HIGH PRESSURE ENABLED SYNTHESIS OF ULTRAHIGH ASPECT RATIO MATERIALS FOR SUPERCONDUCTIVE AND OPTOELECTRONIC APPLICATIONS

A Dissertation in Chemistry
by
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ABSTRACT

High aspect ratio materials are of interest in both the microscale and nanoscale. These materials are small in the transverse direction and can be synthesized to be hundreds of thousands or even millions of times longer on the axial direction. When a material is arranged in this manner, it offers opportunities to exploit weak effects in the material due to the large interaction between the material itself and the photons and/or electrons that travel through the material. These structures could be necessary for the next generation of photonic, spintronic, photovoltaic, and electronic devices. The actualization of materials, specifically semiconductors at the micro scale and metals at the nanoscale, in this type of geometry presents a challenge because conventional synthesis techniques do not possess the ability to grow materials in such extreme aspect ratios.

The focus of this dissertation will be furthering the development of a high pressure templated growth in the pores of microstructured optical fibers. These meter long, ultra-high aspect ratio materials have been utilized for decades in the telecommunication, medical, and industrial fields; however, they are limited in materials that could be incorporated into their structure via traditional drawing techniques. When fabricated with hollow cores, they offer a template that is capable of handling high pressures and moderately high temperatures, as well as a nearly atomically smooth surface to act as the substrate to deposit materials.

Two types of synthesis will be described. First is a high pressure chemical vapor deposition technique that was pioneered by former members of the Badding lab. The focus will be on a novel approach to high aspect ratio zinc oxide deposition in which water is created via the reverse water gas shift reaction to act as the oxygen source of the metal.
oxide. The high pressures involved in the deposition drastically affect the material quality as well as the chemical kinetics and thermodynamics involved in the reaction. The second synthesis described will be metal nanowires that are created via a pressure-assisted melt filling technique. High pressures are necessary to overcome the surface tension and the non-wetting characteristics of many metals on silica and form them into the high aspect ratio shapes. A focus will be on gallium’s interesting surface chemistry and ability to create metastable crystal structures in confined geometries. Investigations into the superconductivity of gallium as well as gallium-indium structures are of interest due an interest in 1-D superconductivity, which long nanowires are required due to proximity effects of contacts to the superconductive wires. One particular structure is utilized to create a non-destructive memory element that is a nano-realization of a Josephson memory device.
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AAO</td>
<td>Anodic aluminum oxide</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DEZ</td>
<td>Diethyl zinc</td>
</tr>
<tr>
<td>DMZ</td>
<td>Dimethyl zinc</td>
</tr>
<tr>
<td>Ebeam</td>
<td>Electron beam lithography</td>
</tr>
<tr>
<td>EGaIn</td>
<td>Gallium-indium eutectic</td>
</tr>
<tr>
<td>HPCVD</td>
<td>High pressure chemical vapor deposition</td>
</tr>
<tr>
<td>MCD</td>
<td>Molten core drawing</td>
</tr>
<tr>
<td>MFP</td>
<td>Mean free path</td>
</tr>
<tr>
<td>MOF</td>
<td>Microstructured optical fiber</td>
</tr>
<tr>
<td>PAMF</td>
<td>Pressure assisted melt filling</td>
</tr>
<tr>
<td>PAPF</td>
<td>Pressure assisted physical filling</td>
</tr>
<tr>
<td>PCF</td>
<td>Photonic crystal fiber</td>
</tr>
<tr>
<td>PIT</td>
<td>Powder in a tube</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>QRRK</td>
<td>Quantum Rice-Ramspegier-Kassel</td>
</tr>
<tr>
<td>RWGS</td>
<td>Reverse water gas shift</td>
</tr>
<tr>
<td>TMA</td>
<td>Trimethyl aluminum</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-Liquid-Solid</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence</td>
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</tbody>
</table>
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Chapter One

An Introduction to high aspect ratio materials

High aspect ratio materials have been of interest on both the microscale and nanoscale. Various materials such as semiconductors, metals or polymers are all of interest for different functionality, but all high aspect ratio materials are quite small in the transverse direction and long or even much longer in the axial direction. On the microscale, these materials have been in existence for centuries. One example is the highest aspect ratio material that humans have ever made in silica optical fibers.\(^1\) These fibers take advantage of total internal reflection which was first applied to glass rods and fibers in the 1920’s, originally for the purposes of medical endoscopy, periscopes and video transmission technology.\(^2\) Today new versions of these silica fibers span the world’s oceans creating high speed internet connections that reach every continent except Antarctica. When materials are arranged in high aspect ratios like this, there is a fundamental challenge in fabrication; however, they offer opportunities to exploit weak effects in said materials due to the large interaction between the material itself and the photons and/or electrons that travel through the material. These structures could be necessary for the next generation of photonic, spintronic, photovoltaic, and electronic devices that require control over the size, shape, and morphology of the materials.\(^3,4\)

Nanoscale high aspect ratio materials such as nanowires or nanorods, typically have an aspect ratio around 500, where they are tens of nanometers in the transverse direction and a couple hundred micrometers in the axial direction at most.\(^4\) These materials are of interest not only for their high aspect ratio structure but also the large differences in the properties of nanoscale materials when compared to their bulk counterparts, such as their
thermodynamic and kinetic properties as well as quantum confinement. These materials have become relevant in numerous fields including physics, chemistry, and biology. One particular material of interest is an “old” material that is being utilized in new ways. Metals have been largely investigated in the bulk, but their nanoscale properties have shown new and interesting physical and electronic properties, especially when arranged into high aspect ratio nanowires or nanorods. These interesting properties include catalyzed motion, nanowire assembly dynamics, optical properties, superconductivity, and phase anomalies.

1.1 Synthesis of high aspect ratio optoelectronic materials

For the purposes of these studies, a “high aspect ratio” material will refer to any material that has an aspect ratio higher than 100. Some materials may be considered to be high aspect; however, it is a relative term ranging everywhere from nanorods that have an aspect ratio of 10, where the axial and longitudinal dimensions are on the same prefix unit of measurement. Other materials, specifically those that will be described in this dissertation extend to aspect ratios that are on the scale of 1,000,000 and larger.

1.1.1- Silica optical fibers

On the micrometer length scale, silica fibers are the undisputed champions of high aspect ratio materials. These silica fibers not only have significant technological applications in telecommunications, as mentioned earlier, but are also important in many scientific fields as they offer fundamental platforms for sensing, non-linear optics, light manipulation, and imaging. Optical fibers originated as “single material” step index fibers made entirely of silica and guide light by total internal reflection via refractive index differences. To have more tunability for photonic bandgap guidance, higher refractive
index differences were needed, which led to the development of the air/silica microstructured optical fiber (MOF).

![Diagram of optical fiber creation](image)

Figure 1.1: Creation of optical fibers via drawing. The optical fiber begins as a preform that is centimeters in diameter which is heated in a furnace and drawn to the end diameter which is typically micrometers in diameter. A protective polymer coating is applied prior to the fiber being spooled to protect against scratches to the glass surface that may cause the fiber to break.

These silica fiber capillaries are produced by a high temperature drawing technique as shown in Figure 1.1. The silica fiber capillaries begin as a silica glass tube with centimeter to millimeter dimensions called a preform. The preform is heated to high temperature (~ 2000°C) in a tower furnace which is typically a few stories high. The macroscale dimensions possessed by the preform are replicated on the microscale and
nanoscale in the optical fiber capillary. The fiber drawing process enables nearly any arrangement or pattern of pores to be fabricated into optical fibers. Furthermore, the silica surface is nearly atomically smooth,\(^{11}\) and the capillary diameter variations are as little two nanometers over centimeter length scales.\(^{12}\)

Figure 1.2: Various microstructured optical fibers. The size, shape, and position of the hollow areas run axially along the length of the fiber. They can be controlled very accurately due to numerous advances in the fiber drawing technique. The center image is an example of a silica preform.\(^{13}\)

MOFs are an interesting subset of optical fibers as the structures can affect many of the properties of the fiber, most importantly the guidance of light through the fiber. The melting and draw technique described above allows for virtually any pattern of holes of different shapes and sizes to be fabricated with precise locations in the transverse plane as shown in Figure 1.2. Compared to other glasses, silica’s low slope viscosity curve aids this process and allows for intricate structures to be drawn on nanometer scale dimensions.
1.1.2 – Optoelectronic material integration with MOFs

While silica fibers and MOFs have revolutionized optics and many other fields, there is still a need to add materials such as semiconductors for greater range of functionality. Semiconductor devices within optical fibers is advantageous for high-speed processing of telecommunications data without coupling the signal to a wafer.\textsuperscript{14} Extending electronic devices to flexible, longer length scales is appealing for applications such as chemical sensing,\textsuperscript{15} power generation,\textsuperscript{16} and biomedical devices.\textsuperscript{17,18} Optical fibers are ideal for these applications and have been demonstrated as three-dimensional and woven electronics.\textsuperscript{19,20} Table 1.1 is a very short list of materials that could be of interest in high aspect ratio geometries coupled with their common applications. There are obviously many other semiconductors that have optical properties of interest, this table lists just a few.

The integration of such materials poses a significant challenge. It is easy to see certain limitations such as the need for a material to have an accessible glass or liquid phase in a similar temperature range to the melting point of silica. Many other issues arise when working with semiconductor materials including thermal, chemical, and mechanical mismatches of the optoelectronic material and the silica. Additionally, at high temperatures, there is the possibility of unwanted reactions as well as atomic diffusion which would cause impure materials.
Table 1.1: Common semiconductors and their applications. Bandgap Energy data is from *Springer Handbook of Electronic and Photonic Materials*.

<table>
<thead>
<tr>
<th>Material</th>
<th>Bandgap Energy (eV)</th>
<th>Application(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si:H</td>
<td>1.7-1.8</td>
<td>Optoelectronics, solar cells, flat panel displays</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.74</td>
<td>Solar cells</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42</td>
<td>Light emitting diodes, high-speed electronics, and solar cells</td>
</tr>
<tr>
<td>GaN</td>
<td>3.44</td>
<td>Light emitting diodes and power amplifiers</td>
</tr>
<tr>
<td>GaSb</td>
<td>0.73</td>
<td>Infrared detectors and light emitting diodes</td>
</tr>
<tr>
<td>Ge</td>
<td>0.67</td>
<td>Thermal imaging</td>
</tr>
<tr>
<td>InAs</td>
<td>0.36</td>
<td>Infrared detectors</td>
</tr>
<tr>
<td>InP</td>
<td>1.35</td>
<td>High power optoelectronics</td>
</tr>
<tr>
<td>InSb</td>
<td>0.17</td>
<td>Infrared detectors and thermal imaging sensors</td>
</tr>
<tr>
<td>Si</td>
<td>1.11</td>
<td>Transistors, detectors, and solar cells</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.7</td>
<td>High power infrared lasers and IR transmission</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.37</td>
<td>Transparent electrodes, transistors, light emitting diodes and UV lasing material</td>
</tr>
</tbody>
</table>

1.1.3 – Molten core drawing

The Ballato group at Clemson University developed a molten core drawing (MCD) technique to draw optical fibers that consist of mainly group IV semiconductors.\(^{21-24}\) Recently they have also had some success in drawing III-V semiconductors via MCD,\(^{25}\) but the technique is still quite limited. The MCD process starts with a rod of the semiconductor material being placed inside a cladding glass tube to construct the preform. When the preform is heated to the glass transition temperature of the silica, it is above the melting point of the semiconductor core, and the fiber is drawn. Despite the fact that the semiconductor is molten and the silica is above its glass transition temperature, the
cladding is still rigid enough with a sufficiently low viscosity to be drawn into the fiber geometry.

This technique has been used to create circular as well as square step index fibers.\textsuperscript{26} The Ballato group anticipates that the process can also be extended to MOFs. While this method is fantastic at making very long lengths of fibers and can be done using equipment that is found in a modern optical fiber drawing facility, it still has set backs. First is that the high temperatures needed for the drawing process causes significant diffusion of impurities from the cladding to the core. In the case of something like a silicon core, oxygen often diffuses from the silica cladding into the core which can limit to the power the fiber is capable of handling. Small cored fibers are also difficult to produce using this method as diffusion can cause the complete oxidation of the core if it is too small.\textsuperscript{24} The group has introduced a reactive MCD method which utilizes a sacrificial oxygen getter such as silicon carbide,\textsuperscript{27} and it will be interesting to see if the group can create small, pure silicon core optical fibers in the future.

One other issue that MCD poses is the fact that semiconductor materials and metals tend to have a much higher coefficient of thermal expansion than silica. Table 1.2 compares a few important optoelectronic materials and their corresponding coefficient of thermal expansion. When materials are drawn at such high temperatures the mismatch between the cladding and core material becomes quite apparent. The Ballato group has reported growth of a single crystal germanium optical fiber;\textsuperscript{23} however, the single crystal is cracked periodically throughout the length of the fiber which is most likely due to the thermal expansion mismatch. Because of these issues the group is moving efforts toward
glasses that have thermal expansion coefficients that are similar to those of the desired semiconductor material to be drawn.

Table 1.2: Coefficient of linear thermal expansion of various materials that may be of interest for high aspect ratio materials. It should be noted that Silica’s value is vastly smaller than the semiconductors and metals. This mismatch causes materials quality issues. *Mercury is liquid at this temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Coefficient of linear thermal expansion $(10^{-6} \text{ K}^{-1}, 20 \degree \text{C})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>0.59</td>
</tr>
<tr>
<td>Silicon</td>
<td>2.5</td>
</tr>
<tr>
<td>Germanium</td>
<td>6.1</td>
</tr>
<tr>
<td>ZnSe</td>
<td>7.2</td>
</tr>
<tr>
<td>ZnO</td>
<td>2.9</td>
</tr>
<tr>
<td>Gallium</td>
<td>18.3</td>
</tr>
<tr>
<td>Gold</td>
<td>14.2</td>
</tr>
<tr>
<td>Mercury</td>
<td>61*</td>
</tr>
<tr>
<td>Tin</td>
<td>23.4</td>
</tr>
</tbody>
</table>

Compound semiconductor fibers, such as III-V, have been created as well. The first MCD III-V optical fiber was created of indium antimonide.\textsuperscript{25} It was created using a phosphate glass cladding which was compatible with the relatively low melting semiconductor (527 \degree C). While this fiber was not capable of optical transmission measurements due to impurities from the diffusion process, the fiber was drawn as a proof of concept that the MCD technique was applicable to compound semiconductors; however, special consideration must be taken when deciding upon the semiconductor to be used in the MCD technique. As shown in Figure 1.3, a zinc selenide fiber was attempted to be drawn from a piece of ZnSe that was placed inside a silica cladding. Upon heating the preform to draw the fiber at a temperature of 2000 \degree C, the ZnSe developed an appreciable vapor pressure inside the cladding due to the sublimation rather than melting of the compound. This pressure caused a small explosion of the preform before it could be drawn into a fiber.
Figure 1.3: Failed attempt to drawing a ZnSe optical fiber. Upon heating of the structure to drawing temperatures (~2000 °C), the ZnSe began to sublime causing pressure to form within the glass cladding. This pressure caused the softened glass to explode.  

1.1.4 – Powder in a tube

One other method that utilizes an approach that is quite similar to the MCD technique is a powder in a tube (PIT) technique. This method tends to be used for much smaller cores and relatively short length fibers when compared to MCD. In this method, silicon powder is packed quite densely into silica tubes that have an inner diameter close to 1 mm, which is then heated and stretched on a bench top fiber drawing apparatus to produce fibers that have final diameter that range between 10 and 100 microns. This process is typically used to create fibers that are centimeters in length and only used for testing purposes, but there is no reason to suggest that this technique could not be adapted to large fiber drawing towers. The PIT technique has produced interesting fibers such as
an n-doped silicon core fiber,\textsuperscript{31} but in a manner similar to the MCD technique, the high temperatures that are needed for drawing causes cracks to form within the core.

1.2 – High aspect ratio metals at the nanoscale

While semiconductor materials for optoelectronic applications are best suited at the micrometer scale, high aspect ratio metals have a great deal of interesting chemistry and physical properties when they are in nanoscale geometries. Current nanowire synthesis of metallic structures that are between 50 and 200 nm in diameter utilize techniques that are largely limited to hundreds of microns in length. While this length scale is all that is necessary for certain applications such as nanowire assembly or catalyzed motion, for other applications larger length scales are necessary.

1.2.1 – Anodic aluminum oxide templates

One of the most popular methods of producing metallic nanowires employs anodic aluminum oxide (AAO) templates which were developed in the 1950’s.\textsuperscript{32} To create an AAO template, aluminum is anodized and etched to produce a template design with multiple pores. The pore diameter can be controlled by adjusting the anodizing and etching conditions. Once the AAO template is created, metallic nanowires can be produced by filling the voids via deposition,\textsuperscript{33} electroplating,\textsuperscript{34} or hydraulic pressure.\textsuperscript{35} The nanowires that are created are then isolated by etching away the AAO template leaving the wires behind.

This method has numerous advantages such as unidirectional growth, varying composition in one direction, controlled arrays of metallic wires, and very accurate and precise control of wire diameters.\textsuperscript{5} There are also numerous drawbacks, despite the years that have been devoted to improving this technique. One of the biggest issues is the length
at which the wire can be grown. In recent publications an “ultra-long” wire was described as having a length of 130 micrometers and an aspect ratio of roughly 500. While this is impressive there is still a need in some fields of study such as 1-D superconductivity to have wires that are much longer than this. One other issue with the AAO technique is that there is a good deal of processing that is needed when attempting to make contact to a single nanowire. The AAO template creates hundreds or more nanowires in a single synthesis. In order to make contact to a single wire for measurements and studies, a combination of dispersion of the wires onto a substrate, etching, and deposition of electrodes are required.

1.2.2 – Electron beam lithography

Electron beam lithography (e-beam) is another method that can be utilized to create high aspect ratio nanostructures. In this technique, a focused beam of electrons can draw custom shapes onto a surface that is covered with an electron beam-sensitive film. This beam changes the solubility of the resist which allows for the removal of certain portions of the film by the immersion into a solvent. Wires can then be created by means of physical vapor deposition (PVD) over the entire wafer. If a nanowire shape was dissolved by the solvent, the metal will stick directly to the silicon wafer and everywhere else, the metal will be on the polymer film that was left behind. A different solvent from that which was used to create the nanowire trench is used to “lift off” the remaining polymer that leaves only the metal that was deposited on the bare silicon portions of the wafer. This technique has been used in the past to investigate various metals and their superconductive properties. Two issues that arise from this technique are first, the quality of the metal that is deposited is not always of highest quality. It is typically amorphous or very highly
polycrystalline which results in poor physical properties such as lowered conductivity and optical transparency. Additionally the surfaces of these wires tend to be quite rough causing scattering sites to form and lower the materials quality even further. Despite these drawbacks, e-beam growth of metallic nanowires has been of interest due to the ease of fabrication and the long lengths that these wires can be fabricated into; however, the inability to lift these bound wires from the silicon substrate can cause interference with certain measurements.

1.2.3 – Free standing growth of nanowires

There are a variety of free standing growth mechanisms that can be used to create high aspect ratio nanowires; however, one of the most popular techniques is vapor-liquid-solid (VLS) growth. This technique is very similar to chemical vapor deposition (CVD) growth in that chemical precursors are reacted from the gas phase to form the desired materials, but VLS differs in that rather than the chemical reaction going straight from the gas to solid phase, it goes through an intermediate liquid phase as shown in Figure 1.4. The precursors are absorbed by a liquid on a substrate (typically gold or other metal nanoscale droplets) to the point where the liquid becomes supersaturated and deposition occurs in an axial manner between the droplet and the substrate. While this technique is capable of single crystal deposition, the wires cannot grow to very long lengths before becoming quite brittle rather than malleable.
Figure 1.4: Schematic of the VLS growth mechanism. The silicon substrate is first coated with a thin gold layer which is annealed to create a gold-silicon eutectic droplet as shown in the center of the figure. This eutectic is then infiltrated with a silicone precursor such as silane molecules that causes supersaturation of silicon in the droplet. This causes deposition on the silicon substrate of silicon whiskers.

1.3 – Integration micro and nanoscale materials post-drawing of MOFs

Most of the drawbacks to conventional techniques for growing high aspect ratio materials at the micro and nanoscale can be remedied by utilizing the MOF structure as a template for growth. One of the biggest challenges arises from the difficulty of infiltrating molecules into such high aspect ratio pores.

1.3.1 – Deposition from solution

Films of various semiconductors such as ZnS, ZnSe, ZnO, Ge, CdS, and PbS can be deposited in the MOFs utilizing the precipitation of material from a solution of their salts.\textsuperscript{41,42} This process has been primarily used to create very large, hollow core optical fibers for infrared power delivery and sensing applications. One issue with this technique is the film quality. Surface roughness is on the order of 10 nm and complete filling of the pores with this technique has yet to be reported and is likely not a reasonable expectation as the nanometer and small micrometer sized capillaries would restrict the liquid’s mass transport properties due to surface tension restraints.
1.3.2 – Chemical vapor deposition

Chemical vapor deposition has been utilized in the semiconductor industry for years and is typically done on flat substrates to create thin filmed materials. This technique can be expanded to 1-D structures utilizing a high pressure CVD (HPCVD) method that was pioneered by the Badding lab at Penn State University in collaboration with the Sazio group at the University of Southampton. Conventional CVD is not well suited for high aspect ratio materials creation due to the lack of mass transport inside small pores such as the MOF geometries. The lack of mass transport is likely due to the atmospheric or vacuum conditions that traditional CVD utilizes for the deposition. High pressures can aid in the mass transport of precursors and drive the chemical reaction to meters in length in microscale pores. This technique will be described in far more detail in Chapter 2 of this dissertation.

1.3.3 – Pressure assisted melt filling

The Russel group at the Max Planck Institute has used a pressure assisted physical filling (PAPF) technique that can allow for the integration of materials that have melting points below the softening temperature of glass (~1400 °C) and were considered to be incompatible with silica at drawing temperatures. Many liquids, gases, metals and colloids have been infiltrated into MOFs via the PAPF technique and the specifics of this particular method will be described in detail in Chapter 3 of this dissertation as it can be a very useful technique to create high aspect ratio materials, particularly homogeneous and heterogeneous metallic nanowires.
1.4 – Microstructured optical fibers as a template for optoelectronic and metallic materials growth

Many of the techniques described above have made significant advances in diversifying the number of materials that can be created in a high aspect ratio geometry both at the micro and nanoscale. The compatibility issues between semiconductor materials and fiber drawing techniques as well as the high temperature processing leading to large amounts of diffusion cause quite a limitation on the number of various materials that can be created using this method. When a chemist sees the MOF structure, an opportunity for templated growth of materials becomes apparent; however, there is the issue of actually infiltrating these structures. The focus of this dissertation will be how pressure can assist a chemist in creating high aspect ratio materials at the microscale and nanoscale inside these MOF templates.

1.5 – References


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Chapter 2

High aspect ratio depositions via high pressure chemical vapor deposition and atomic layer deposition

As mentioned in Chapter 1, traditional methods for synthesizing high aspect ratio materials in MOF templates are limited. A high pressure chemical vapor deposition (HPCVD) method has been developed in the Badding lab\(^1\) that allows for the conformal coating of MOFs with metals,\(^2\) amorphous semiconductors,\(^3,4\) polycrystalline\(^5\) and large single crystal semiconductors,\(^6\) as well as compound semiconductors.\(^7\) Throughout this chapter the deposition of silicon via silane (SiH\(_4\)) pyrolysis will be referenced as it is a well-studied model system to explain the thermodynamics and kinetics of the HPCVD technique. These principal aspects of HPCVD can be applied to the synthesis of zinc oxide (ZnO) and those same aspects can be applied to atomic layer deposition (ALD), specifically of alumina (Al\(_2\)O\(_3\)).

2.1 - Limitations of conventional CVD and ALD

Conventionally, CVD and ALD are done at atmospheric or vacuum conditions, and can be enhanced by the addition of plasma for increased reaction rates as well as producing new and interesting semiconductor films. These well-known techniques are some of the most widely used fabrication methods for the deposition of planar thin films. The CVD reactors are carefully designed to accomplish two main goals. First is to cover very large area planar substrates, as in the case of some hot wall CVD reactors which can be tens of meters in size. The second is to deposit a very precise and uniform layer thickness onto the substrates. This is achieved by carefully balancing the reaction rates of the precursor onto the surface and the precursor transport. While these techniques have been optimized for
planar films, they are very limited in their ability to uniformly coat or fill extreme aspect ratio voids such as those discussed in Chapter 1 with MOF structures. The ability to conformally coat structures that are geometrically complex, three-dimensional and hierarchically organized across a range of length scales would be of value in the semiconductor industry. A few examples of where this type of deposition may be interesting are in pillar array photovoltaics, microfluidics, biological templates, three-dimensional optical materials, and in telecommunications.

2.2 – Pressure’s effect on mass transport

Traditional CVD is largely unable to generate conformal semiconductor coatings in deep trenches or voids. This inability is mostly due to the mean free path (MFP) of the precursor molecules inside the reaction chamber. The MFP of a gas molecule is inversely proportional to pressure and can be calculated using kinetic theory of gases:

$$MFP = \frac{k_B T}{\sqrt{2\pi d^2 P}} \quad (Equation \ 2.1)$$

where $k_B$ is Boltzmann’s constant, $T$ is the temperature of the gas, $P$ is the pressure of the gas, and $d$ is the diameter of the gas molecule.

The mean free path of a H$_2$ molecule at 400 °C is approximately 300 nm at atmospheric pressure. This pressure corresponds to typical atmospheric CVD pressure range. Most CVD work is done at lower pressure which will only cause an increase in the MFP. In a typical HPCVD reaction the pressure is closer to 35 MPa, and these sorts of pressures decrease the MFP to closer to 1 nm as seen in Figure 2.1. Essentially in conventional CVD effusion is the dominating mechanism to cause transport into small openings. In HPCVD, the molecular MFP of 1 nm allows for pressure driven molecular transport by hydrodynamic flow into micro and nanoscale voids.
Figure 2.1: Mean free path of a hydrogen molecule as a function of pressure at 400 °C.\textsuperscript{12} The typical pressure regimes of conventional CVD is highlighted in green while pressures used in the Badding lab for HPCVD are highlighted in blue.

At this point the rate of mass transport to micro/nanoscale features becomes almost equal to the rate of transport to macroscale features, and thus HPCVD has the ability to conformally coat surfaces that have structure with a thin film of a chosen semiconductor where conventional CVD techniques are inadequate as they rely on effusion as shown in Figure 2.2.
Figure 2.2: Diffusion vs effusion into small holes. Infiltration of nanoscale holes and pores with gas molecules with a decreased MFP result in diffusion, while a larger MFP causes effusion.

In conventional CVD, hydrodynamic flow plays a key role in the deposited film. In HPCVD, a typical reaction is done in microcapillaries and the flow of gases through these capillaries has been characterized by experimental studies of helium gas flow.\textsuperscript{14} The volumetric flow rate through the microcapillaries was measured as a function of pressure at constant capillary diameter and as a function of diameter at a constant pressure. Figure 2.3 shows the flow scales with the square of pressure, and with the fourth power of diameter. It should be noted that in very large capillary diameters, this data deviates from that shown in Figure 2.3. This is due to the laminar flow in microcapillaries becoming turbulent at larger capillary sizes. The reactions that will be described in this dissertation will be largely considered to be in the compressible laminar flow regime and thus, flow can be approximated and expressed as:

\[
Q \propto \frac{\pi \Delta P^2 D^4}{8 \eta L} \quad \text{(Equation 2.2)}
\]

where \(\Delta P\) is the pressure difference, \(D\) is the diameter, \(\eta\) is the viscosity and \(L\) is the length of the capillary.
The mass flow rate is proportional to: a) diameter of the capillary to the fourth power and b) the difference in pressure squared.

The rate of mass transport can thus be tuned with pressure and length, assuming the diameter of the capillary is consistent, which provides the HPCVD technique with the same hydrodynamic flow control that conventional CVD has at its disposal.

2.3 – Overview of the HPCVD technique

One of the biggest differences between CVD and the HPCVD technique developed in the Badding lab is that gasses are mixed and held in the same reservoir before they get to the targeted deposition location. In conventional CVD, there are individual input locations where precursors can be added, and thus any sort of reactions between individual precursors can be largely ignored until they reach the desired reaction location. In HPCVD, the reactants must be mixed prior to deposition, and so precursor selection is very important in HPCVD as they must be able to react when they reach a heated zone and avoid any sort of prereactions at relatively low temperatures such as room temperature. This will be discussed in detail later in this chapter. For a visual aid as to how the HPCVD technique is different from conventional CVD, please refer to Figure 2.4.
Figure 2.4: Schematic comparison of conventional CVD and HPCVD.\textsuperscript{7} a) Conventional CVD, which requires individual delivery of precursors into the large reaction chamber. This allows for a variety of precursors to be used without any consideration for “prereactions”. A small pressure differential causes flow toward the heated substrate for deposition. b) HPCVD process in which high pressure precursors enter into the silica capillary from the left with the opposite end open to atmospheric pressures. In this case precursor selection is crucial as all precursors are contained in the same vessel prior to entering the capillary. When the reactants reach the heated area, deposition begins in an annular film fashion on the walls of the capillary and byproducts are exhausted through the open end of the capillary downstream.

The general process for HPCVD involves a high pressure mixture containing chemical precursors (or in the case of silicon deposition, only one precursor is required) at relatively low concentrations (typically less than 5% of the total mixture concentration) and a carrier gas, which is typically He or H\textsubscript{2}, depending upon the desired reaction. The carrier gas raises the total pressure of the mixture to somewhere between 35 and 70 MPa, again depending on the desired reaction. This high pressure mixture is contained in a stainless steel vessel which is constructed using specialized high pressure parts from High Pressure Equipment Company located in Erie, PA. Many of the precursor compounds are air sensitive, such as silane, germane, and organometallics which are all pyrophoric when exposed to atmosphere. They are loaded using one of two methods. The first is simply filling a vacuumed reservoir with the vapor pressure of the precursor. Obviously this
method is only applicable to precursors that have an appreciable vapor pressure. The other method is limited to depositions that need precursor pressures higher than the vapor pressure. In these cases, a known volume and pressure of a gas is condensed into the reservoir utilizing liquid N\textsubscript{2}. Depending upon the desired precursor concentration, the condensation can be repeated numerous times. Once the precursor is in the reservoir, carrier gas is pressurized using a stainless steel diaphragm pump from Superpressure (a Newport subsidiary located in Jessup, MD).

After the reservoir is sufficiently pressurized, it can be connected to a MOF of any size or structure, followed by numerous evacuations using a dry scroll vacuum pump and purges using high purity He gas to ensure that any oxygen or water that may have been in the connection is removed. At this point, the reservoir can be opened allowing the pressurized mixture to flow through the capillary and is typically exhausted through the other end of the capillary which is open to the atmosphere. Heat is provided to the desired deposition zone via an external resistance furnace. This furnace is controlled using a PID controller as well as a solid state relay which combine to send the appropriate current through the resistance wire of the furnace causing heat to form in the furnace. These furnaces are built and profiled by our lab, and can be adjusted to fit any temperature profile that may be needed. When the precursor and carrier gas reach the heated area of the MOF, the reaction is initiated and a semiconductor film begins to form. At this point, any unreacted precursors, carrier gas, as well as reaction byproducts exit the other end of the fiber.

While high pressure gasses, especially pyrophoric precursors, can sound quite dangerous, many precautions are taken to ensure that the entire process is safe. First the
stainless steel reservoirs are often rated to well over double the pressures that are placed in them. When they are constructed, they are tested thoroughly with inert gases to ensure there are no leaks or weak points that could cause catastrophic failure. Additionally the glass capillaries are incredibly strong. They also hold such a small volume of reactive gas, that if the fragile, yet strong glass happens to break, the pyrophoric gases that are contained have a minimal amount of risk involved, and the flow of these gases can be stopped relatively quickly.

### 2.4 – High Pressure’s effect on chemical reactions

As discussed above, the HPCVD technique can be used to force chemical precursors into high aspect ratio features such as the micro and nanoscale pores in MOFs which would not be possible in conventional CVD. While the high pressures do enable the transport of chemicals into small pores, there are numerous other benefits that arise due the increase in pressure. The pressure effects both the reaction thermodynamics and the kinetics. These effects will be discussed in this section. Most of the fundamental thermodynamic and kinetic discussion will be done on the pyrolysis of SiH₄ which decomposes to form silicon. This reaction is well studied and the concepts developed from this reaction translate well to most other HPCVD reactions.

#### 2.4.1 – High pressure and thermodynamics

Typically when looking to induce chemical reactions, we as chemists are trained to think that raising the temperature is the solution. The temperature increase will give the system the energy required to overcome activation barriers. This certainly is true as raising
the temperature in most reactions will cause an increase in the chemical potential and cause a reaction to take place as seen in the Gibbs free energy equation:

$$\Delta G = V\Delta P - S\Delta T$$

(Equation 2.3)

where $\Delta G$ is the change in Gibbs energy, $V$ is the volume of the system, $\Delta P$ is the change of pressure in the system, $S$ is the entropy of the system and $\Delta T$ is the change in temperature of the system.

One property that is often overlooked is the fact that similar activation of chemical reactions can be achieved by changing the pressure of the system without any changes in temperature. From the equation of state of a system, the effects of pressure on thermodynamic quantities can be calculated. For H$_2$, increasing the pressure of a system results in an increased chemical potential as shown in Figure 2.5. An example where this becomes an important aspect to consider is in the hydrogen embrittlement of steel. High pressure H$_2$ gas is capable of reacting with the carbon in steel and weakening it.$^{15,16}$ This increased chemical potential due to pressure changes allow for reactions to be done at far lower temperatures, while still maintaining appreciable growth rates.
2.4.2 – Kinetics of high pressure SiH₄ pyrolysis

At high pressures, it is easy to imagine that molecular collisions of precursor molecules increase. This increase has a drastic effect on the reaction kinetics of a system, and the effects of pressure on the pyrolysis of SiH₄ have been studied extensively.

The mechanism and reaction pathway from SiH₄ to amorphous or crystalline silicon products in conventional CVD has been shown to have numerous gas phase and surface reaction steps. While there is still a good amount of debate as to the full mechanism due to the fact that there is evidence that there is a change in reaction order from low to high pressures, the first step of the reaction is widely considered to be collisionally activated. This first step causes the SiH₄ to form silylene (SiH₂).

\[ \text{SiH}_4(g) \rightarrow \text{SiH}_2(g) + \text{H}_2(g) \]  
(Reaction 2.1)

While bimolecular collisions with carrier molecules and other SiH₄ molecules are present, the rate for this reaction is typically written in the unimolecular form:
\[ -\frac{d[SiH_4]}{dt} = k[SiH_4] \]  \hspace{1cm} (Equation 2.4)

When written like this, the rate expression is dependent on the total pressure as well as the temperature and the identity of the colliding gas molecules. The silane molecule does not have low frequency vibrations, so the unimolecular decomposition is not at the high pressure limits under conventional CVD conditions.\(^{22}\) This unimolecular decomposition can have a rate constant calculated as a function of the total pressure (accounting for the SiH\(_4\), as well as the carrier gas, which in this case is He) using quantum Rice-Ramsperger-Kassel (QRRK) theory as shown in Figure 2.6. Here the temperature was held at 420 °C, and the rate constant increased from \(1.6 \times 10^{-7} \text{ s}^{-1}\) at 13 Pa, which is a very typical pressure for traditional CVD depositions of silicon, to \(4.6 \times 10^{-4} \text{ s}^{-1}\) at 10 MPa, the high-pressure limit. This increase of \(~10^3\) increase in the reaction rate couples with the \(~10^5\) increase in the reaction concentration (13 Pa versus the 1.7 MPa partial pressure in the HPCVD reaction) ensures that there is a considerable increase in the rate of decomposition of silane to silylene.
After the formation of SiH$_2$ there is a series of other reactions that eventually lead to the formation of solid silicon. Every step in the series very well may experience a similar increase to the rate constant due to collisional activation at high pressures. Experimentally, the deposition rate is found to increase roughly 30 fold at 450 °C, from 0.01 Ås$^{-1}$ at 13 Pa$^{23}$ to ~0.3 Ås$^{-1}$ for the HPCVD of SiH$_4$ silicon at a partial pressure of 1.7 MPa. The acceleration shown experimentally is not nearly as large as would be expected based on the increase in SiH$_2$ concentration at high pressures.$^3$

When coupled with the thermodynamic effects at high pressure, these kinetic effects lead to substantially higher rates of reaction and allow for many reactions to be done at lower temperatures than what may be needed with conventional CVD. Studies are currently underway to have a better understanding of the effects of high pressure on the decomposition rate of SiH$_4$ pyrolysis. This study is being done by a collaboration between
theory/modeling expert, Dr. Ali Borhan of the Chemical Engineering department at Penn State University and the Badding group.

2.4.3 – Confinement effects on HPCVD

As described above, the increase in pressure and thus increase in concentration of precursor molecules causes an acceleration of deposition. One reason that HPCVD is typically not done in CVD reactors aside from the safety issues involved in large volume reactors, is that it causes homogeneous particle formation in the gas phase as opposed to the desired heterogeneous film growth at the surface. When the pyrolysis of SiH₄ is carried out in smaller reactors, though, the reaction at the surface becomes much more active than the reaction in the gas phase. As shown in Figure 2.7, there is a clear limit as to how large of a reaction chamber can be used to ensure film growth rather than the “fines” that are Si particles that are formed in the gas phase which eventually grow large enough to precipitate out of the gas phase and onto the surface.³

![Figure 2.7: Synthesis of silicon from silane pyrolysis as a function of confinement. In agreement with previous studies,²¹ HPCVD of silicon inside a large volume (diameter larger than 2.5 mm) capillary results in the formation of silicon particles on the left. In the center, a 1 mm capillary shows an intermediate surface to volume ratio where the surface reaction and reaction in the gas phase are roughly equal. The right shows heterogeneous film growth which is favorable to any pore that is less than 300 μm in diameter.](image)

When the reactor is large, in this case a few millimeters in diameter, the gas phase reaction dominates and the particles are clearly formed. When the reactor is shrunk to about 1 mm in diameter, there is a competition between gas phase and surface reactions which
results in both a film growth and particle growth. When the reactor is sufficiently confined, only the surface reaction occurs and well-developed films on the wall of the reactor are observed. The threshold in the case of silane pyrolysis seems to be around $300 \, \mu\text{m}$ in diameter. In the confined case, any particles that may form in the gas phase have very little time to grow into large particles before hitting the reactor wall and becoming embedded in the film growth. The time required for a nucleated particle to reach the pore wall scales as $x^2/D$, where $x$ is the pore diameter and $D$ is the gas phase diffusivity of the particle. It is easy to see that $x^2/D$ is orders of magnitude larger for any capillary that is larger than $300 \, \mu\text{m}$ when compared to a smaller pore like the $6 \, \mu\text{m}$ pore shown in Figure 2.7.

2.5 – Deposition of binary semiconductor compounds

Many of the benefits to HPCVD of group IV semiconductors such as silicon and germanium can also be used in creating III-V and II-VI compound semiconductors. Past and current members of the Badding lab have done the groundwork in depositing numerous binary compounds such as $\text{ZnSe}$, $\text{ZnS}$, $\text{ZnS}_x\text{Se}_{1-x}$, $\text{GaAs}$, $\text{GaN}$, and numerous others. Here I will discuss the deposition of $\text{ZnO}$ via the reverse water gas shift (RWGS) reaction in MOF templates.

2.5.1 - Motivation for the production of high aspect ratio $\text{ZnO}$

The growth of $\text{ZnO}$ has garnered a large amount of interest over the past couple decades for its semiconductor properties. It has a direct and wide band gap, high thermal conductivity, high electron mobility, and a large exciton binding energy. For these reasons it has been a pursued material for sensing, solid-state lasing, piezoelectric and optoelectronic applications. For many of these applications, high aspect ratios are beneficial as it provides more interaction between the $\text{ZnO}$ and the photons and/or
chemicals. There have been previous attempts of depositing ZnO in MOFs. First was done in our lab where a well-developed high aspect ratio ZnSe microwire was oxidized via high temperatures and introduction of high pressure oxygen to form ZnO.\(^7\)

This deposition method did create ZnO; however, it was a very porous material as seen in Figure 2.8 a. One other attempt was made via deposition from solution, a technique that was discussed in Chapter 1. The growth from this technique was only able to create very thin films of ZnO as seen in Figure 2.8 b, and when thicker films were attempted, the growth failed to produce well developed films. It created nanopillars of ZnO materials that grew laterally from the MOF wall.\(^28\) As the ZnO is wanted for its optical properties, porosity and film thickness are important features that need to be controlled in a better fashion.

![Figure 2.8: Deposition of zinc oxide in MOFs.](image)

2.5.2 – Choosing proper precursors for the ZnO deposition

One disadvantage to the HPCVD method as opposed to conventional CVD is that all the precursors for the overall reaction must be held at high pressures in the same
reservoir before they are allowed to flow through the MOF for the reaction to take place. Unfortunately for HPCVD, many of the precursors used in conventional CVD will react at room temperature if mixed. In the case of ZnO, typically an organo-zinc compound, such as diethylzinc (DEZ) or dimethylzinc (DMZ) are reacted with water to create ZnO layers. DEZ and DMZ are liquid at room temperature and have appreciable vapor pressures, which is ideal for both CVD and HPCVD. The DMZ compound was chosen based on its large vapor pressure (~30 kPa at room temperature), the availability in electronic purity levels, and compound stability. When the alkyl group attached to the zinc atom are extended to longer chains, in general the compound decomposes more readily. Water is also needed to create the ZnO film as shown below:

\[
\text{Zn(CH}_3\text{)}_2 (g) + \text{H}_2\text{O (g)} \rightarrow \text{ZnO (s)} + 2 \text{CH}_4 (g) \quad \text{(Reaction 2.2)}
\]

This reaction happens at room temperature and because of this, it is necessary that the water is introduced or produced at the site of the reaction rather than added to the stainless steel reservoir prior to the depositions.

### 2.5.3 – Chemical encapsulation for HPCVD precursor containment

A solution to the “pre-reactions” that would occur in HPCVD is an interesting technique that was developed in the Badding lab, coined “chemical encapsulation”. In this method chemicals that are unreactive at room temperatures create the reactive precursors for the film growth when temperatures are raised to appropriate levels. This was first used for the deposition of ZnSe where DMZ and hydrogen selenide are typically needed as precursors\(^{29}\); however, they react at room temperature. To avoid this the researchers chose to use DMZ and dimethylselenide in the presence of hydrogen gas. All three gases do not
react with each other at room temperature, but when heated, the following reactions occur to form the desired semiconductor:

\[
\text{Se(CH}_3\text{)}_2 (g) + 2 \text{H}_2 (g) \rightarrow \text{SeH}_2 (g) + 2 \text{CH}_4 (g) \quad \text{(Reaction 2.3)}
\]

\[
\text{SeH}_2 (g) + \text{Zn(CH}_3\text{)}_2 (g) \rightarrow \text{ZnSe} (s) + 2 \text{CH}_4 (g) \quad \text{(Reaction 2.4)}
\]

In this case the hydrogen selenide was “encapsulated” and formed \textit{in situ} at the deposition location. A similar method is needed to encapsulate water and create it \textit{in situ} at the reaction area for the deposition of ZnO.

2.5.4 – Reverse water gas shift at high pressures

The RWGS reaction has been known since the 19\textsuperscript{th} century; however, with the ever expanding interest of Mars exploration, it has become a popular candidate of late to produce water on a planet such as Mars that has an atmosphere that is roughly 95\% CO\textsubscript{2}.\textsuperscript{30,31} The simple reaction is shown here:

\[
\text{CO}_2 (g) + \text{H}_2 (g) \rightarrow \text{H}_2\text{O} (g) + \text{CO} (g) \quad \text{(Reaction 2.5)}
\]

This is a prime candidate to create water \textit{in situ} for the deposition of ZnO. At atmospheric pressure, this reaction typically occurs in appreciable amounts at ~600 °C.\textsuperscript{32} This temperature is far too high to react with the DMZ which begins to decompose at temperatures closer to 300 °C.

As mentioned earlier in this chapter, the chemical potential of H\textsubscript{2} can be increased with pressure to make the gaseous molecule far more reactive. With this in mind, an experiment was run to determine what temperature would yield appreciable amounts of water at higher pressures. A reservoir was filled to 35 MPa with a mixture ratio of 20:1 H\textsubscript{2}:CO\textsubscript{2}. A 6 µm internal diameter MOF was attached to the reservoir, fed through a resistance furnace and then attached to mass spectrometer to measure the chemical species.
from the exhaust of the MOF. A small amount (less than 0.1% of the total mixture) of argon gas was added to the reservoir to act as a baseline for measurements. As shown in Figure 2.9, water formation was observed at temperatures as low as 150 °C. This temperature is ideal for the reaction with DMZ to form ZnO.

![Figure 2.9: Formation of water at high pressure via the reverse water gas shift reaction. The MOF that was attached to the reservoir was fed into a mass spectrometer, and the water signal increases as a furnace surrounding the fiber further upstream is ramped from 100 °C to 400 °C over the course of one hour. When the HPCVD reservoir is closed, the water signal decreases quickly. Argon was also used in trace amounts as a baseline for the experiment.](image)

2.5.5 – HPCVD and processing of ZnO

There are many parameters to consider when depositing a binary compound via HPCVD and chemical encapsulation. They include factors such as deposition temperature, furnace heating profile, precursor and carrier gas ratios, length of the fiber, and numerous others. These variables are often optimized by a series of multiple depositions and intuition.
For the deposition of ZnO via the RWGS reaction, temperatures of around 250 °C were found to be optimal when all other variables are held constant. At this temperature there is sufficient water production and the DMZ does not break down and form zinc that precipitates out in the form of zinc islands like it would at higher temperatures. Good film growth occurs using a ratio of 2250:250:1 of H\textsubscript{2}, CO\textsubscript{2} and DMZ respectively. This deposition is shown in Figure 2.10. Under these conditions, the deposition creates a good film over multiple centimeters.

![Figure 2.10](image1.png)

Figure 2.10: Deposition of zinc oxide utilizing the reverse water gas shift reaction. a) Shows an optical micrograph of the transparent ZnO. b) Shows an SEM micrograph of the cross-section of the ZnO filled MOF.

Raman spectroscopy (Figure 2.11) reveals that the material deposited was indeed ZnO, but it also revealed something interesting in that there was a sufficient amount of an unknown alcohol that was created as a byproduct of the reaction. While methanol is the most likely byproduct, the spectra matches far closer to ethanol than it does to methanol. While this is a very interesting result and could be investigated for applications in fuel production and possible catalytic effects that ZnO may have on the RWGS reaction, it is beyond the scope of this dissertation. It will, however, be explored in more depth by Haw-Tyng Huang and Alex Hendrickson, junior members of the Badding group, it is not advantageous from a materials deposition point of view.
Figure 2.11: Raman spectra of the zinc oxide deposited from the RWGS reaction. The red spectrum shows a ZnO standard. The black line represents the ZnO as deposited. It should be noted that there is an impurity of an alcohol as shown by the peaks between 2800 cm\(^{-1}\) and 3600 cm\(^{-1}\). This impurity can be annealed out of the ZnO as shown in the blue spectrum which is after a 5 minute anneal at 900 °C.

Post deposition annealing is required for both the removal of the alcohol that is produced and trapped in the ZnO, but also as a method of eliminating the central pore in the deposited film. This central pore is a possible scattering site for any light that may be interacting with the ZnO and thus it would be advantageous for it to be removed. As shown in Figure 2.11, a 5 minute anneal time in a 900 °C furnace allows for the removal of the contaminants. Figure 2.12 shows that this annealing step also causes a significant crystal rearrangement within the microwire suggesting that with the proper tuning of the annealing parameters, the central pore left by the deposition can be closed to form a solid high aspect ratio microwire of ZnO.
Figure 2.12: Annealing of a zinc oxide microwire. After a 5 minute anneal at 900 °C, the structure of the crystalline ZnO has significantly rearranged itself. This annealing step was necessary for removing impurities, but it also suggests that solid microwires could be possible under the right annealing conditions.

2.6 – References


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Chapter 3

Pressure assisted melt filling of metals into silica nanocapillaries

As discussed in Chapter 1, pressure can be utilized to force liquids (metals in particular) into small capillaries. These metals can have quite high aspect ratios and the wires that are created are relatively free of impurities due to the fact that there are no chemical precursors being used. In this chapter pressure assisted melt filling (PAMF) will be discussed and the nano-structures that can be created using gallium-indium eutectic (EGaIn) mixtures.

3.1 – Pressure assisted melt filling fundamentals

The PAMF technique is largely limited to materials that have a melting point below that of the softening temperature of the silica MOFs which is around 1400 °C and also has an appropriate non-wetting surface interaction with the SiO$_2$ surface. By and large most metals of interest fit these requirement; however some other materials that may be of interest in filling the MOFs such as some polymers or tellurite glass have strong wetting properties to the silica glass, and this leads to annular film formation with a central hollow bore rather than a solid, fully filled “plug” of the desired material.

3.1.1 – Filling dynamics for PAMF

The filling dynamics are largely dominated by the capillary effect. This effect can be described using the Washburn equation.\(^1\) Neglecting any gravitational forces, which in the case of nanopores is an excellent approximation, especially at the high pressures that are used, the possible filling length $L$ is given by:

$$L = \frac{1}{2} \sqrt{(2R\gamma\cos\theta + R^2\rho)t/\eta}$$  \hspace{1cm} (Equation 3.1)
Where $\rho$ is the applied pressure, $\gamma$ is the surface tension of the metal, $\theta$ is the contact angle of the metal on the silica, $R$ is the radius of the pore, $\eta$ is the dynamic viscosity of the metal, and $t$ is the filling time.

An additional assumption that can be made is if the contact angle to the silica is greater than $90^\circ$, which is the case for most metals and semiconductors on silica, a minimum pressure can be calculated:

$$\rho_{\text{min}} = -\frac{(2\gamma/R)\cos\theta}{\text{(Equation 3.2)}}$$

where $\rho_{\text{min}}$ is the minimum amount of pressure required to fill the pore of radius $R$.

A good visualization of the minimum diameter of MOF that could be filled with various materials using pressures available to our laboratory can be seen in Figure 3.1. This is a prime example of why high pressures are required for the small nanoscale pores. If this technique was attempted with vacuum rather than high pressures, the minimum pore that could be filled with these three materials are between 20 and 30 microns (not shown in Figure 3.1). This is due to the fact that absolute perfect vacuum would only have a difference in pressure of roughly 1 atm, whereas the application of high pressures can have a pressure difference of over 600 atm when compared to atmospheric pressure.
Figure 3.1: Visualization of the smallest diameter pore that is fillable by gold, gallium and germanium. The maximum pressure that can be utilized by the current apparatus is ~680 atm, so the smallest diameter pore that can be filled with gold, gallium and germanium is 43 nm, 38 nm, and 32 nm respectively.

3.1.2 – Pressure assisted filling methods of various materials

The filling technique that is utilized to fill the silica MOFs depends largely on the melting point of the material. If the material has a melting point below the failure point of PEEK tubing or EpoHeat, a polymer tube and epoxy respectively that we use to connect the pressurized stainless steel vessel to the silica MOF, a technique such as that shown in Figure 3.2 can be utilized. Here the desired material is placed into a melting point tube that has been cleaved to approximately 1.5 cm in length. That melting point tube is then placed on the end of a cleaned and cleaved MOF, which is then attached to a high pressure reservoir. The pressure is applied and the material is driven into the MOF due to the pressure differential between the high pressure reservoir and the atmosphere which is on
the other end of the MOF. This technique has a limit of about 100 °C, so it is largely limited to polymeric materials, water, or in the case of the large portion of this chapter, gallium metal and its numerous alloys that it has with other metals.

Figure 3.2: Schematic of the pressure assisted melt filing technique for low temperature melting metals such as gallium. A melting point tube is cut to ~1 cm in length and filled with the metal of choice. One end of the nanoscale MOF is placed in the liquid metal while the other end is left open to the atmosphere. Pressure is applied and the metallic nanowire is grown as a result of the pressure differential.

There are other materials such as gold, tin, silver or germanium that could be filled, but would require a different approach for filling. A schematic of an all silica spliced fiber technique is shown in Figure 3.3. First a silica MOF with an outer diameter of about 350 µm and an inner diameter of about 75 µm is cleaned and cleaved. At this point, a 50 µm in diameter wire of the desired material is inserted into the MOF. If the wire is not available in this form (as is the case with most metals not utilized for wiring of electronics), another option is melting the desired material on a hot plate and using the assistance of a vacuum pump to suck the material into the 75 µm pore. Once the material of choice is in the MOF, it must be moved away from the end so that a fresh cleave can be done to ensure a clean
end face. This MOF is then spliced to the desirable nanoscale MOF in a Vytran glass processing instrument. Special care is taken to adjust the splicing parameter so that the splice is mechanically strong, but also delicate enough to keep the pore of the MOF open. In the case of any MOF that has a pore smaller than 5 µm, it was necessary to inflate the pore prior to splicing by applying the appropriate pressure and heat the MOF above the softening temperature of silica. Details of this inflation will be discussed later in this chapter. Finally the fiber is placed in a furnace and heated to the melting point of the desired material and nitrogen gas is applied to provide the driving force for the material to enter the desired MOF.

This technique is far more flexible and safe than other techniques that accomplish the same goal such as pressure-cell filling. It is also far easier to adapt to selective filling, and it also requires only a small amount of the desired filling material. It is also generally better for filling large arrays of MOFs rather than traditional drawing methods discussed in Chapter 1. This is largely due to the higher percentage of metals that are a part of the larger “preform”. The metals can cause instabilities during the drawing of the fiber and can lead to numerous structural irregularities.
Figure 3.3: All silica pressure assisted melt filling technique schematic.\textsuperscript{8} a) A gold wire is placed into a relatively large silica capillary. b) The wire is pushed back by a tungsten wire to create room for a clean cleave. c) The capillary is then spliced to a photonic crystal fiber (PCF) or MOF. d) The spliced section is heated to the melting point and high pressure nitrogen gas is applied. e) The PCF or MOF is filled to the desired length and then cooled for solidification.
To date, the smallest filled MOFs that have been filled using this technique with various materials is shown below:

Table 3.1: Record of the smallest metal wires created using the PAMF technique. The gallium, Gallium-Indium and tin wires were created in the Badding lab at Penn State, while the gold wire was made by the Russel group at the Max Planck Institute.8

<table>
<thead>
<tr>
<th>Metal</th>
<th>Smallest wire diameter to date via PAMF</th>
<th>Gaps in resultant wire</th>
<th>All silica splice technique required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallium</td>
<td>50 nm</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Gallium-Indium</td>
<td>50 nm</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Tin</td>
<td>150 nm</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Gold</td>
<td>120 nm</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

3.2 – Compatibility of the metal and glass MOF

One issue that has been a nuisance over the past decade in both the HPCVD discussed in Chapter 2 and the filling discussed here, is the compatibility of the silica MOF template and the materials that fill it whether they be deposited or melt filled into the capillary. There are two main issues that cause problems. The first is the thermal expansion mismatch that arises on the cooling of the MOF after filling or annealing. The second is the interaction between the surface of the silica MOF and the material that is filling it.

3.2.1 – Thermal expansion mismatch of MOFs and metals

Silica has widely been known to have an incredibly low linear thermal expansion coefficient. While this does have numerous benefits to the materials property of the silica itself such as its remarkable ability to undergo large as well as rapid temperature changes without cracking, it also poses a problem in material compatibility between the silica and other materials such as metals and semiconductors as seen in Table 1.2.

As shown in Figure 3.4, a 150 nm MOF is filled with tin and non-periodic, yet very regular breaks occur in the wire that is formed as a result of the PAMF technique. These
gaps are exacerbated when investigating much higher melting point materials such as gold, germanium, or silver. While some groups have utilized these gaps as a means for creating scattering sights within the MOF when light is guided through a neighboring core as a means to study surface plasmon-polaritons, it is not very useful in creating an ultralong, continuous nanowire for studies such as those described in Chapter 4 of this dissertation.

![Figure 3.4: An optical micrograph of a tin nanowire created via PAMF. Highlighted with the yellow circle is a gap that forms in the wire. These are seen every 50-200 µm along the length of the wire.](image)

These “breaks” in the resultant metal wire were attempted to be remedied by two methods. The first and easiest method was a very slow cooling rate of the MOF after it had been filled with the metal. This had been shown in previous studies with ZnSe to alleviate cracking issues on the micrometer scale; however, it yielded no benefits when applied to the metallic nanowires grown in this study.

The other method to alleviate the gap issue was to fill the wire and while pressure was still being applied to the liquid metal contained in the MOF, cool the wire slowly and asymmetrically so the crystallization occurs toward the source of the metal. This method did result in a smaller number of cracks in the tin wire, but it was unable to completely remove the breaks despite trials with very high pressures (680 atm) and very slow recrystallization (cooling over a 24 hour period).
3.2.2 – MOF surface interaction and reactivity with filling substance

The choice of metals or semiconductors to fill the MOFs is largely based on the intrinsic properties of that material. As mentioned earlier, gold can be used to study surface plasmon-polaritons, germanium could be filled to create single mode light guiding fibers, or some metals could be used to study superconductivity. It will be discussed in more detail in chapter 4, but superconductivity in ultralong nanowires is very interesting from a low temperature physics point of view. Tin, aluminum, and zinc were initial targets for wire creation, and each metal had its own issues that caused them to be discarded as possible metals for those studies.

Tin was discussed in section 3.2.1 where the metal would shrink when cooled causing gaps along the length of the wire. Aluminum is completely incompatible with the PAMF technique as liquid aluminum immediately reacts with the MOF:

\[
4 \text{Al (l)} + 3 \text{SiO}_2 (s) \rightarrow 2 \text{Al}_2\text{O}_3 (s) + 3 \text{Si (s)}
\]  
(Reaction 3.1)

This reaction is shown clearly in Figure 3.5, where the attempted PAMF experiment failed immediately upon the melting of Aluminum. Zinc’s interaction with the surface of the silica MOF was not advantageous as it would create annular films inside the MOF rather than forming a solid plug to be pushed with a pressurized gas into the nanopore. This could be remedied with the proper surface functionalization of the silica glass in the MOF, but that would also ruin some of the valuable properties of using the MOFs in the first place such as the atomically smooth nature of the glass surface. For the purposes of this study, a metal that has no reactivity with silica, and has the proper wetting properties to fused silica is required.
Figure 3.5: Aluminum’s reaction with a silica capillary. As can be seen from the two optical micrographs above, the aluminum (the dark portion inside the transparent silica capillary) upon melting immediately reacts with the silica capillary causing structural damage. It is clear that aluminum is not an appropriate metal for the PAMF technique.

3.3 – Gallium: PAMF’s solution for ultralong nanowire growth

Gallium is one of the more interesting metals on the periodic table. It has an incredibly low melting point second only to mercury. It is well known in the prank memories of “old school” chemists. Sam Kean’s fantastic book: *The Disappearing Spoon: And Other True Tales of Madness, Love, and the History of the World from the Periodic Table of the Elements* details the prank (as well as numerous others) in that scientists used to make spoons out of gallium metal and serve tea alongside the spoon. With the low melting point of ~30 °C, an unsuspecting guest would stir their tea and the spoon would seemingly disappear. What was actually occurring was that the spoon had melted and fallen to the bottom of the tea cup. While it has fallen out of favor with the scientific world for pranks as it is toxic if ingested, gallium’s low melting point and numerous other properties make it ideal for use in the PAMF technique.

3.3.1 – Gallium’s thermal expansion and crystal structure benefits

Thermal expansion can cause issues with numerous metals and semiconductors when confined in silica MOFs due to the mismatch between the two materials. Gallium
does have a high coefficient of thermal expansion (comparable to most metals); however, the temperature difference between the point of solidification and room temperature is much smaller. For instance, the coefficient of linear thermal expansion for tin and gallium are $23.4 \times 10^{-6} \text{K}^{-1}$ and $18.3 \times 10^{-6} \text{K}^{-1}$ respectively. Not only is gallium’s thermal expansion smaller, tin also has to cool ~207 K from its solidification point whereas gallium only requires a 5 K temperature differential to cool from solidification to room temperature. This helps to keep the gallium in one solid wire.

Gallium also has a very unusual property in that its most common crystal structure is water-like and expands upon solidification. Bismuth is the only other metal that has such a property. This is largely due to a dimer that forms in the center of the base unit of the gallium crystal. This dimer lends numerous interesting properties to the gallium solid, but a 3.1% expansion from the liquid to solid phase\textsuperscript{10} is of most interest when discussing gallium’s ability to completely fill a MOF’s nanopore upon solidification rather than having the gaps that are seen in tin, gold, and other metals.

3.3.2 – Gallium and gallium oxide’s wetting properties to silica

As discussed above, the surface chemistry between the silica MOF and the substance that is filling the MOF are very important in determining the liquid’s behavior upon filling. If the metal or semiconductor fully wets the MOF wall, it will tend to form annular films rather than solid wires. If the material does not wet the wall very well, then it will be far likely to exacerbate the gaps discussed earlier due to the material wanting to minimize contact with the silica wall. One other thing that could happen is if the pressure used to fill the MOF is released before the material is fully solidified, which could be the
case for a material like water or mercury that has a tendency to supercool and remain a liquid at room temperature, the material is likely to just flow back out of the nanopore.

Gallium metal itself does not wet silica very well with a contact angle of 126° between the liquefied metal and fused silica\textsuperscript{11}; however, gallium spontaneously forms a thin and passivating surface oxide layer at room temperature in the presence of oxygen. It is largely considered to be a nuisance,\textsuperscript{12} especially considering this oxide skin forms even at parts per million oxygen levels causing many measurements on pure gallium to be very difficult.\textsuperscript{13} It has recently been discovered that this skin can be utilized as it tends to envelope the liquid and provide mechanical stability. Because of this the metal can be molded into non-equilibrium shapes that would typically be disallowed by surface tension.\textsuperscript{14,15} The oxide skin is the key to making gallium and gallium alloy wires in the nanopores of silica MOFs as shown in Figure 3.6.

**Figure 3.6:** Filling schematic of a small pore and the difference between mercury on the left and gallium on the right. The filling of the two is similar when under pressure; however, after the release of pressure, mercury will escape out of the pore, while gallium and its alloys tend to stay in place.
Figure 3.7: Gallium oxide’s usefulness in filling a silica MOF. The gallium is filled via pressure from left to right and as shown in the first schematic, as fresh gallium is exposed to atmospheric oxygen, it will continue to create gallium oxide that will coat the surface of the MOF. This provides the stability for the gallium and its alloys to remain in the capillary after the pressure is released from the MOF.

Figure 3.7 is a schematic of the filling of the gallium and its alloys. The metal is injected into the pore, and the metal itself does not wet to the wall, but the gallium oxide that is formed on the filling front of the metal does wet the MOF as well as the gallium contained inside the oxide shell. Without the shell, the gallium metal will undergo capillary action to minimize its surface energy with the silica. This was confirmed in an experiment in which the nanopore MOF was sealed on one end and evacuated with a scroll pump for two hours. It was then transferred to an argon atmosphere where the gallium metal was filled via argon pressure. After the appropriate time for the nanopore to fill, the pressure was released and then sealed end of the fiber was opened to relieve any pressure that may have accumulated due to the filling mechanics. The gallium metal in the pore quickly “recapillaried” back toward the initial source of the gallium, observed via optical microscopy.

Figure 3.8 a shows the cross section of an empty MOF with an inner pore of roughly 100 nm in diameter and b shows an optical image of the same wire filled with the gallium metal. The wire is continuous along the length of the fiber and have been grown up to a
meter in length (verified via optical microscopy). The longest continuous wire verified via electrical conductivity was 10 cm long. These two wires have an aspect ratio of 10,000,000 and 1,000,000 respectively. Compared to what is readily available in the scientific literature, these are some of the highest aspect ratio metallic nanowires that have ever been created. The wires are also in the alpha crystal structure, confirmed via low temperature measurements on a 6 mm portion of the MOF. The superconductive transition temperature is 1.1 K which matches the transition temperature of the bulk gallium metal. This will be further discussed in Chapter 4.

Figure 3.8: Nanoscale MOF and a gallium nanowire. a) Shows an SEM micrograph of the cross section of a nanoscale MOF that measures roughly 100 nm in diameter. b) An optical micrograph (episcopic illumination) shows the gallium wire created in the pore via PAMF. The wire is continuous and remains in the pore after the pressure is released.

3.4 – Adding interesting structures to the metallic nanowires

Heterogeneous nanostructures have been of interest for their ability to add more functionality to the nanomaterial. The different structures include core-shell nanowires\textsuperscript{16–18} and particles,\textsuperscript{19–21} “pea in a pod” structures,\textsuperscript{22–24} or segmented nanowires that could be created via traditional methods.\textsuperscript{25–27} These heterogeneous structures are often created to create junctions,\textsuperscript{28} devices,\textsuperscript{29} or to simply combine the two different intrinsic properties of the materials into one location, such as combining catalytic materials with magnetic materials for site specific catalysis.\textsuperscript{30} These structures are often made in a template and two separate depositions or syntheses are done to deposit the two separate materials. For the PAMF technique this could be possible by depositing a substance in the pore of the MOF.
such as silicon as discussed in Chapter 2, and then the material is filled to create a core-shell structure. One other option that will be discussed here is filling the MOF with a material that will spontaneously create a heterogeneous structure due to the solidification of the molten material.

3.4.1 – Gallium-indium eutectic

Gallium has numerous interesting properties as discussed earlier, and many of those properties translate well when it is alloyed with other materials. One material of interest is its periodic table neighbor, indium. When the two substances are mixed they are a eutectic mixture as shown in the phase diagram in Figure 3.9. The eutectic point is at roughly 75% gallium and 25% indium by weight and has a melting point of 15.5 °C. It has many of the same properties as pure gallium where it will form an oxide skin, but it is also liquid at room temperature which has driven interest in applications such as reconfigurable electronic devices, conductive stretchable polymers, as well as ink jet printing for wearable electronics are just a few examples of applications of this liquid metal system. EGaIn has also become popular in the field of microfluidics due to its relatively low fluid viscosity, and its moldability due to the same thin oxide skin described with pure gallium.

One area of interest in EGaIn that is less studied is the unusual phase separation phenomena that exist when the system is solidified at lower temperatures. As shown in the phase diagram, it would be expected that when the EGaIn system is at its eutectic point and cooled, it should phase separate. This phase separation would be beneficial when creating heterogeneous nanowires in the nanopore MOF templates, but the EGaIn system has a phenomenon when confined to geometries smaller than 1 µm in that it will tend to alloy rather than phase separate as would be expected. We have confirmed this as shown in
Figure 3.10 where a nanowire created via PAMF that was exactly at the eutectic point was a homogeneous wire. When the wire’s composition is either gallium or indium rich; however, we are able to create heterogeneous structures.

Figure 3.9: The phase diagram of the gallium and indium system. Diagram created utilizing data collected from Svirbely and Selis. The eutectic point is 14.2% gallium by atomic percent which corresponds to roughly 25% gallium by weight.

3.4.2 – Exploring the EGaIn system by adjusting concentrations

Wires were created by mixing gallium and indium to the desired concentration ratios and then filled into the nanopore of the MOF which was roughly 100 nm in diameter. These wires are not easily removed from the MOF template, which means many of the traditional techniques for materials characterization such as SEM or TEM on the wires are
difficult. Because of this X-ray fluorescence (XRF) was used and will be described in more detail later in this chapter.

Figure 3.10: X-ray fluorescence data of three different concentrations of the EGaIn system. a) and b) EGaIn system is at 75% indium and 25% gallium by weight. a) shows an indium dominated region with gallium breaks and b) shows a gallium dominated area with indium breaks. These two areas alternate along the short length of wire that was examined via XRF. c) EGaIn system is shifted to the gallium side of the eutectic point with 90% gallium by weight. The entire wire is gallium dominated with periodic indium breaks. d) Shows the EGaIn system directly at the eutectic point. This wire is homogeneous along the length of the wire, and has a mix of both gallium and indium. The signals of gallium and indium are in arbitrary units where the highest signal is dark in color and low signal fades to white.
As seen from the XRF data in Figure 3.10, when the gallium concentration is decreased to 25% by weight, the wire will form two distinct regions. One region (A) is an indium dominated region with small gallium dominated regions and the other region (B) is the inverse where gallium regions are broken by indium regions. These regions alternate about every 10 µm. Wires that are far to the opposite side of the eutectic point at 90% gallium by weight (C), the entire wire is a gallium enriched area that still has indium signal is disrupted every 2 µm by an indium enriched spot. Finally, a wire that is exactly at the eutectic point of 75% gallium by weight (D) shows a homogeneous wire that has both gallium and indium in the mixture.

The EGaIn system is of interest upon crystallization as gallium has at least four different metastable crystal structures, many of which arise when the metal in nanoconfined. Previous studies used differential scanning calorimetry to show that there are three metastable states that the eutectic alloy will form and the phase is dependent upon the extent of confinement the alloy is under.\textsuperscript{36} Laue micro-diffraction has been done on the 150 nm EGaIn wires at the Advanced Photon Source and the results show that the wires are crystalline and that the crystal grains are close to 10 µm for a sample that is exactly at the eutectic point. Coherent diffraction imaging of the wires can be done if the exact crystal structure is determined,\textsuperscript{37} but the cryogenic temperatures required for diffraction on such a small sample and the relatively large grains that the wire freezes into makes it difficult for diffraction to be done in order to determine the crystal structure.

To alleviate this issue, a different confinement geometry was utilized where the EGaIn was dispersed via ultrasonic vibration into a poly(methyl methacrylate) (PMMA) matrix. This is shown in schematic form in Figure 3.11. This method not only increases the
amount of metal in the sample to about 3% by volume, compared to less than 0.005% in the silica capillaries, but it also creates an environment where powder diffraction is possible as there seems to be no preferred orientation of the particles within the PMMA matrix. TEM micrographs and electron diffraction in Fig 3.12 show that the particles are dispersed in a variety of sizes. Electron diffraction suggests that the smallest particles, which would match the size of the capillary environment, freeze into a hexagonal crystal structure, which does not match any known structure of gallium nor indium. The larger particles freeze into a single crystal structure. It is possible that the EGaIn did freeze into a polycrystalline material, and we were lucky enough to cut the PMMA directly through a grain in the structure, but that seems very unlikely. The crystal structure (just as with the smaller particles) does not match any known structure of gallium nor indium.

![Diagram showing the creation of EGaIn nano-dispersions in PMMA.](image)

**Figure 3.11:** Schematic of the creation of EGaIn nano-dispersions in PMMA. First the PMMA is prepared for polymerization by removal of protections groups and dried with calcium sulfate. That PMMA has EGaIn immersed into it and is exposed to an ultrasonic vibration bath for the dispersion of the EGaIn into particles. The polymer is partially polymerized and vibration is stopped allowing a gradient of particles within the PMMA. Larger particles sink while the lighter particles stay toward the top of the PMMA. While the different sized particles are moving, more heat is applied to the system to fully polymerize the PMMA.

Previous studies have suggested that the suppression of phase separation is due to the diffusion of indium atoms in the mixture being slowed by nanoconfinement.\(^{38,39}\) Our experiments above (as shown by the XRF data) show that the indium atoms can freely

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diffuse over relatively long distances through the solidification process. This experiment supports that the suppression of phase separation seen in the Ga-In system is due to metastable states that arise upon nano-confinement, as suggested by other previous studies.\textsuperscript{34,40,41} It also shows that we can control the structure of the nanowire based on the composition of the eutectic mixture that is placed in the silica capillary.

![Figure 3.12: TEM and electron diffraction of the EGaIn dispersed particles. The samples are prepared using a cryogenic ultramicrotome in the Materials Characterization Lab at Penn State University. a) Shows a rather large EGaIn particle amongst numerous smaller particles. This technique is not very monodispersive in particle sizes. The electron diffraction shows that the large particle is single crystal in nature and does not match any known gallium nor indium crystal structure. b) A small cluster of sub 200 nm particles is observed with a crystal structure that once again does not match any known gallium nor indium structure. The structure appears to be hexagonal in nature.](image)

### 3.5 – XRF of EGaIn nanowires

X-ray fluorescence resolution has traditionally been limited to hundreds of nanometers\textsuperscript{42} which was not well suited for numerous biological, environmental, and material science samples. Sector 26 of the Center for Nanoscale Materials in the Advanced Photon Source at Argonne National Laboratory developed an X-ray microscopy facility that incorporates diffraction, fluorescence and full-field imaging capabilities.\textsuperscript{43} The Hard X-ray Nanoprobe Beamline incorporates Fresnel zone plate optics for focusing of the X-ray beam rather than the more traditional KB mirrors. This provides an X-ray spot that is sub 30 nm and is quickly approaching 10 nm resolution. The beamline can operate from 3
to 30 KeV making it ideal for investigating gallium (10.3 KeV K-edge) and indium (4.2 KeV L-edge). The beamline is also equipped with a precision laser sensing and control system. This system monitors the position of the sample and scanning zone plate in three-dimensional space. The measurements are then fed back to a digital signal-processing system which controls piezoelectric-actuator-driven flexure stages underneath the scanning zone plate in order to maintain the proper zone plate to sample orientation.

A cryogenic cooling system uses liquid nitrogen to hold the temperature of the specimen within 0.01 K of the set temperature. This is very important as the slightest change in temperature can cause thermal drift. This is seen in Figure 3.10 as the nanowires themselves are quite straight as seen in the optical micrographs of them; however, they appear to be quite curvy when looking at XRF data. Many of the XRF maps that are shown took hours to collect. The cooling system utilized the boil-off from the liquid nitrogen to cool the samples and from time to time it would “burp” liquid nitrogen into the cooling system, and so constant monitoring of the measurement was required.

3.6 – Post processing of MOFs to create smaller pores

The superconductive properties of 1-D metallic nanowires have been of interest for numerous years. A true 1-D system for superconductive studies is considered to be a nanowire that has a diameter that is less than the coherence length, which is the distance between the electrons that form Cooper pairs of the metal of interest. A basic tenet of solid state physics is that in 1-D systems superconductivity should be destroyed due to thermal\textsuperscript{44–47} or quantum phase fluctuations\textsuperscript{48–52} While thermal fluctuations has been extensively shown experimentally, quantum phase fluctuations have more difficult to conclusively show as most studies are done using nanowires that are only a few microns in length and
between 50 and 200 nm in diameter. Studies have shown that the contacts to these nanowires to take measurements can influence its superconducting behavior over micrometer length scales. While these proximity effects are of great interest, they make it difficult to separate the intrinsic superconducting behavior of the wire due to 1-D confinement from behavior arising from the contacts made to the nanowire. By having longer wires made in MOF templates, we plan to overcome these issues.

As discussed earlier, metallic wires were created using gallium and EGaIn as the two substances were best suited for creating continuous, electrically conductive wires. To study 1-D superconductivity, it is important that the diameter of the fiber is smaller than that of the coherence length of the metal being used. Gallium’s coherence length is around 100 nm. MOFs with an inner pore of 150 nm were the smallest available for initial studies of these kind and thus there was a need to make the pores smaller.

**3.6.1 – Depositing thin films in nanoscale MOF pores**

As discussed in Chapter 2, the Badding lab has developed high pressure methods of depositing annular films of various materials. These films can be used to narrow the pores of MOFs so that the metal can be inserted into a pore that is of the proper size. In order to have the same characteristics of the MOF, the films that are deposited need to be very uniform in nature over long lengths. In order to accomplish this, furnaces needed to be developed that were uniform over a long length. Additionally the deposition needs to be slow so that the timing of stopping the deposition can have a larger time window. A typical silicon deposition using our systems deposits roughly 300 nm per hour of deposition. Because of this, concentration of the precursor, silane, was lowered from its typical concentration of ~3% of the total pressure down to about 0.1%. Additionally the...
temperature of the deposition was lowered from the typical deposition temperature of 400 °C down to 300 °C where the deposition rate is slowed, but not to the point where the deposition is negligible.

Figure 3.13 demonstrates a good example of the nano-pore of the MOF being closed in from around 150 nm to roughly 35 nm in diameter. While this method showed a good amount of promise there were a few drawbacks to narrowing the pore via this technique. First is that the precursor concentration naturally creates a gradient as the deposition occurs along the length of the MOF. At the micron length scale, a difference in 10-15 nm from one end of the deposition to the other is not an issue, but when dealing with these very small pores, and a system that is very dependent upon the diameter, these differences can cause issue with consistency in the low temperature measurements. Due to the concentration gradient along the length of the fiber, the deposition was not even and formed more of a taper than a consistent annular film. The other issue that arose from this deposition was that it appeared to have a very high rate of deposition when first exposed to the heat of the furnace. Whether this is some sort of thermal shock or just a large concentration of silane at the beginning of the fiber, it still caused the fiber to plug and halt deposition further down the MOF. This was overcome by adding an additional small furnace to the front of the deposition furnace to gradually heat the gas before it gets to the deposition region.
Figure 3.13: Pore narrowing via HPCVD of silicon. Silane is pyrolized via HPCVD as discussed in Chapter 2. The pore here narrows from roughly 150 nm to about 35 nm in diameter. The inner pore that remains appears to be quite a different shape than the perfectly circular MOF shown on the left.

3.6.2 – Atomic layer deposition at high pressures in the MOF

Atomic layer deposition (ALD) is an alternative deposition technique that could be used to create atomically precise film thickness inside the MOFs. ALD differs from CVD in that rather than sending one particular gaseous mixture and having bulk deposition of a material, there are two separate gas mixtures that each deposit a monolayer of precursors in a self-terminating mechanism. After the system is purged to remove any unreacted precursor, the second self-terminating precursor is sent to react and form a new monolayer. High pressure ALD has not been investigated to the best of our knowledge, and upon a literature search, “high aspect ratio” ALD is limited to be on aspect ratios of a few thousand,\textsuperscript{58} where as we are attempting to fill pores with aspect ratios closer to a million.

3.6.3 – Aluminum oxide ALD as model system for high pressure deposition

Aluminum oxide deposition was chosen as the first system to be investigated for high pressure ALD as it is one of the most investigated ALD reactions and the mechanism is very well known.\textsuperscript{59,60} The reaction is outlined in Figure 3.14 and it starts with a silica
substrate, in this case, the silica substrate is the MOF wall. The MOF surface is ultraclean and nearly devoid of any hydroxyl groups as these groups tend to cause scattering of light, so the surface was specifically designed to not have them present. Trimethylaluminum (TMA) is then reacted with the surface of the MOF, and then purged leaving a monolayer of aluminum bound to the MOF wall and two methyl groups still bound to the aluminum atom. The MOF is then purged with ultrapure nitrogen gas (which is also used as the carrier gas for the precursor molecules) to remove the unreacted TMA and the methane byproduct of the reaction. Water is then sent into the MOF to displace the methyl groups on the aluminum and replacing them with hydroxyl groups. After the fiber is purged once more, the TMA is once again used to react with the hydroxide groups and the process is repeated.

The deposition equipment that the Badding group uses for HPCVD was used for this deposition and there were many drawbacks associated with it. This largest shortcoming is the fact that the HPCVD system is not equipped to switch from one gas to another efficiently. Large amounts of precursor is lost between the switching from TMA to water in the reaction. Due to this issue, only very thin layers (less than 1 nm) of aluminum oxide were able to be deposited for these preliminary studies. Traditional methods such as SEM were not appropriate for determining if the aluminum oxide was deposited.
3.6.4 – Waveguide Raman and its ability to detect monolayer growth

The Badding lab has developed a method to monitor monolayer growth within a specialized MOF which has numerous pores surrounding a solid silica core as shown in Figure 3.15. This solid silica core is capable of guiding visible light over very long lengths, but a small amount of the light “leaks” out into the surrounding pores of the MOF. This allows for examination of a material that has a very high surface to volume ratio. It is very similar to Fourier transform infrared spectroscopy and the use of an attenuated total reflectance crystal, in which the surface is probed far more than the bulk.

Figure 3.16 shows successive precursors of TMA (referred to from here out as step A) and water (step B) being sent down the waveguide Raman MOF. There are four peaks of interest in the Raman spectra. First are the symmetric and antisymmetric methyl
stretches located at 2925 cm\(^{-1}\) and 2982 cm\(^{-1}\) respectively. These two stretches correspond to the methyl groups that are attached to aluminum atoms. These two peaks are only present after step A has been done and step B has yet to occur. The other two peaks are at 2910 cm\(^{-1}\) and 2960 cm\(^{-1}\) which correspond to the symmetric and antisymmetric stretches of methyl groups that are bound to silicon atoms on the wall of the MOF itself. As shown in the Raman spectra, these methyl groups are unreactive with step B of the ALD cycle and they remain at the MOF’s surface through successive cycles of A and B. These methyl groups are not likely to cause any materials deficiencies; however, if they are necessary to be removed, the MOF can have the surface hydrated by flowing water through the MOF and heating it to cause hydroxyl groups to populate the silica surface. By doing this the methyl group will no longer bind to the silicon atom in the MOF wall as it is already populated by a hydroxyl group.
Figure 3.15: Waveguide Raman MOF. An SEM image shows the cross section of this wire. Finite element modeling depicts the optical intensity of 632.8 nm guided through the central core. b) a small amount of the light intensity leaks into the surrounding pores providing an excellent opportunity to probe the surface of the pore rather than the bulk that may be deposited into the pore.\textsuperscript{61}
Figure 3.16: Waveguide Raman spectra of HPALD of aluminum oxide. The red line represents a spectrum taken after step A of the cycle. The blue line is the spectrum after step B of the cycle. Upon successive steps, the two spectra appear to be very similar to the two spectra shown here.

Monolayer coverage was monitored by means of a cutback measurement in which the fiber is gradually shortened from the end that is not coupled into the Raman microscope. The antisymmetric methyl vibration of the methyl group attached to the aluminum atom after step A of the deposition was monitored for different lengths of the same waveguide Raman MOF. As shown in Figure 3.17, the signal decreases linearly with fiber length indicating that the coverage along the entire length of the fiber is consistent. This chemistry is interesting as it opens up the ability to deposit atomically accurate film thicknesses and ALD also opens up numerous materials that may be very difficult to deposit via HPCVD. Here the precursors are stored in separate high pressure reservoirs and so the need to carefully select precursors that will not react with one another like in HPCVD is no longer
applicable to the HPALD system. This chemistry is going to be continued by junior member of the Badding lab, Alex Hendrickson.

![Graph](image)

Figure 3.17: Analyzing the monolayer coverage of HPALD via fiber cutback method. This is a plot of the normalized peak intensity of the antisymmetric CH$_3$ stretching peak attached to the aluminum atom located at 2960 cm$^{-1}$ as a function of the MOF length. The linear fit shows even coverage of the monolayer.

3.6.5 – Tapering of MOFs using Vytran glass processing station

One of the greatest tools available in the Badding lab for post draw processing of fibers is the Vytran GPX-3000 that was purchased in 2014. The system allows for even heating of MOFs and the ability to splice fibers to hold high pressures as well as inflate and taper the fibers for a variety of reasons including but not limited to creating couplers, spectral filters and nonlinear optical elements. The pressure required to keep a cylindrical hole from collapsing is related to the surface tension of the particular liquid by:

\[ P = 2\gamma/d \]  

(Equation 3.3)

Where $P$ is the hydrostatic pressure to maintain the hole diameter. Any pressure higher will cause an inflation and lower pressures will allow for the collapse of the hole, $\gamma$ is the surface tension of the liquid and $d$ is the diameter of the hole.
While the viscosity of silica glass does change very rapidly with respect to temperature close to the softening point of 1700 °C, overall, the surface tension does not change much with temperature. Using a very commonly-quoted value of 0.3 J/m$^2$, Equation 3.3 can be simplified in terms of pressure in bar and hole diameter in micrometers as:

$$P \text{ (bar)} = \frac{6}{d \text{ (µm)}}$$  \hspace{1cm} (Equation 3.4)

As an example, if the MOF has an inner pore of 1 µm, it would require 6 bar to maintain that hole diameter. Pressures below 6 bar would cause the hole to collapse and pressures above 6 bar would cause the hole to inflate.

We have utilized this method for three different applications. The first is that when performing the PAMF in MOFs with materials that have melting points higher than 100 °C (the failure point of PEEK tubing traditionally used to hold pressures in the MOF). The MOF that is spliced to a larger MOF containing the desired filling material is often small for the needed applications, such as nanowires. Any MOF that has a diameter of less than 5 µm, it is necessary to slightly inflate the pore(s) of the MOF so that the splice can be done without them collapsing into solid silica. An example of this is shown in Figure 3.18.

![Figure 3.18: All glass fiber PAMF technique via glass splicing. The MOF on the left is a 100 nm single pore fiber that was ballooned via high pressures and heat, cleaved and then spliced to a 70 µm fiber on the right. Without the ballooning of the pore, the splice would have failed due to a collapsed nanopore and thus no filling could be obtained.](image-url)
The second technique is to utilize the tapering of the MOF to smaller sizes for the purposes of creating the 1-D superconducting nanowires. As shown in Figure 3.18, a MOF with a nanopore of roughly 150 nm can be tapered down to a size of about 35 nm. This allows for the pores to be altered after they have been drawn by our collaborators at Southampton University. One major drawback to this method, however, is the fact that it is not very repeatable from trial to trial, despite having the exact same parameters. It is very similar to the issues with HPCVD of silicon in the nanoscale MOF pores in that it’s reliably consistent when dealing with microscale pores to within 20-30 nm, but when on the nanoscale, the exact same taper can be done on the same fiber and the results could be very different from one another. Luckily, our collaborators were capable of drawing nanoscale MOFs for our 1-D superconductivity studies, as they were capable of drawing a fiber that is roughly 60 nm in diameter, and so the need for tapering of fibers to consistent waist diameters is no longer needed.

The last technique involves the 60 nm MOF that was infiltrated with gallium metal. When performing any superconductive studies on these wires, it is necessary to cut the MOFs into smaller sizes to fit in the refrigeration units. When cutting the wires to 6 mm pieces, roughly one out of every seven gallium wires with a diameter of 150 nm were able to be contacted externally with a small droplet of gallium metal. This is likely because when the gallium wires are cut they are either still liquid as gallium has a tendency to supercool, especially when placed in confined geometries, or they are solid and in either case, the cleaving of the fiber causes the gallium wire to come out of the fiber ends. This was remedied by cutting the MOFs under a small puddle of molten gallium so that once it is cut, rather than air rushing into the voided space, gallium rushes in. This increased the
success rate to roughly one out of every three that successfully make electrical contact to the nanowire in the MOF. When the 60 nm MOF was filled and cut, the success rate dropped drastically to one out of every 100 making electrical contact. To make the success rate more reasonable, the 60 nm fiber was inflated every 6 mm along the length of the fiber using ~500 bar of ultrapure nitrogen gas and the Vytran glass processing station. After it was filled with the gallium metal, it was carefully cleaved at the inflated region and the success rate became a much more reasonable 25% success rate. Now that sub 100 nm nanowires of gallium have been created and electrical contact has been made, transport measurements at low temperatures will be explored.

3.7 – References


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Chapter 4

Superconductivity studies of ultralong metal nanowires

Strictly speaking, superconductivity is destroyed in any 1-D system due to phase fluctuation, whether they be thermal or quantum.\(^1\)\(^-\)\(^8\) This effect has been investigated using mostly amorphous and polycrystalline nanowires that are typically a few microns in length and between 50 and 200 nm in diameter. The important question of where quantum fluctuations begin has remained controversial. Previous studies have shown the role of the electrodes in affecting the behavior of the nanowires. Ultralong, high quality nanowires should resolve these issues. This chapter will discuss the superconductive properties of pure gallium wires as well as EGaIn wires, some of which are homogeneous and some of which are heterogeneous in nature.

4.1 – Superconductivity in pure gallium nanowires

The synthesis of pure gallium wires was discussed in Chapter 3. These wires were created using the PAMF technique and had a diameter of roughly 150 nm. The coherence length of gallium is \(~100\) nm, and so as expected and shown in Figure 4.1, the gallium wires act largely like bulk gallium in that the superconductive transition temperature (Tc) is at 1.1 K. These wires did provide useful information in that the wires had a resistance that is roughly 1.6 times higher than bulk gallium. Having a resistance this close to bulk gallium shows that the wires are of very high quality. This is coupled with the residual-resistance ratio, which is quite high and indicates that these wires are of higher quality than those that are created via e-beam assisted evaporation and crystalline nanowires grown by electrodeposition in track-etched membranes. The reasons for this quality is likely two fold.
First is that we are starting with very high quality metals, often in the range of 99.99% purity. These metals are not created by any sort of chemical reaction, and are only subjected to physical changes such as melting and solidification. The other possible reason for this high quality is the MOF itself. The walls of the MOF are nearly atomically smooth. This would result in less scattering sites for the electrons traveling through the wire during transport measurements.

Figure 4.1: Transport measurement of 150 nm gallium wire. This wire is 6 mm in length and shows a transition temperature at 1.1 K which is the same as a bulk sample of gallium.

4.1.1 – Sub 100 nm gallium wires

The diameter of the wire has to be smaller than 100 nm to have a chance of studying any 1-D superconducting phenomena. The methods outlined in Chapter 3 of this dissertation that involved any deposition of materials on the wall of the nanopore of the MOF would not be ideal due to the fact that the glass MOF must be inflated to ensure proper contact to the metallic nanowire. If this inflation is done prior to the deposition, the pockets that are created will disrupt the flow of precursors through the MOF, and this turbulence would cause issues with conformal coatings over long lengths. Efforts were
made to create a smaller pore in the MOF by tapering the fiber; however, this tapering effect would cause the resulting nanowire to not have a consistent diameter over the long length scales that are needed for this study. Because of this our collaborators at Southampton University were asked to and successfully were able to create a MOF that as shown in Figure 4.2 has a diameter that was ~70 nm and tapered over 50 meters to ~50 nm. This slope of 0.0004 nm/mm difference would mean that a MOF that was cut to our normal low temperature experiment size of 5 to 6 mm would have a diameter difference of 0.002 to 0.0024 nm from one end of our metallic nanowire to the other. This is small enough of a difference to effectively say that the nanowires have a constant diameter over the lengths that we are studying.

Figure 4.2: SEM of the cross section of the sub 100 nm MOF. These two pores are on the opposite ends of a 50 m spool of fiber. The first has a diameter of roughly 70 nm and the second has a diameter of roughly 50 nm. This 20 nm difference over 50 meters is gradual enough that it can largely be ignored over a length of our samples which are typically 5-6 mm in length.

It made most sense to start with the 50 nm end of the wire to push as far into the 1-D realm as possible. Figure 4.3 shows the transport measurement of one of these wires, and it is still acting as though it is bulk in nature. There is no evidence of thermal nor quantum phase slips in the pure gallium wire. While these results are interesting in that
they show a wire that is theoretically 1-D in nature and does not show any signs of decreased superconductivity. It would be beneficial to see a system where the superconductivity does indeed break down. There are signs of 1-D superconductivity in a pure gallium wire, but created via a different mechanism.

Figure 4.3: Transport measurements over various magnetic fields of 50 nm gallium wire. This wire is once again acting in a bulk gallium manner. No evidence of quantum or thermal phase slips are seen.

4.1.2 – Core-shell nanowires created via phase separation of EGaIn

As mentioned in Chapter 3, heterogeneous structured nanowires can be created by adjusting the relative concentrations of gallium and indium in the EGaIn system. One composition that was of interest due to its transport measurements in a 150 nm diameter MOF was a 90% gallium by weight mixture which is heavily gallium doped when compared to the eutectic point (remember that the eutectic point is 75% gallium by weight).
As shown in Figure 4.4, the wire has a relatively large percentage of resistance become superconducting close to 2 K. This accounts for roughly 93% of the wire’s total resistance. The additional 7% can be assigned to the alpha-phase of gallium as it has the indicative Tc of 1.1 K. One observation of note is that the transition at 1.1 K is not a clean superconductive transition. These pieces of information has lead us to believe that the wire is core shell in nature where the pure gallium precipitates out of the wire and is surrounded then by the EGaIn system. Considering that the liquid EGaIn both prefers the cold walls and the EGaIn wets the silica wall of the MOF more than pure gallium, it is reasonable assume that the wire will have some sort of core-shell structure, even if the core does not run the full length of the wire.

![Figure 4.4](image1)

**Figure 4.4:** Transport measurements of a 90% gallium by weight 150 nm wire. The first shows a rather large superconducting transition at roughly 1.5 K. The second image shows a far more sluggish transition between 1.1 K and 0.8 K. This sluggish transition could be evidence of quantum and thermal phase slips, but more studies are needed to confirm.

This mixture of 90% gallium by weight was used in the MOF with the 50 nm inner diameter pore and the transport measurements for that wire were just as interesting. As shown in Figure 4.5 the transition at 1.1 K is still present, but it does not completely go to 0 ohms of resistance. The residual resistance is roughly 300 ohms. These studies will be continued by Jiang Wei of the Chan group in the physics department here at Penn State.
University. The concentrations of the components of the EGaIn system will continue to be investigated as well as other gallium mixtures including the binary systems with zinc, tin, and aluminum.

![Graph](image)

Figure 4.5: Superconducting transition at 1.1 K in a 90% gallium by weight, 50 nm wire. This wire shows that even to the lowest attained temperature of 0.5 K, the nanowire still does no fully reach superconducting status. The residual resistance is 300 Ω.

4.2 – Single-fluxon controlled resistance switching in ultralong EGaIn nanowires

The search for interesting superconducting physics in these wires was not completely void in these studies. One particular wire geometry and material profile became quite interesting and will be discussed here. Modern techniques have made it possible to observe a dramatic modulation of resistance induced by the addition of a single electron into a quantum dot, such as a single electron transistor.\textsuperscript{13–18} Recent experiments have shown that it is also possible to detect electrical signatures due to a change in the state of a single electron spin in a variety of physical systems.\textsuperscript{19–22} Single flux quantum sensitivity has also been observed in superconducting loop devices based on Josephson junctions.\textsuperscript{23,24} However, the size of the unit based on this structure is still larger than tens of micrometer.\textsuperscript{25} We report a switching between a superconducting and a resistive state by
the addition of a single magnetic flux quantum in sub- 150 nm geometry. This is made possible by the availability of centimeter-long superconducting EGaIn nanowires with multiple gallium nanodroplets residing along the length. This “peas in a pod” configuration of two superconducting materials with different transition temperatures and critical fields is crucial for this purpose; the normal gallium nanodroplets surrounded by superconducting EGaIn alloy in 150 nm diameter wire are natural locations where fluxons can be trapped. Large portions of this chapter, including numerous figures are reproduced with permission from “Single-Fluxon Controlled Resistance Switching in Centimeter-Long Superconducting Gallium-Indium Eutectic nanowires” Copyright 2015 American Chemical Society.

4.2.1 – Pea pod structured EGaIn nanowires

The nanowires studied in this experiment were created utilizing the PAMF technique discussed earlier in this dissertation. The wires were made using a 75.5% gallium by weight EGaIn mixture. The wires are typically grown ~20 cm at a time and then cut into 6 mm segments to fit easily in the physical property measurement system that is placed in the refrigeration unit for low temperature studies.

As shown in Figure 4.1, a pure gallium wire shows a superconducting transition at 1.1 K, same as the bulk value. The room temperature resistivity value of pure gallium wire is 1.6 times the bulk value. This indicates that the nanowires inside the glass fiber are of higher quality than those fabricated by e-beam assisted evaporation and also those grown by electro-deposition in track-etched membrane. EGaIn nanowires with gallium concentration slightly higher than the eutectic point (75% Ga by weight) show two resistance steps, the first from 11 kΩ to 60 Ω between 3.5 and 5 K and the second to zero
resistance more sharply at 1.1 K as seen in Figure 4.6. This can be understood as the phase separation of the wire into two distinct regions. The first can be assigned to an alloyed gallium-indium material. This is the first report of any superconducting transition for an alloy of gallium and indium. The second transition matches the Tc of bulk gallium.

![Graph showing resistance as a function of temperature](image)

Figure 4.6: Resistance as a function of temperature of 75.5% by weight gallium wire that is 150 nm in diameter. A two stage superconducting transition is observed. The first is around 3.5 K and is assigned to an alloyed EGaIn material. The second is at 1.1 K which matches pure gallium.

We have directly confirmed that the phase separated residual gallium forms nanodroplets surrounded by EGaIn by X-ray fluorescence (XRF) spectroscopy as seen in Figure 4.7. The gallium nanodroplets are likely to be of different sizes, residing randomly along the nanowire like peas in a pod. The droplets are predicted to be random in size and location due to the fact that the inner wall of the MOF is nearly atomically smooth and thus there are no seeding locations for the gallium to start to phase separate from the mixture. If all gallium nanodroplets were very small, the resistance of the nanowire would remain
zero so long as EGaIn is superconducting, independent of whether the gallium nanodroplets are normal or superconducting. We assign the 60 Ω resistance to a relatively large normal Ga nanodroplet with very thin EGaIn layer, which is driven normal by the excitation current of 5 nA.

Figure 4.7: XRF and schematic of the gallium droplets in the nanowire. Shown first is the XRF data of gallium collected at the Advanced Photon Source at Argonne National Laboratory. The scale to the right has low gallium signal in the purple and blue and high gallium signal in reds and oranges. Highlighted in the XRF 2D plot are two “hot spots” which are evidence of pure gallium droplets that are located throughout the wire. The schematic shows a good representation of the wire based on the transport measurements and XRF data.

This assignment is confirmed by voltage–current measurements that show many steps in voltage with increasing current suggesting the presence of multiple gallium nanodroplets with different diameters and surrounded by EGaIn shells of different thicknesses with different critical currents which range from nanoamps to tens of microamps in this work. The critical magnetic fields at which vortices can tunnel through the EGaIn shells also depend on the thickness of the EGaIn shells for a fixed excitation current; this is confirmed by R vs H scanning at fixed current as shown in Figure 4.8.
Figure 4.8: Resistance vs magnetic field of the EGaIn nanowire. Measurements were made after cooling from 8 K under zero magnetic field and no fluxons trapped in the small gallium droplet initially. The current is fixed at 10 µA (a), 30 µA (b), and 60 µA (c). The critical field depends on the EGaIn shell surrounding the gallium droplets, not the droplet itself. The critical magnetic fields which can tunnel the EGaIn layers are different as the shell’s thickness changes due to varying gallium droplet sizes. The various steps in (b) and (c) confirm the various sizes of gallium droplets located in these wires.

4.2.2 – Hysteretic resistance switching behaviors

The qualitative difference in the magnetoresistance below and above the gallium Tc of 1.1 K is quite interesting as shown in Figure 4.9. When the temperature is 1.2 K, the magnetoresistance stays constant at 60 Ω at low fields and increases with magnetic field. When the magnetic field is higher than 500 Oe, the wire’s resistance plateaus to the normal state value of 11 kΩ near 2800 Oe. The critical magnetic fields will be designated as Hc1 and Hc2 to correspond to the low and high critical fields respectively.
Figure 4.9: Magnetoresistance of the EGaIn nanowire. (a) The magnetoresistance results are qualitatively different below and above Tc = 1.1 K. At T = 1.2 K, the magnetoresistance results show that resistance (R) stays constant at 60 Ω at low field and increases with magnetic field (H) for H > 500 Oe, which plateaus to the normal state value of 11 kΩ. The magnetoresistance at 0.5 K shows a two-step transition. A sharp transition occurs at a specific value 490 Oe, which we designated as Hc1, and then there is a gradual increase in resistance toward the normal state value with increasing magnetic field. There is no well-defined critical field for the second transition. For specificity, we choose Hc2 as the field value where resistance of the nanowire is 90% of the normal state value. Between Hc1 and Hc2 the EGaIn is in the mixed state. (b) Hc2 as a function of temperature (T). Beyond Hc2(T), the EGaIn is normal.

When the wire is held below the 1.1 K Tc of the pure gallium droplets, there is a hysteretic switching event that occurs between two resistive states of 0 Ω and 60Ω as shown in Figure 4.10. In this case, when the magnetic field is increased to Hc1, the resistance abruptly jumps from zero to 60 Ω and stays at this value even as the magnetic field is returned to zero. When the magnetic field is swept to the negative field, the resistance drops back to zero at a point specified as -Hc1’ followed by returning to 60 Ω when the field reaches the point of –Hc1. This behavior continues as the magnetic field is swept back to the positive magnetic field position and follows a symmetric loop. One thing of note is that the absolute value of Hc1’ is always less than that of the absolute value of Hc1. If this loop is attempted at 1.2 K (slightly above the Tc of pure gallium), this hysteretic loop is no longer observed.
Hysteretic behavior was also observed in resistance when temperature was swept in cooling and warming cycles with the magnetic field held constant. During the warming process the superconducting transition to 60 Ω is found at 1.1 for any field below 330 Oe as shown in Figure 4.11. The same Tc is found when the wire is cooled under zero magnetic field irrespective of the maximum temperature reached in the warming cycle. Similarly, no hysteresis is seen in a temperature cycle under 200 Oe if the maximum temperature is only increased to 2 K; however, if the temp is increased to 8 K in the cycle, then the Tc is suppressed to 0.8 K during the cooling portion of the cycle under that same 200 Oe field.
A complete view of the hysteretic behavior in both magnetic field and temperature scans can be seen in Figure 4.12.

![Figure 4.12: Three dimensional plot of resistance as a function of magnetic field and temperature. In the first plot temperature is fixed at various temperatures and resistance shown as a function of magnetic field. The second has various fixed magnetic fields and resistance shown as a function of temperature.](image)

A good summarization of the hysteretic behavior in both magnetic field and temperature scans can be seen in Figure 4.13. No hysteretic behavior is seen if the measurement path is kept inside the black solid line as shown in paths a and d. This black line represents Hc1 as a function of temperature of the EGaIn, the phase boundary separating the Meissner state and the mixed state. We define this zero resistance state obtained at the end of paths a or d as state A. Hysteretic behaviors happen when the black line is crossed during the measurement such as paths b and c. Although both paths b and c end at the same low field and low temperature region, the resistance is different in that b ends in a superconductive state and c ends in 60 Ω resistive state. These final states are referred to as state B and C respectively.
Figure 4.13: History dependent measurement of the transition temperature and critical magnetic field. The orange line coincides to the Tc of a pure gallium nanowire in a zero field, and the green line corresponds to the transition temperature of a gallium nanodroplet in the presence of magnetic field. The solid black line shows Hc1 as a function of temperature of the EGaIn shell. When the magnetic field is < Hc1, the EGaIn is in the Meissner state. When Hc1 < magnetic field < Hc2, EGaIn is still superconducting but magnetic fluxons can freely tunnel into the wire. The black dotted lines schematically separates regions of magnetic field that would capture different numbers of fluxons. Paths a, b, c, d show four different measurement scan paths where we begin by cooling from 8 K under no magnetic field. The paths have two different colors. Blue represents a 0 Ω state while the red represents a 60 Ω (or higher) state. Note that switching between these two states are seen in a, b, c. This switch is not present in path d as it remains superconductive throughout the path.

4.2.3 – Fluxon trapping model

The hysteretic resistance switching behavior and the three different history dependent states can be understood by a fluxon trapping model. As noted above, normal gallium nanodroplets are obvious locations where fluxons can be trapped considering the EGaIn shell that surrounds these droplets. One particular location that is possible is in a very small gallium droplet. As mentioned earlier there is no real control over size or location of these droplets, so one could imagine a fluxon going through a relatively small
gallium droplet and not have the ability to leak out provided that the surrounding shell of EGaIn is in a superconductive state. While this simple one droplet fluxon trapping model is the simplest, it does not describe the system viewed here as if the fluxon was trapped in one small droplet, this would not cause a resistive state as the superconductive current could simply flow by the gallium droplet unhindered. Because of this, a more complex model is needed.

The simplest model that can exhibit both trapped fluxons and a nonzero resistance is one that contains two gallium nanodroplets of different sizes in close proximity to one another. This model fits the states A, B and C. These states include a zero fluxon (A), one fluxon (B) and two fluxons (C) that are trapped in a small droplet located near a larger droplet. The thin EGaIn layer surrounding the larger droplet behaves much like a weak link not capable of capturing a fluxon, and the 60 Ω resistance state appears when the larger gallium droplet becomes normal. This is the case when the temperature is raised above the orange line in path a in Figure 4.13. The orange line is independent of external magnetic field because the gallium droplet “sees” no magnetic field due to the Meissner effect of the EGaIn shell. The Meissner effect also assures that no fluxon is captured by the smaller gallium droplet.

In the case of path b, when the black line is crossed from high to low temperatures, a single fluxon is trapped by the smaller gallium droplet. As a result of the magnetic field due to the circulating currents supporting this fluxon, it is necessary to go to a lower temperature before the larger gallium droplet becomes superconducting. This temperature is designated by the bright green line on Figure 4.13. This green line separates the superconducting and normal phases of the larger gallium droplet in the presence of the
magnetic field due to a single trapped fluxon in the smaller nanodroplet and the external field.

![Diagram of regions I and II](image)

Figure 4.14: A model with two neighboring gallium nanodroplets that is consistent with all the experimental observations. The different microscopic states of the two neighboring gallium nanodroplets controlling the zero and 60 Ω states of the nanowire as shown in regions I (low field) and II (intermediate field) of Figure 4.14. Each arrow depicts a fluxon. Superconducting and normal regions are shown respectively in blue and red. The region of direct/inverse proximity effect between normal gallium nanodroplets and superconducting EGaln shell is shown by gradient color between blue and red. The smaller gallium nanodroplet is surrounded by a sufficiently thick EGaln shell that makes it possible to trap 1 or 2 fluxons when EGaln is superconducting. The diameter of the larger gallium limits the thickness of the surrounding EGaln and prevents the trapping of even 1 fluxon. When the larger gallium nanodroplet is superconducting, the nanowire shows zero resistance. 60 Ω appears when the larger gallium nanodroplet is driven normal by one trapped fluxon with additional external magnetic field in region II or by two trapped fluxons in the smaller nanodroplet in both regions I & II. The regions I and II are defined in the phase diagram of Figure 4.14.

Finally, along path c, when the black line is crossed at a much higher magnetic field than that in the path b, two fluxons are trapped in the smaller nanodroplet. The circulating current is now so large that the neighboring large gallium droplet is incapable of superconductivity, even at zero magnetic field and the lowest temperature achieved in this study of 0.5 K. This explains how a state with nonzero resistance (in this case 60 Ω) can
be stable even under a magnetic field of 0 Oe. The stability is due to the trapping of fluxons in the smaller gallium nanodroplet while the resistance is from the larger droplet. We note that the number of trapped fluxons depends on the external magnetic field. Figure 4.14 schematically depicts the regions that trap zero one and two fluxons by dashed lines in the phase diagram in Figure 4.13.

4.2.4 – Modeling fluxon trapping in the gallium nanodroplets

The model explained above is qualitatively consistent with all the observations. It is not possible to make the model quantitative due to the lack of detailed and precise information about the configuration of the gallium nanodroplet pair. Semi-quantitative statements can be made regarding the plausibility of the fluxon trapping model. According to the XRF data, the gallium droplets are elliptical in shape with dimensions ranging from tens to hundreds of nanometers. It is reasonable to infer that when the long axis of the larger elliptical gallium droplet reaches 300 nm, its width would be close to 150 nm, the diameter of the MOF’s inner pore. The outer skin of this droplet would be the EGaIn shell forming a weak link which is incapable of capturing a fluxon. The long axis of the smaller nanodroplet is likely smaller than 300 nm. The distance between two gallium nanodroplets should be larger than the magnetic penetration length $\lambda$ (about 10 nm) but smaller than the coherence length $\xi$ (about 40 nm) of the EGaIn shell. Thus, we estimate the droplet separation distance to be about 40 nm in length. The magnetic field from the trapped fluxons can be simply estimated by fluxon number divided by the area of the smaller gallium nanodroplet which yields ~600 Oe for one trapped fluxon and ~1200 Oe for two trapped fluxons.
An important question to be answered is whether the surrounding EGaIn around the smaller nanodroplet is capable of trapping two magnetic fluxons. To address this question, we consider a related geometry of a thin superconducting ring to model the state in which the EGaIn is superconducting but the smaller gallium droplet is normal. The maximum number of trapped fluxons in this geometry has been previously studied.\(^\text{30}\) From the London equation:

\[
\nabla \times (\lambda^2 \mu_0 j + A) = n_{\text{flux}} \Phi_0
\]  

(Equation 4.1)

Where \(\lambda\) is the penetration length, \(\mu_0\) is the magnetic permeability, \(j\) is supercurrents, \(A\) is vector potential, \(n_{\text{flux}}\) is the number of fluxons, and \(\Phi_0\) is flux quanta.

The maximum number of trapped fluxons is limited by the condition that the induced circulating currents are less than the critical current of the superconductor, which in this case is the EGaIn shell. This number is given by:

\[
n_{\text{max}} = \frac{\sqrt{2}\frac{3\sqrt{2}}{\xi} r_{\text{avg}}}{3 \sqrt{(3\lambda)}}
\]  

(Equation 4.2)

Where the radius, \(r_{\text{avg}}\) is about 100 nm in our samples, and the coherence length, \(\xi\), is about 40 nm for EGaIn.

Since at least one fluxon can be trapped inside the nanodroplet, the penetration depth cannot be larger than the smallest thickness of the EGaIn wall surrounding the relevant gallium droplet. Therefore, with \(\lambda \approx 10\) nm, we obtain \(n_{\text{max}} \approx 2\), which is consistent with our physical explanation that qualitatively matches all observed data.

4.3 – Prospects of the fluxon trapping memory element

We note that the quasi-1D geometry is crucial for the system described above. In a 2D or 3D system, the trapping or expulsion of a single fluxon does not cause any
macroscopic changes in the resistance as the superconductivity can simply flow around the trapped locations. The long lengths of the nanowires investigated here are important for this study because the effect depends upon a relatively rare configuration of a pair of gallium droplets in close proximity to one another. Measurements were carried out on a total of 11 wires and evidence of shape hysteretic switching between two metastable states in magnetoresistance scans similar to those reported here were seen in four wires. This study can be viewed as a nanorealization of a previously proposed Josephson memory element\(^3\) that can store and retrieve binary data in a nondestructive manner. It suggests it is feasible to develop nanoscale single fluxon devices in a controllable manner, such as an addressable logic and memory device fabricated by means of e-beam nanolithography in which the “peas in a pod” configuration of two superconducting materials with different Tc and Hc. Future experiments in that direction, especially to determine the most optimal configurations are currently underway.

4.4 – References


Chapter 5

Conclusions and future outlooks

The ability to create high aspect ratio materials at the microscale and nanoscale will continue to be of interest for years to come. The number of materials that can be formed into these 1-D like structures will become larger in type and method of fabrication. The approaches utilized here have focused on high pressure deposition methods, both chemical vapor and atomic layer, as well as pressure-assisted filling techniques. High pressure has enabled the creation of these high aspect ratio materials when used for templated growth in microstructured optical fibers that would not be obtainable by current, conventional synthesis methods. As discussed in Chapter 2, HPCVD can be utilized to deposit interesting materials such as oxides and semiconductors. Traditional drawing techniques and regular deposition techniques cannot be utilized to create these structures due to a variety of reasons. One large issue that stood in the way of the deposition of oxides was the choice of precursors. Since the precursors are all contained in the same high pressure reservoir, they must be compatible with one another at room temperature. The synthesis route that was taken for ZnO deposition was reacting DMZ and water, where the water is created \textit{in situ} via the reverse water gas shift reaction between hydrogen and carbon dioxide. The ZnO that was deposited could be utilized as a UV lasing medium or with the pore left in the center it could be used in microfluidic chips as a piezoelectric microvalve. The high pressures involved allowed for the RWGS reaction to happen at a temperature that is compatible with organometallic precursors. This method can and will be expanded to other valuable oxide materials such as titanium oxide, vanadium oxide, indium tin oxide and doped versions of these oxide. One doped oxide that is of particular interest is aluminum.
doped zinc oxide for a transparent, conductive material. Chapter 2 also laid the groundwork for high pressure ALD. Since ALD requires that one precursor be exposed to the substrate at a time, it will be far easier to follow conventional ALD reaction schemes in the high aspect ratio MOFs without the need for chemical encapsulation like HPCVD.

Pressure assisted melt filling was used in Chapter 3 to create high aspect ratio metallic nanowires. These wires are much longer than conventional nanowire syntheses are capable of creating by orders of magnitude. The wires are homogeneous and heterogeneous, depending upon the material that is deposited in the nanoscale MOFs. Gallium is by far the most versatile metal to place in the high aspect ratio nanopores, provided that the filling front has oxygen readily available to form a gallium oxide surface. The gallium oxide that is formed creates a thin layer on the surface of the wire that allows the gallium to be molded into non-equilibrium shapes that typically would not be permitted by the surface tension of the metal. These long nanowires are necessary when investigating 1-D superconducting physics. The long lengths ensure that data collected from measurements are properties of the wire itself rather than the contacts or the interplay between contacts and the wire. While it remains to be seen as to whether these wires truly are 1-D in nature and superconductivity is suppressed, early indications suggest that gallium which is slightly doped with indium provides some suppression, especially in wires with a diameter smaller than the coherence length of gallium (100 nm). Further investigation will be done with gallium metal being doped with various other superconducting materials such as aluminum, which has an incredibly large coherence length of 1.6 \( \mu \)m. Additionally, the heterogeneous structures that were created such as the core-shell nanowires, would be of interest, particularly if a wire were created with a
ferromagnetic material and a superconducting material, as the interplay between the two types of materials are of interest in superconducting physics. The pressure assisted melt filling technique could also be of interest when combined with the HPCVD synthesis technique. If a material such as germanium were deposited in a relatively large internal diameter MOF (~50 µm), but not completely filled, the small pore that remains could be filled with a metal such as tin. Upon annealing the sample, the germanium, which is an indirect band gap material, would be doped with the tin which would cause strain in the structure. With enough strain a direct band gap semiconductor material would be created. The creation of a direct band gap would expand the photonic capabilities of the germanium material and could potentially be advanced as a lasing medium or used as a diode in the fiber geometry.

One particular gallium-indium mixture was the focus in Chapter 4, where the slightly gallium enriched eutectic mixture created an interesting pea podded structure in a 150 nm inner diameter MOF was observed. The superconducting physics involved with this structure showed a very large hysteretic loop in resistance as the magnetic field was swept from positive to negative fields. Depending on the history of this sweep, the wire could be in two different resistive states while at the same temperature and magnetic field. These two resistive states were explained by the trapping of magnetic fluxon(s) in the gallium droplets along the length of the wire. The entire system can be described as a nano-realization of a Josephson memory element that can store and retrieve binary data in a nondestructive manner. This study will be expanded into a nanoscale single fluxon device that is more addressable. It can be created by means of e-beam nanolithography in which the pea pod structure is created using two superconducting materials. The only
requirements of the materials are that they are superconducting and have different superconducting transition temperatures and different critical magnetic fields.

The future is certainly bright in the field of high aspect ratio materials, particularly at the micro and nanoscale. Many of the experiments and projects described in this dissertation will be continued, and I look forward to seeing the great devices that can be created utilizing the groundwork that was established here.
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