DEVELOPMENT OF A HIGH THROUGHPUT IMPEDANCE MEASUREMENT DEVICE FOR NEW MATERIALS DISCOVERY

A Dissertation

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Karen L. Williams

________________________________________
Paul J. McGinn, Director

Graduate Program in Chemical and Biomolecular Engineering
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Doped perovskites are a material of interest due to their ability to conduct protons in a temperature range desirable for intermediate temperature fuel cell applications. Despite much research aimed at improving the performance of these materials, the contributions of various material parameters to the conductivity are not well understood. In the case of Y-doped BaZrO$_3$, published reports often disagree about its conductivity and structure. By employing combinatorial methods, the effect of compositional or process variations can be studied in a more rapid manner in order to identify potential candidate compositions, and possibly gain a better understanding of the material. In this work, a high-throughput impedance test cell was designed and built in order to test thin film samples by electrical impedance spectroscopy. Blanket thin film samples deposited by pulsed laser deposition (PLD) were created and tested, and a masking scheme was developed for fabrication of combinatorial libraries. Testing with the high-throughput
cell revealed challenges to ensure the quality of acquired data, and the importance of the quality of electrical contact being made with the library wafers. For samples where high film quality was combined with reliable contacts, calculated properties for conductivity and activation energies were in agreement with literature values. Testing on BaZr_{0.9}Y_{0.1}O_{2.95} (BYZ10), a candidate electrolyte for intermediate temperature fuel cell applications was inconclusive due to experimental difficulties in obtaining high quality data. It is recommended that for improved cell performance, refinement of the contact design is needed in order to facilitate more robust electrical contact between the cell and the wafer.
For my dad – I miss you.
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CHAPTER 1:
INTRODUCTION AND BACKGROUND

The objective of this work is to develop a device that will use electrical impedance spectroscopy (EIS) to rapidly screen candidate materials for desirable electrical properties. Specifically, it will be used to identify electrolyte materials for potential use in intermediate temperature fuel cells, but it may be applied to any solid materials for which EIS is a suitable characterization tool. Another major component of this work included the adaptation of a pulsed laser deposition system for combinatorial library fabrication. This work is based primarily on perovskite-type proton conducting materials. This introduction will provide a brief overview of fuel cell technology, proton conducting oxides and their potential use as fuel cell electrolytes.

1.1 Fuel Cells

As energy demands grow and fossil fuel sources dwindle, much research has been focused on development of alternate sources of energy, among them wind, solar and hydro power. One of the most promising prospects for making the shift from a fossil fuel based society to one based on renewable energy is the fuel cell: a unit which converts chemical energy to electrical energy.
1.1.1 Fuel Cell Basics

The concept of a “fuel cell” was first introduced in 1839 with a straightforward demonstration of the reversal of the electrolysis of water (Grove, 1839). One cell consists of three basic parts: the anode, the cathode, and the electrolyte. At one electrode, a material is fed to the cell and an ionization reaction occurs. These ions then pass through the electrolyte while the electrons that were liberated in that reaction pass through an external circuit, thus generating electricity. At the second electrode, the ions and electrons recombine along with a second material to complete the overall reaction taking place. The electrolyte must be chosen so as to allow the desired ions to pass, yet keep the feed materials separated, and be electrically insulating to prevent a short circuit. Electrodes must be electrically conductive and, oftentimes, support a catalyst.

There are many types of fuel cells, most often defined by the electrolyte that they incorporate. Foremost among these types are the polymer electrolyte membrane fuel cell (PEMFC), the phosphoric acid fuel cell (PAFC), the molten carbonate fuel cell (MCFC) and the solid oxide fuel cell (SOFC). The choice of electrolyte is an important one, as it dictates what the mobile ion will be, the mechanism whereby that ion will traverse the electrolyte, and at what temperature that transfer should occur. A summary of some fuel cell types, the mobile ion for each, and their approximate temperature range may be seen in Figure 1.1. Most well-known fuel cells may be categorized as either low- or high-temperature fuel cells.
1.1.2 Low Temperature Fuel Cells

Low temperature fuel cells are defined as those that operate at ~200°C or below. Examples of low temperature fuel cells include the PEMFC and PAFC. Both of these cells carry with them an upper temperature limit. The PEMFC must remain hydrated in order for proton transfer to occur, and cannot be operated above 100 °C. This temperature is dictated by the electrolyte and the transport mechanism that occurs. As indicated by the name, the PEMFC employs a polymer electrolyte, typically Nafion™ or some other polymer with sulphonated side chains. These side chains create local hydrophilicity within the generally hydrophobic polymer matrix. The presence of hydrated regions (weak acid regions) is what allows the transport of protons across the electrolyte. Nafion™ and related materials have enjoyed much popularity in fuel cell
applications because they are chemically resistant, mechanically strong, and electrically insulating while allowing the transfer of protons.

The PAFC operates at slightly higher temperatures (around 200 °C), and is somewhat similar to the PEMFC. Liquid phosphoric acid in a SiC matrix is used as the electrolyte and is held in place within the matrix by capillary forces. Typically, PAFC technology has been installed commercially for stationary applications, such as back up power systems for hospitals, hotels, and other buildings. It is an attractive alternative to the lower temperature PEM cell due to its ease of construction and higher tolerance for CO₂ in the feed stream. Even though phosphoric acid exhibits low volatility, operation of these cells will require periodic electrolyte replenishment. And as with the PEM cell, strict controls are essential to keep the operating temperature between 150 and 220 °C in order to maintain satisfactory performance.

Operation at these lower temperatures is problematic for both the PEMFC and the PAFC. Most notably, both require the use of expensive electrocatalysts (typically Pt or a Pt alloy) to drive the electrode reactions. Aside from the cost of these catalyst materials, the introduction of Pt into the system adds to the difficulty of maintaining cell performance over time. CO is a poison to Pt, and it is therefore essential to remove impurities in the feed stream in order to ensure continued operation at a satisfactory level, requiring auxiliary equipment and energy which detracts from the overall efficiency. Even with these measures, it is likely that the catalyst will periodically require regeneration.
1.1.3 High Temperature Fuel Cells

The use of high temperature fuel cells can address many of the problems associated with the low temperature cells described above. “High temperature” refers to cells operating at 600°C or higher, such as the molten carbonate fuel cell (MCFC) and the solid oxide fuel cell (SOFC).

In an MCFC, the electrolyte is made up of lithium-potassium carbonate salts heated to about 650°C. At these temperatures, the salts exist in a molten state that can conduct ions between the two electrodes. In contrast, the solid oxide fuel cell is unique in that it consists of all solid state construction, and is the most commercially advanced high-temperature cell. The electrolyte is typically an oxide ion conductor and must operate at high temperatures (800 – 1000°C) in order to facilitate ion transport across the electrolyte and obtain reasonable power outputs.

These operating temperatures offer several advantages, while they are also accompanied by their own set of problems. Running at higher temperatures eliminates many of the key problems associated with lower temperature fuel cells: reactions at the electrodes proceed much more quickly, and the need for expensive noble metal catalysts is eliminated or reduced. Aside from the cost of the catalyst, its potential elimination also would do away with the issue of catalyst poisoning from impurities in the feed gas, most notably CO poisoning of Pt based catalysts. The SOFC and MCFC can handle these impurities without losing efficiency. Additionally, the operating temperature of these cells is high enough for fuel reforming, so the use of fuels with energy densities higher than that of pure hydrogen, for example methane, may be used without the need for auxiliary equipment. Overall system efficiency may be further increased by
incorporating exiting gas streams at high temperatures into a combined heat and power (CHP) system: using them to turn turbines to drive generators and create more electricity.

High temperature operation does come with some drawbacks, however. The most challenging issues associated with high temperature fuel cells come from a materials standpoint. Materials for the electrodes and the electrolyte must not only be chosen based on their performance, but must also be thermally and chemically compatible during both construction and operation. More expensive materials are needed to withstand such temperatures, and construction methods must be carefully chosen, as different materials often need processing at different temperatures. Cost of construction of these cells is generally higher than that of the lower temperature cells because they require more elaborate processing. Thermal mismatch will lead to stress on the entire system, and shorten its lifetime, while chemical instability at high temperatures will render the cell useless.

1.1.4 Current Research Trends and the Intermediate Temperature Fuel Cell

Due to the problems associated with both low and high temperature fuel cell systems, much interest has been generated in the development of intermediate temperature systems. These cells would potentially incorporate the advantages, and reduce the problems, associated with each. Intermediate temperatures would allow for the reduction or elimination of expensive precious metal catalysts and remove the need for the strict humidity control associated with systems which rely on water as a transport medium, such as the PEM. At the same time, choice of potential component materials,
cell lifetime, and ease of fabrication will be greater than those associated with high temperature cells.

While the development of an intermediate temperature cell seems to be the obvious solution to a host of problems associated with existing low- and high-temperature cells, researchers have found development of such a cell to be a difficult task. Methods that have been attempted to resolve this issue have been primarily based on the conventional SOFC, and include attempts to improve electrode kinetics through the use of new materials and fabrication techniques, as well as reductions in electrolyte thickness to reduce internal resistance (deSouza, S. 1997; Srivastava, P.K. 1997; Gorman, B.P. 2005). Another promising approach to reducing SOFC operating temperatures is the development of new electrolyte materials that are more highly conductive at the desired conditions. Yet this avenue of investigation has also proven to be daunting to researchers. Materials that are known conductors in the target range of temperatures either exhibit conductivities that are too low to be practical in fuel cell applications, or are unstable in the reducing/oxidizing conditions of a fuel cell. Recent attention has been focused on proton conducting electrolytes – a shift from the traditional concept of SOFC’s which employ O$_2^-$ as the conductive species. These may include polymers (e.g. Nafion™), solid acids (Haile, S.M. 2001), and solid oxides. Even taking into consideration this variety of materials with their different proton conduction mechanisms, a so-called “temperature gap” exists from around 100 – 500 °C within which no known material exhibits necessary conductivity values for fuel cell applications (Figure 1.2), which are typically considered to be around 1 S/cm. Proton conducting oxides are one
group of materials drawing attention from the scientific community which has the 
potential to bridge this gap.

Figure 1.2: Conductivity of known materials at various temperatures
(Norby, 1999)

1.2 Proton Conducing Oxide Electrolytes

The use of doped oxides is not new to the field of SOFC research, as they are well
known to be oxide ion conductors. In fact, the most widely used oxide-conducting
electrolyte for conventional SOFCs is 8% yttria-stabilized zirconia (YSZ – Zr$_{0.92}$Y$_{0.08}$O$_{2-\delta}$). Proton conducting oxides typically incorporate a dopant to facilitate ion conductivity.
In the early 1980s it was shown that some doped oxides could actually act as proton conductors within certain temperature ranges in hydrogen containing atmospheres (Takahashi, T. 1980). Since the original discovery, protons were verified as the dominant conductive species (Iwahara, H. 1993), and the mechanism by which this type of conduction happens was studied (42 Kreuer, K.D. 2000). Generally, substitution of an ion with a lower oxidation state for one with a higher oxidation state (substituting \( \text{Y}^{3+} \) for \( \text{Ce}^{4+} \) in \( \text{BaCeO}_3 \), for example) creates oxygen ion vacancies in the crystal lattice, as illustrated in Kröger-Vink notation:

\[
D_2O_3 \xrightarrow{\text{B}} 2D'_B + V^{\!*}_O + 3O^\circ_O
\]

Where \( D \) is the dopant and \( B \) is the B-site atom in the perovskite \( \text{ABO}_3 \). An oxygen vacancy is created for every two dopant atoms that are incorporated into the lattice. When this material is subsequently exposed to a humid atmosphere, the vacancies are filled by hydroxyl ions:

\[
H_2O + V^{\!*}_O + O^\circ_O \rightarrow 2OH^\circ_O
\]

Following this protonation step, the hydrogen ions “hop” from one oxygen site of the lattice to the next to traverse the electrolyte. Rapid rotational motion of the O-H group allows for the reorientation of the proton towards an adjacent oxygen ion. Studies show that the lattice locally “softens”, and a transient bond is formed between the proton and two oxygen ions before the final “hop” is made (Figure 1.3)( Islam, M.S. 2000).
When these materials are subjected to high temperatures, the main conductive species switches from protons to oxide ions, but generally proton conduction is dominant below 800 °C (Boehm & McEvoy, 2006). This can be attributed to the water incorporation step in the process, which has been shown to be exothermic (Islam, M.S. 2000). Oxide ion conduction occurs by a mechanism similar to that which proton conduction occurs. The oxygen vacancies created by the substitution of lower valency cations serve as spaces for the oxygen ions to “hop” through the material. However, the oxygen ion here is transferred in a “free” state, while transferred protons are bound to oxygen ions. Both oxide ion conduction and proton conduction in solid oxides is dependant on the existence of oxygen vacancies, and materials thus created are generally capable of conducting both species. Which ion dominates is a function of atmosphere and temperature. It is important to note that materials such as YSZ and other binary oxides have not exhibited the same level of protonic conductivity that some doped perovskite compounds have been found to demonstrate (Iwahara, H. 2004). Based on empirically observed trends, structural factors seem to have an impact on proton mobility.
in these doped perovskites. Materials with a high molar volume (large lattice constants) and which are more ideally cubic tend to exhibit more proton mobility. An ideally cubic structure will contain oxygen vacancies which do not differ from one another. A standard way to classify the degree of ideality in ABO$_3$ perovskite materials is through the use of a tolerance factor. A tolerance factor of 1 is an ideally cubic structure. Proton mobility in materials with a tolerance factor of less than one has been shown to be diminished, and this is possibly due to the existence of two unique oxygen vacancies, as opposed to one (Kreuer, 2003).

Use of a proton-conducting oxide in a fuel cell carries with it some inherent advantages. In contrast to the conventional oxide ion conducting SOFC electrolyte, one based on a proton conductor would produce water at the cathode, and not at the anode where it can dilute the fuel (Iwahara, H. 1982). Thermodynamic studies indicate that SOFCs based on proton conductors are more efficient in the conversion of chemical energy to electrical power than those based on oxide ion conductors (Demin, A. 2001). All solid state construction eliminates concerns about electrolyte losses associated with the PAFC, while concerns about hydration and humidity levels that accompany the PEM would be mitigated. The temperature range at which proton conduction is dominant in these materials falls within the temperature range desired for an intermediate temperature fuel cell. Fabrication of electrolytes in thin film form will serve to further increase their performance by reducing the overall resistance. Proton conducting thin films have been fabricated by a variety of methods, including pulsed laser deposition (PLD) (Ito, N. 2005), sputtering (He, T. 1996), colloidal spray deposition (Lee, T.H. 2005), screen printed precursors (Meulenberg, W.A. 2006), and slurry coating (Yamaguchi, S. 2004).
Solid oxide proton conductors that have received the most attention in research laboratories are those based on cerates and zirconates. The original proton conducting oxide work by Takahashi et. al. focused on SrCeO3 based compounds, and much work has been done on this compound, as well as SrZrO3 (Iwahara, Yajima, Hibino, Ozaki, & Suzuki, 1993), BaCeO3 (Dynys, Berger, & Sayir, 2006; Ito, Iijima, Kimura, & Iguchi, 2005; Peng, Wu, Yang, & Mao, 2006; F. Zhao & Chen, 2010), and BaZrO3 (Bohn & Schober, 2000; Iwahara et al., 1993; Sun et al., 2010). To date, doped barium cerate compounds have been shown to be the most conductive out of the known proton conducting oxides. However, these compounds have stability issues, often reacting with CO2 to form CeO2 and BaCO3 (Haile, S.M. 2001; Ryu, K.H. 1999). In addition, the stability of cerate based compounds is questionable after prolonged exposure to a humid atmosphere (Taniguchi, N. 2001). Doped BaZrO3 is another popular basis for proton conducting oxides and, despite its reduced conductivity when compared with BaCeO3, has received much attention due to the increased stability that it offers.

1.3 Problem Statement

Investigations of proton conducting oxides have thus far been largely a trial and error kind of process. Some selected materials have been synthesized one by one and tested for proton conduction and use in an ITSOFC, yet a large number of systems have yet to be investigated. While computer modeling in conjunction with experimental observations have identified certain factors such as structure, lattice ideality (tolerance factor), and dopant levels to be significant factors in conductivity levels (Kreuer, K.D., 2003), attempts at a comprehensive model to predict new candidate materials has been
largely unsuccessful (Norby, T. 1997). In fact, even some structural questions remain as yet unresolved in the research community. For example in the case of Y-doped BaZrO3, some researchers contend that the compound exists as a single phase which transitions from cubic to tetragonal to cubic with increasing Y concentration (Kreuer, K. et al., 2001). Other groups contend that this material consists of two different perovskite phases given certain doping levels and processing conditions (Azad et al., 2008; Kojima, Tanaka, Oyama, Higuchi, & Yamaguchi, ). Without a clear consensus on something as fundamental as molecular structure and existent phases, the scientific community will not be able to state with certainty the factors which govern the proton conductivity exhibited by these materials, which in turn will prohibit the prediction and design of materials with higher conductivities.

This work seeks to address the difficulty involved in new materials discovery in a field such as solid oxide proton conductors - where modeling and traditional experimental techniques have failed to yield a comprehensive and widely accepted theory of how and why a material possesses certain desired properties. The fabrication of a test apparatus to rapidly screen materials of different compositions and make an informed choice of a candidate material to scale up and test more extensively will greatly aid in the ability to understand these materials. While the original design is based on proton conducting oxides for intermediate temperature fuel cells, the testing equipment could be used to evaluate other materials for different electrical properties well beyond the scope of this work.
2.1 Combinatorial Chemistry

Given the difficulty encountered in modeling all the factors which may predict materials with high proton conductivity, and the disagreement in the research community about what factors may be relevant (e.g. debate about interactions between the dopant and the incorporated proton (Kreuer, K.D. 1997; Karmonik, C. 1998), the use of combinatorial, or high-throughput, methods can aid in the discovery of more candidate materials. Instead of creating a material of a single composition, then testing it, and moving on to the next, a combinatorial approach creates an entire library of materials with varying compositions, and tests each one, either in series or parallel, to determine which materials have potential for a given application and merit more investigation.

There are two major kinds of combinatorial libraries: discrete libraries, in which specific areas on a substrate contain predefined compositions, and constant composition spread libraries, which exhibit a concentration gradient across a given area. Xiang et. al. first proposed the use of a physical masking technique to create discrete thin film libraries, creating a grid on the substrate where each square could be tested for various properties. Two masking sets were used to generate samples of various compositions (Xiang, X.D. 1995). In general, this technique employs a stationary mask which is
moved into position for the deposition of a material, and, depending on the system, may be rotated and/or exchanged for a new, differently patterned mask for subsequent depositions of a second material. Each mask exposes only those sections of the substrate desired for the layer being deposited, and the composition of each discrete sample is controlled by the ratio of the number of layers of one material to the other. Later work in creating these libraries saw the development of new masking patterns (Xiang, X.D. 1998; Xiang, X.D. 1999).

A constant composition spread (CCS) library may be made in two different ways. The first is the use of off-axis deposition to take advantage of the natural concentration gradient that exists across a substrate during deposition. In this case, the flux of material being deposited is positioned on one side of the substrate while the flux of a second material is positioned at the other side of the substrate, 180° from the first material. It results in a substrate with pure or mostly pure materials at the edges, with a composition gradient as one moves from one side to the other. This may also be extended to create ternary composition spreads, with fluxes positioned at 120° intervals (Figure 2.1). This type of combinatorial materials synthesis was realized as early as 1965 (Kennedy, K. 1965) using an evaporation technique. Constant composition spreads have since been created with other deposition techniques, including pulsed laser deposition. Christen, et. al. applied the PLD-CCS technique to create binary and ternary phase diagrams as well as epitaxial superlattices (Christen, H.M. 2002).
An alternate technique for creating CCS libraries is the use of a constantly moving physical masking technique. Using this method, a mask with an opening cut in a predefined shape is moved through the deposition flux, exposing different parts of the substrate to the flux for different amounts of time. At the end of the routine, a wedge of material with a constant thickness gradient is left. Another material may be deposited with the mask moving in the opposite direction to obtain a second layer with a thickness gradient opposite to the first. The end result is a film which varies linearly across the deposit from one pure material to the other (Figure 2.2). Hasegawa et al. applied this mobile masking method to create ternary composition diagrams by controlling the speed of the mask as it moved in one direction. For deposition of a single component, the film thickness was varied along the substrate from a full monolayer of thickness to zero. Substrate rotation and subsequent similar depositions of two other compounds yielded a single substrate with the ternary composition spread, all three binary spreads, as well as a pure layer of each compound (Hasegawa, K. 2004). Recently, some groups have applied mathematical modeling in order to determine the optimal spacing and shapes that should
be incorporated in these masks to make the process more efficient {{75 Yamamoto, Y. 2004; }}.

Figure 2.2: Creating a composition gradient with mobile masks during material deposition

Thin film techniques can be extremely useful in the field of combinatorial chemistry, and many of the approaches described above have been developed for use in conjunction with various vapor deposition techniques. The thin film structures that may be created using these methods are extremely versatile and varied. And because these films are small in scale, a large number of compounds may be synthesized and studied without wasting valuable materials.

This work seeks to apply a thin film combinatorial approach to discovery of new materials for use in fuel cells. The basic concept is to create a library of samples of differing compositions, complete with thin film electrical contacts, and subsequently test them using EIS to determine proton conductivity. The wafer library design was originally inspired by work done by this group (Cooper & McGinn, 2007) in the field of
combinatorial testing of fuel cell catalysts; however the scope and layout were ultimately dictated by system capabilities, as will be discussed in detail later.

2.2 Library Fabrication Techniques

The materials libraries and single thin film samples examined in this work were all deposited by pulsed laser deposition or sputtering, either separately or in conjunction with one another. Libraries were built on 2 inch diameter Si wafers with a 300nm SiO₂ buffer layer. Individual films were deposited on Si, quartz, and glass for preliminary testing.

2.2.1 Photolithography

Patternning for thin film electrical contacts was accomplished through photolithography. A photomask of the desired pattern was made, and photoresist type AZ 5214 was used in the image reversal mode in order to expose the desired wafer area. After deposition of the conductive thin film, the remaining photoresist was lifted off with acetone.

2.2.2 Sputtering

Electrical contacts for library fabrication were sputtered onto wafers using an RF magnetron sputtering system. Sputtering was the preferred method for this step in the process due to its superior ability to deposit conductive species and the quality (uniformity and smoothness) of the deposited film. Titanium nitride was ultimately chosen as the electrical trace material since it has been used successfully in the past.
(Cooper & McGinn, 2007) and would not oxidize at desired test temperatures. A Ti target was used while N₂ was admitted to the chamber during deposition in order to reactively sputter the TiN onto the substrate. The material was sputtered at 150W with a sputter chamber pressure of 5 mT. Argon flowing at 16 sccm was the sputter gas, while 4 sccm of 25% N₂ (balance Ar) was used as the reactive gas.

2.2.3 Pulsed Laser Deposition (PLD)

Thin films of candidate electrolyte materials were deposited using pulsed laser deposition (PLD). PLD of thin films is a relatively recent development in materials science, yet has gained in popularity very quickly. While the process had been in some use prior to the late 1980s, a real explosion in PLD occurred when the ability to deposit high temperature superconductors was demonstrated in 1987 (Dijikkamp, D. 1987). The ability of this process to deposit high quality stoichiometric films in a relatively short time period, along with its ease of operation, makes PLD an attractive alternative to many other deposition technologies.

PLD is a relatively simple process. A pulsed laser strikes a target material, thereby causing a small portion of this material to ablate and subsequently deposit on a substrate opposite the target. The ejecta contains both neutral and ionic species, and electrons, and is most often referred to as a plasma plume. PLD is unique in that the energy source (laser) is operated outside of the deposition chamber, which avoids contamination problems inherent in other processing methods, such as sputtering. It may be run under high vacuum conditions, or with a background gas to control deposition profiles or ensure proper stoichiometry (such as depositing oxide materials in an oxygen
The pulsed nature of this method is another unique feature that helps to promote the nucleation and growth of high quality films. The large instantaneous deposition rate for one pulse allows for a large number of nucleation sites, while the time between pulses, when the laser is not firing, allow the adatoms present to settle into low energy positions (Shen, J. 2004). The apparatus that will be used to accomplish the objectives of this project consists of a 248 nm KrF excimer laser and a deposition chamber. The chamber may be held under vacuum or filled with a background gas while a deposition is being made, or after deposition has completed during an in-situ anneal. The system is currently set up to provide oxygen, nitrogen, or argon as background gases, however this may be changed as dictated by the specific processing conditions necessary to deposit a given material. The deposition chamber (Figure 2.3) consists of a carousel capable of holding up to six targets of 1 inch diameter (or three 2-inch targets), a substrate holder capable of holding up to 2 inch diameter wafers, and a masking system capable of movement in both the x- and y-direction. The substrate has rotational capabilities, may be moved in the z-direction and is set up such that it may be equipped with a contact mask for defining discrete sample pad areas. The chamber is equipped with a load lock system to allow the user to change substrates without having to break vacuum in the main chamber. The chamber also contains a heater for deposition at elevated temperatures and in-situ annealing. A combination of mobile and stationary masks was developed to create combinatorial libraries, the details of which will be described in Chapter 3.
Films were deposited in constant energy mode (the voltage of the laser was controlled in order to maintain a set constant energy output). Energies between 120 mJ and 180 mJ were typical throughout the course of this work. Repetition rates of 10 or 20 Hz were used for all films. Temperature and background gas pressures varied widely throughout this work.
2.3 Material Synthesis (Pechini, 1967)

2.3.1 Yttria-doped Barium Zirconate (BaZr\(_{1-\delta}\)Y\(_\delta\)O\(_3\))

Yttria-doped Barium Zirconate (BaZr\(_{1-\delta}\)Y\(_\delta\)O\(_3\)) was synthesized using a modified Pechini \{232 Pechini, Maggio P. 1967\} process. The metal ion precursors that were used were barium nitrate (Ba(NO\(_3\))\(_2\) - 99%), yttrium nitrate hexahydrate (Y(NO\(_3\))\(_2\)•6H\(_2\)O – 99%), and zirconium dintrate oxide hydrate (ZrO(NO\(_3\))\(_2\)•xH\(_2\)O). An assay of the Zr-precursor found x = 2.3. The metal salts were dissolved in water in stoichiometric amounts to achieve a dopant level of 10% (\(\delta = 0.10\)). This dopant level was chosen as a suitable starting point because it has been shown to yield good conductivities in the literature, and its study by other groups would provide a means by which to evaluate the results of this work (Bohn & Schober, 2000; Higuchi et al., 2005; Slade, Flint, & Singh, 1995). Citric acid and ethylene glycol were then added under heat and stirring. The molar ratio of citric acid to ethylene glycol and organics to metals was 3:2 in both cases.

The solution was placed in 150 °C oven overnight to dehydrate. The result was a fine, fluffy powder. The powder was ground with a mortar and pestle and placed in an alumina boat and calcined at 1200 °C for 8 hours. Such a high calcination temperature is necessary to ensure decomposition of any BaCO\(_3\) that may have formed. XRD analysis of the calcined powder confirmed that BaZr\(_{0.9}\)Y\(_{0.1}\)O\(_{2.95}\) (BYZ\(_{10}\)) had formed and that all BaCO\(_3\) had decomposed. The calcined powder was again ground with a mortar and pestle and then pressed into pellets. A 1 inch diameter pellet with approximately ¼ inch thickness was fabricated to be used as a PLD target, while smaller pellets with 1 cm diameters and thicknesses varying between 2 – 4 mm were created for bulk impedance
testing. All pellets were sintered at 1500°C for 8 hours, and achieved ~60% of theoretical density.

2.3.2 The Li-V-Si-O System

Some work was also done on a material of interest as an electrolyte in Li-ion battery research – Li$_3$V$_{1-\delta}$Si$_{\delta}$O$_4$ (LVSO). This material was synthesized by the solid state reaction of LiCO$_3$, V$_2$O$_5$, and SiO$_2$ with a metals ration of Li:V:Si = 3.4: 0.6: 0.4. Excess Li was used in order to offset Li loss during sintering and deposition. The powders were milled and calcined, and the structure was confirmed with x-ray diffraction.

2.4 Material Characterization

2.4.1 Electrical Impedance Spectroscopy

Electrical impedance spectroscopy (EIS) is an extremely powerful tool in electrochemistry and may be used to find the electrical properties of a variety of systems. In EIS, a specific voltage is applied to the cell of interest with a small perturbation (AC signal). The response (phase shift/change in amplitude) is measured, from which the impedance can be found. Impedance is related to resistance, as both are a measure of opposition to electrical flow, and resistance is a special case of impedance for DC current applications only. In general, impedance ($Z$) is a complex quantity, measured in ohms ($\Omega$) that may be defined as

$$Z = \frac{E}{I}$$
Where E is the potential and I is the current.

Typical impedance data is presented in the form of a Nyquist plot, where the real part of the impedance is plotted on the x-axis, and the negative imaginary part of the impedance is plotted on the y-axis. This usually results in one or a series of so-called impedance arcs, as shown in Figure 2.4. High frequency data is located closest to the origin, while low frequency data is located further down the positive x-axis. The impedance measurements obtained in the Nyquist plot, also referred to as a complex plane plot, may be analyzed by choosing an analogous electrical model that would yield the observed behavior, known as an equivalent circuit. While there are many circuits that might exhibit the observed behavior of the data, the chosen model must relate to what is known of the material under investigation. For ceramics, the equivalent circuit shown in Figure 2.5 was first proposed by Bauerle in 1969 (Bauerle, 1969) and is still taken to be the appropriate model for these materials with some minor adjustments, such as replacement of the capacitors with constant phase elements (Haile, S.M. 1998) in order to better model the non-homogeneous nature of real systems. In the Bauerle circuit, each arc (corresponding to an RC-circuit in the model) corresponds to a specific physical process: bulk conductivity, grain boundary conductivity, and electrode effects. Ideally, these processes occur in distinct time domains, and all arcs are well defined, but in practice these arcs are often found to overlap one another.
Figure 2.4: Example of a complex plane impedance plot for the shown equivalent circuit.

Figure 2.5: Bauerle’s equivalent circuit

Extraction of conductivity values from raw impedance data is a relatively straightforward process, especially if the impedance arcs are well defined. The measured resistance of the sample under test is simply the distance across the real impedance axis that is spanned for a given impedance arc. That is to say, for an ideal semi-circle of data, the diameter of that semi-circle is the resistance of the sample. This value, along with the
dimension of the sample and the electrodes, may then be used to find the conductivity according to:

\[ \sigma = \frac{1}{\rho} = \frac{t}{AR} \]

Where \( t \) is the thickness of the sample, \( A \) is the electrode area, and \( R \) is the measured resistance. It is important to note that this value for conductivity is the total conductivity of the material and there is no distinction between different ionic conductivities or electron hole conductivity. However, it is known that the temperatures at which measurements are being taken in this work are thermodynamically favorable for proton conduction, and unfavorable for significant oxide ion conduction (Boehm & McEvoy, 2006). Additionally, all samples were heated under humidified N\(_2\) prior to and during testing to ensure there was little oxygen in the system, as well as to protonate the sample prior to testing.

The biggest drawback to EIS is that the data that it yields is highly susceptible to misinterpretation. This is especially evident when one or more processes are occurring within the same time domain. For example, if a researcher is expecting to see three distinct impedance arcs, and only observes two, he then must perform further experiments in order to elucidate which processes should be assigned to which section of the data, or to determine if a larger time domain needs to be sampled to find the third arc. Often, it is extremely insightful to observe impedance data at a variety of temperatures. The temperature dependence of ionic conductivity follows an Arrhenius relationship:

\[ \sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \]
Where $T$ is the absolute temperature, $\sigma_0$ is a constant, $k$ is the Boltzmann constant, and $E_a$ is the activation energy. By collecting data at different temperatures, $E_a$ can be extracted from a plot of $\ln(\sigma T)$ versus $\frac{1}{T}$, and that value can then be compared to literature values to confirm that the presumed process is the one which is being observed in the data.

EIS may also be problematic for work with thin film samples. Measurement of large resistances, as well as issues with signal to noise ratios may cause thin film data to be more difficult to interpret than bulk data. However, as long as the researcher is aware of this issues and takes the proper steps to mitigate them while ensuring that the resultant data is not affected, EIS can be an extremely insightful tool.

In this work, all impedance measurements were taken with a Solatron model 1260 FRA equipped with a dielectric interface, which allows for the measurements of large resistances. The measured frequencies were typically in the range of 1 MHz to 1 mHz, depending on the sample properties. A perturbation signal of 10 – 500 mV was used. In cases where the higher AC signal was applied, higher and lower perturbations were tested to ensure the accuracy of the data. ZView© software was used to analyze all data.

2.4.2 X-ray Diffraction

X-ray diffraction was used extensively throughout this work in order to confirm the structure of powder and thin film samples at various stages of their processing. Powders and some thin film samples were characterized on a Scintag X series diffractometer, which utilizes a point detector. Additionally, a Bruker D8 diffractometer
was also used in the characterization of thin films and libraries. The D8 employs an area
detector, and the ability to define points on the wafer for testing and then collect data
from each point using an automated program.

2.4.3 Imaging

Both optical and scanning electron microscopy (SEM) were used to image the
samples produced in this work. An Olympus microscope equipped with a camera served
as an important tool for evaluating films for cracking, spalling, and the presence of
particulates. SEM was performed with an Hitachi S-4500 equipped with an electron
dispersive spectroscopy (EDS) system for atomic composition analysis. SEM was used
to determine film quality and morphology of the films, while EDS was used to evaluate
compositions of films, PLD targets, and bulk samples.

2.4.4 Film Thickness and Deposition Rates

The deposition rates and thickness profiles of various materials deposited by PLD
under different conditions was examined using profilometry and spectral reflectance
techniques. An Alpha Step 500 profiler was used to quickly and easily obtain deposition
rate information on deposited materials. For thickness mapping of transparent samples
deposited on Si wafers, a Filmetrics F40 was used to perform spectral reflectance
measurements. Use of the Filmetrics system requires that the user input the refractive
index of the material being measured. For some materials, this information was not
readily available and this property had to be approximated based on similar materials.
Use of spectral reflectance in conjunction with profilometry served to impart a high
degree of confidence in the accuracy of the data obtained for materials for which the refractive index had to be approximated.
CHAPTER 3:  
LIBRARY DESIGN AND FABRICATION

This chapter will detail the steps to create the libraries for testing in the test cell developed in this work. Film quality, geometry around the wafer, electrical contacts, and stoichiometry of various samples were all issues that had to be addressed. The following sections will detail the steps in the process that culminated in the final layout, materials, and processing conditions needed to create one wafer library for testing.

Previous work in this group has focused on sputtered combinatorial libraries for catalyst fabrication and wet cell electrochemical testing. An example of a library created by sputtering can be seen in Figure 3.1. Using this library as a model, a similar concept for library fabrication by PLD was formulated; however the layout had to be adjusted in order to be compatible within the PLD system. The major factors in choice of library layout were the largest area in which a thin film of uniform thickness could be deposited and the maximum mask size that the PLD chamber could accommodate.
3.1 Uniformity, Particulates and Thickness Mapping

Two of the major drawbacks to using PLD as a deposition method are uniformity of the film thickness across the substrate and the presence of particulates. Due to the nature of the plume that is created when the laser hits a target, ejecta is not well dispersed and does not cover a large area. Consequently, resultant film thickness gradients exist even over small areas. Some groups have attempted to formulate a mathematical relationship to describe the plume (Anisimov, S. 1993; Singh, R. 1990) and have studied the effects of various parameters on the film thickness distribution (del Coso et al., 1999). Generally, films are thicker in the middle and thinner on the edges, which can be problematic in many applications, including fabrication of combinatorial libraries. Masking schemes that create layers of materials in wedges are much simpler when the deposit is uniform within a given working area. An uneven distribution would require a complicated routine in which mask velocity would have to vary with position. Distribution problems can be remedied by methods such as off-axis deposition combined with substrate rotation, as well as the use of a mechanical dispersant which acts on the
material plume to filter out larger particles and spread the deposition area by increasing the mean free path of the contents of the laser plume.

In order to develop a library layout and masking routine that would be applicable for various materials processed under different conditions, a quantitative evaluation of the distribution of materials fabricated with a variety of processing parameters was performed. These tests would be used to identify a working area of the wafer that exhibits a certain amount of uniformity (< 10% variance), and define how processing parameters could be altered to maximize this area. These tests were confined to oxides, and by taking a small sampling, a more general understanding of the effect of deposition parameters on film thickness distributions could be gained. Each material was deposited on Si wafers, and the thickness of these films was measured using spectral reflectance. Figure 3.2 shows typical examples of the experiments that were performed. The results shown here are representative of the general trends that were observed. As can be seen from the results, film uniformity increases with increasing pressure, and distributions vary slightly based on the type of material being deposited.

Even more problematic than lack of uniformity in PLD is the issue caused by the ejection of particulate matter from the target, which can subsequently lodge in the film. When the laser strikes a target, material is melted and/or vaporized locally. This rapid influx of energy may cause particulates to be ejected from the surface. The process of laser ablation also leads to the formation of “cones” on the target surface. With continued ablation, these cones can break off and lodge as particulate matter in the deposited film, and targets must be monitored for wear and periodically polished to minimize this effect (Willmott & Huber, 2000). Particulates are difficult to avoid and
Figure 3.2: Sample of normalized spectral reflectance data for films deposited by PLD. TOP: SrTiO$_3$ deposited at 10 mT O$_2$ (left) and 50 mT O$_2$ (right). BOTTOM: Y-doped BaCeO$_3$ (left), SrTiO$_3$ (middle), and MgTiO3 (right) deposited under identical conditions.

Many methods have been proposed to mitigate or eliminate them. These methods include the use of magnetic fields (Weissmantel, Rost, & Reisse, 2002) and electrostatic filtering (Hoche, Ulmer, & Rauschenbach, 2008), or the use of a second laser (Tselev, Gorbunov, & Pompe, 2001). But most involve the physical blocking of the particulates from reaching the substrate through the use of a shield or some kind of mechanical filter. The introduction of a rotary blade between the target and the substrate can yield smoother films. Fast moving species (atoms, ions, molecules, and small clusters of matter) pass through the blades, while slower moving species, including large particulates, are
essentially filtered out before reaching the substrate. Iwabuchi et. al. proposed the use of one large shadow mask placed in the plume between the target and the substrate (“eclipse method”) (Iwabuchi, M. 1994). As with the rotary blade, larger and heavier species will be blocked, while lighter, more mobile species will travel around the shadow mask and deposit on the substrate. Chen et. al. showed that the distance of this mask from the target affected the film quality as well (Chen, C. 2001). While this method certainly does reduce particulate matter, leading to smoother, higher quality films, the deposition rate is significantly reduced. Similar approaches apply the basic principle of blocking any direct path to the substrate, and forcing any matter in the plume to make a circuitous route before finally reaching the substrate (Marcu, A. 2000; Hino, T. 2003).}

In this work, the double slit configuration, as proposed by Hino et. al., was tested as a basis for both particulate control and plume dispersion. Two masks with a series of openings as shown in Figure 3.3 are placed between the target and the substrate. The masks are designed such that when one mask is rotated 180° from the other, the openings do not overlap and no direct path through the masks exists. Masks with slit openings of 0.5, 1, and 3 mm were tested, while their distance both from the target and relative to each other were varied. Films were deposited on Si wafers and spectral reflectance measurements were used to determine thickness distribution and evaluate the effectiveness of each slit configuration.
Figure 3.3: Example of a mask used for particulate control and plume dispersion

Three different conditions were varied in order to observe their effects on the uniformity of the films: pressure, slit size, and the distance of the slit masks relative the target and each other. The figures that follow are optical micrographs. The transparency of the oxide films leads to the appearance of thickness bands of color and visible profiles which are suitable for this discussion. The addition of the slit masks resulted in an improvement in film uniformity (Figure 3.4), however, as found with spectral reflectance, the deposition rate was reduced by as much as 80%. This observed reduction in deposition rate is quite large compared to some other literature values ((Iwabuchi, Kinoshita, Ishibashi, & Kobayashi, 1994)) and can likely be attributed to a smaller target to substrate distance within our system.

Figure 3.4: BaZrO$_3$ deposited with no slits (left) and with a set of 1 mm slits (right)
At lower pressures, it was found that the slit geometry was reflected in the film (Figure 3.5). This is due to ejecta coming from the target at an angle, which will effectively avoid any barrier between it and the substrate. This effect may be tempered, although not eliminated completely, by the use of an overspray mask, which would introduce a shadowing effect on the deposited film and prevent any deposition of material arriving at the substrate at an extreme angle.

![Figure 3.5 BaZrO₃ films deposited at 10 mT (left), 25 mT (center) and 50 mT (right) O₂ background pressure](image)

The location of the slits relative to the target and to each other was also studied. While variation of the slit location did have some effect on the final film thickness distribution, the differences within our working limits were minimal (Figure 3.6).

It was also observed that the orientation of the slit masks had an effect on the final film thickness map. When the slits were oriented parallel to the x-axis, the film was seen to “spread”, or become more uniform in that direction. When they were oriented parallel to the y-axis, spreading occurred in the y-direction. This observation is consistent with results reported in the literature (Afonso, Serna, Catalina, & Bermejo, 1990).
Figure 3.6: BaZrO$_3$ films deposited in 50 mT of O$_2$ with 1-mm slit masks 15 mm from the target with 5 mm between them (top left), 20 mm from the target and 10 mm between them (top right), 25 mm from the target and 20 mm between them (bottom left) and 30 mm from the target with 25 mm between them (bottom right)

In addition to providing a method for dispersing the plume and increasing uniformity, the incorporation of the slit masks had a dramatic effect on the amount of particulates that could be found in the film. The dark field images shown in Figure 3.7 show the reduction in particulates that is possible when the masks are in place. However, as can also be seen, the use of the masks did not lead to a complete elimination of the particulate problem.
3.2 Thin Film Fabrication –Other considerations

While particulates and uniformity are important considerations when choosing optimal deposition conditions for library fabrication, they are not the sole determining factor in parameter value choices. In order to create a library suitable for electrical testing, the deposition conditions must also be fine tuned to ensure the deposition of good quality films. Good quality films, in this case, are uniformly thick, with a minimum of particulate matter, as discussed above, but in addition must be stoichiometric, crystalline, and dense. Each of these issues may be affected by PLD parameters such as laser fluence, background gas pressure, and substrate temperature; and optimizing the conditions for one property may be detrimental to another. By necessity, the process was iterative, as changing conditions to improve some properties affected others. It was important to understand what was absolutely necessary, and what imperfections could be acceptable.

For the system used in this work, the two most important parameters in film fabrication were deposition temperature and background gas pressure. Some parameters,
such as laser wavelength, could not be changed, while varying some others, such as laser fluence, repetition rate, or target to substrate distance, were found to have very little effect on the final product. Therefore, efforts were mainly focused on choosing the proper gas pressure and temperature at which to deposit these films.

3.2.1 Temperature

PLD deposition at elevated temperatures will generally lead to more crystalline and dense films. Film density is arguably the most important consideration in film fabrication in this work due to its effect on the mechanical stability of the film and its electrical properties under testing. A porous film will often either peel or flake off of the substrate very easily. The samples being tested in this work will ideally have electrical traces underneath and on top of each sample pad, with only the oxide material being tested to separate them. It was therefore essential to find the conditions under which dense films could be deposited and short circuiting could be avoided. Infortuna et al. showed that the formation of dense oxide films via PLD was strongly dependent on substrate temperature and background pressure during deposition (Infortuna, 2008); specifically higher temperature and lower deposition temperatures will yield denser films.

Generally films deposited at room temperature were found to be amorphous. Additionally, these films were considerably less stable than comparable films deposited at even moderately elevated temperatures. In the case of BYZ10, crystalline films could be fabricated either by a room temperature deposition followed by an annealing step in air, or deposited directly in situ with substrate temperatures $> 600^\circ$C. Other materials, such as LVSO, could only be deposited in a functional thin film form at elevated
temperatures within the PLD chamber. All attempts to deposit this material at ambient temperature and subsequently test or process the samples led to cracking and spalling of the films. These effects were lessened when the material was deposited at an elevated temperature and allowed to anneal in situ in O₂ atmosphere. As a general rule, LVSO films were stable in air and oxygen up to the temperature at which the film had been deposited originally. This is presumably due to an oxygen-poor stoichiometry of the as-deposited film, with cracking occurring upon post-deposition oxygen incorporation into the lattice.

In addition to improvements in mechanical stability and density, deposition with substrate heating serves to produce crystalline films without the need for an extra annealing step. Crystalline films are more desirable in the case of proton conduction because the order within the crystal structure serves to facilitate the movement of ions through the lattice. Although it is possible to crystallize amorphous films after deposition, a number of factors indicated that this was not ideal. Cracking, delamination, and spalling were greatly reduced at elevated substrate temperatures. Additionally, it was found that films deposited on top of metallic trace materials tended to crack when subjected to an ex situ anneal, either due to thermal mismatch or agglomeration of the metallic film under the oxide. Therefore all samples were deposited with an elevated substrate temperature in order to ensure crystallization and mechanical stability. BYZ10 films were deposited at 600 °C in order to fabricate crystalline, dense films, while LVSO films were deposited at 400 °C, which was found to yield stable films under testing conditions.
3.2.2 Background Gas Pressure

Along with temperature, background gas pressure is an important parameter that can have a significant effect on film density and mechanical stability. It was found qualitatively that, as reported by Infortuna et. al., lower background pressure yielded denser films. Films that were deposited at pressures of only 100 mT of O₂ could be easily brushed off of the substrate, rendering them unsuitable for testing of any kind. Unfortunately in this case, an improvement in film quality achieved by lower the working pressure leads to a less desirable thickness distribution, as was shown in section 3.1. However, since it is only useful to test good quality films in order to get an accurate idea of their electrical properties, density and stability were deemed to be more vital components of this work, and a working pressure of 10 mT was chosen for film deposition. At this pressure, some scattering could be provided in the interest of having a uniform working area, while maintaining the integrity of the film: density, stability, and stoichiometry.

One of the significant advantages of the PLD method is the ability to deposit stoichiometric films from a stoichiometric target, but there are some cases in which stoichiometry is not preserved. Compounds which contain significantly lighter or heavier elements may not transfer to the substrate in a stoichiometric manner. Some elements may ablate preferentially, and the surface stoichiometry of the target may change over the course of its use. It was found that BaZrO₃ based compounds yielded stoichiometric films relatively easily when deposited by PLD. Films were deposited under a wide range of conditions including deposition temperature, annealing temperature, O₂ background pressure, and laser repetition rate. The resultant films were examined by XRD and
showed the BaZrO$_3$ pattern consistently. Figure 3.8 shows an example of the effects of background pressure during deposition, where three films were deposited under identical conditions except for background pressure. Films deposited at 10 mT and 25 mT of O$_2$ were found to be stoichiometric, while data on the film deposited at 50 mT was inconclusive. This is likely due to a decreased film thickness as a result of the elevated background pressure, which yielded a sample that was too thin acquire a sufficient signal to noise ratio in the XRD. It is also possible that the elevated pressure had a detrimental effect on the film stoichiometry, or that it simply did not crystallize. Since stoichiometric films were achieved at the lower pressures, which are desirable for denser, more stable films, the question of stoichiometry at higher pressure was not pursued.

Figure 3.8: XRD pattern of BYZ10 films deposited at various pressures
Although improvement was observed in both particulate control and film uniformity with the use of the slit masks, it was ultimately determined that the gains were not significant enough to warrant their use in this project. As can be seen in Figure 3.5, slit masks are not a viable option when using 10 mT background gas pressures due to the reflection of the slit geometry in the final film distribution. With the desire to work with these pressures, it was necessary to work within the smaller uniform area of film that is present without the use of the slit masks. It should also be noted that additional incorporation of combinatorial masks also has an effect on the deposition rate and uniformity of the film, as will be discussed below.

3.3 Sample Layout/ Masking

When designing a method for fabrication of a ternary library, the advantages and the limitations of the PLD system itself had to be taken into consideration. As shown at the beginning of this chapter, the system we are using exhibits off axis deposition, with the majority of the uniform flux limited to one quadrant of the 2-inch wafer. In order to create a set of discrete points taken from a ternary system, each quadrant of the wafer was used to fabricate a different section of the system, as shown in Figure 3.9. As this system will be used to deposit and evaluate ternary systems, each quadrant contains a triangular arrangement of discrete sample pads.
Figure 3.9: Ternary diagram broken up into quadrants and transferred to a 2-inch wafer.

Each discrete pad is a 2mm circle and is defined during deposition with a contact mask (meaning this mask is in direct contact with the substrate) which is spot welded to the substrate holder. The PLD system is also equipped with two linear feedthroughs which allow masks to be moved through the plume during the deposition. The y-axis is equipped with a stationary mask designed to prevent “overspray” – that is, unintentional material deposition on the three wafer quadrants that are not in use at the time. The creation of discrete samples of different compositions as defined by the ternary diagram is accomplished by the use of a mask affixed to the mobile x-axis feedthrough. By moving this mask at a fixed velocity through the plasma plume during deposition, a film with a constant thickness gradient is created. A ternary system may be created by depositing wedges of different materials on top of the first and subsequently annealing the film to ensure good interdiffusion between the layers, as was discussed in Chapter 2.

Since the PLD system is equipped with masks which move only in the X and Y directions with a 90 degree angle between them, and not three masks with 120 degrees between them, care must be taken with the mask design and opening geometry. Yamamoto et al demonstrated the use of a linear action mask to create a ternary system in
thin film form. For this project, a modified version of this linear action mask was created. As shown in Figure 3.10, each opening in the ternary mask is designed to expose the substrate from a different corner of the triangular deposition area. The positioning and direction of movement of the mask is determined by which portion of the triangle is to be exposed for a given layer. The two horizontal openings shown on the right hand side of the mask are used to attach the mask to the feedthrough and have no bearing effect on the combinatorial deposition. As will be shown, the size and exact layout of this mask was determined based on experimental observations.

Figure 3.10: Mask created to deposit ternary libraries, and the resulting ternary spread
In order for this masking technique to be effective, the area through which the mask openings are moving should ideally be a uniform area of deposition. As discussed earlier, uniform areas of deposition can be problematic when using PLD as a thin film fabrication technique. Also, it has been observed that both the degree and location of an area of uniformity will vary with material, even under identical deposition conditions. The final design of the masks, therefore, had to take this variance into account. At the same time, the choice of that area could not initially be made in full confidence since the introduction of masks (in this case, three) would have an additional effect on the final film profile due to shadowing effects. Based on preliminary distribution studies, two different working areas were chosen for initial testing. Using the point of the triangle as a reference, these two areas were defined as 2mm and 4mm away from the substrate center. These choices were based on two different thickness distribution profiles (Figure 3.11) which were deemed to be typical for the equipment being used.

![Figure 3.11: Working area for ternary library deposition 4 mm from center based on SrTiO_3 deposition at 50mT (left) and 6 mm from center based on Y-doped BaZrO_3 deposition at 50mT (right)](image-url)
Two-millimeter circles were chosen as the size of the sample pads, with 1.5 mm spacing between each sample pad. These values were chosen based on this group’s previous work with thin film combinatorial libraries by sputter deposition (Cooper & McGinn, 2007). This size and spacing were sufficient to isolate each sample pad and provide a reasonable amount of space to avoid any short circuits that might occur between the various electrical traces that will be applied to the wafer.

The initial version of the contact mask was designed to incorporate 15 sample pads per quadrant (60 sample locations in the ternary system over all). Masks were fabricated by laser cutting 10 mil (0.001 inch) thick stainless steel. This particular thickness was chosen such that masks would have an appropriate amount of rigidity, yet they would retain the ability to be bent and altered relatively easily if necessary. Laser cutting services were provided by Microscreen®. The overspray mask, which consists of a triangular opening designed to expose only the desired wafer area to deposition, was made such that the exposure extended just to the outside edge of the sample pads with an equilateral triangle with 16 mm edges. The openings in the ternary (mobile) mask were also sized according to this specification. It was found that depositions using this first set of masks were too thin on the outside edge of the desired deposition area. The shadowing effects of the two masks near the substrate were obstructing flux from reaching the substrate and affecting the uniformity (Figure 3.12). As a result, the openings in the two masks (overspray and ternary masks) were enlarged to take this shadowing effect into account. The defining triangle edge was increased to 18 mm, however, this was still not enough to mitigate the observed shadowing effects. Ultimately, the size of the openings in the ternary mask was limited by the geometry of
the PLD chamber itself. Given a specific initial triangle size, the size of the other openings and the spacing between them could not be altered. It was found that the overall length of the mask could not exceed 115 mm. If the mask was fabricated to be longer than this, the left edge of the mask would intercept the laser during deposition through the far right triangle. It was found that rearranging the order of the triangles on the mask relative to each other could free up some additional space, however, a base triangle size of 18 mm was pushing the limit and it was impossible to enlarge the openings much more than this. As a result, the 15 sample pad per quadrant design had to be reduced to use only 10 sample pads per quadrant. The final mask designs can be seen in Figure 3.13.

Figure 3.12: Designing the dimensions of the overspray mask.
Figure 3.13: Final mask design for ternary library fabrication in the PLD: Contact, overspray and ternary (mobile) masks
3.4 Contact Layout

A materials library is useless without a reliable method to test each sample. Therefore, it was necessary to also design a network of electrical traces in order to perform electrical impedance spectroscopy on the finished library. These traces need to be electrically conductive and must be stable under the temperatures of interest. Additionally, they must be able to be fabricated in thin film form in a pattern compatible with the library sample pad pattern.

Since the goal of this work was to test the intragrain conductivities of these materials, and because films grown by PLD often exhibit a columnar morphology, it was logical to attempt to design electrical traces that ran below and above each sample pad. A network of traces had to be designed such that they terminated in pads that could be contacted around the edges of the wafer. In order to save space around the edges, allowing contact areas to be larger, trace lines were arranged such that one line was associated with multiple sample pads, while the selection of two such pads would correspond to only one unique sample pad from the ternary library (Figure 3.14). As shown, the original concept evolved into a more elegant and functional design.

Figure 3.14: (a) original concept for electrical traces and (b) final design of electrical traces that run over and under each sample pad.
In order to test the electrical performance of films fabricated by PLD, thin films of silver were also applied to the wafer to provide electrical contact with the films. Silver is relatively inexpensive and readily available, and has generated some interest for its possible use in integrated circuit technology (Adams & Alford, 2003). It exhibits low resistivity and a high oxidation resistance, which are both desirable qualities in the application to this work. Additionally, Ag has been fabricated in thin film form by other groups by evaporation (Lv et al., 2007), sputtering (Gadkari, Warren, Todi, Petrova, & Coffey, 2005; Hauder, Gstottner, Hansch, & Schmitt-Landsiedel, 2001) and PLD (Scharf & Krebs, 2002).

Preliminary fabrication of silver films by PLD was promising: smooth conductive films were produced on a variety of substrates including glass, quartz and Si wafers. However, when the silver films were combined with the oxide thin films and exposed to processing, post-processing, and test conditions, the film quality was significantly diminished. The silver films exhibited a significant amount of dewetting and agglomeration when exposed to an oxygen atmosphere at moderate temperatures. Even with this agglomeration present, it was observed that electrical continuity was maintained in films that were greater than 100 nm thick, and is confirmed by other groups (Kim, Alford, & Allee, 2002).

While the agglomeration exhibited by the silver films did not affect their conductivity significantly, there were other problems encountered with these films and their proposed application for this project. When electrical traces were fabricated in a parallel plate configuration (one contact under the film, with the second on top, forming a sandwich), short circuit issues were prevalent, and generally unavoidable with any degree
of consistency. The main culprit in this short-circuit issue was found to be particulates which had lodged in the film during deposition. While the double slit method described earlier would be effective in minimizing these large particulates, it could not be guaranteed to eliminate every single particulate, and the decrease in deposition rate, which is already low when depositing metals by PLD, was unacceptable.

Another cause of short circuits in a setup such as this is film quality. If the oxide film under test is not sufficiently dense, and contains pores or pinholes, the material being deposited over it will fill in those holes and contact the bottom electrode. Agglomeration and hillock formation may also play a role because of its effect on the smoothness of the bottom electrode. All these factors led to a re-design of the electrode arrangement in order to definitively avoid short circuits, and it was decided that co-planar electrodes would be preferable.

Preliminary testing of co-planar electrodes proved to be problematic. While no problems were observed in extracting impedance measurements from bulk sample pellets with parallel plate or co-planar electrodes, significant issues were encountered when the same measurements were made on thin films of the same materials. Electrical impedance spectroscopy of thin films carries with it some unique challenges. The small sample size results in measurements that are extremely noisy, or oftentimes unmeasurable due to very large capacitances that are present. The supplied AC signal must be increased, and the electrode length maximized in order to obtain any impedance measurements on the film. For this reason, many groups working with electrical testing of thin, insulating films find it necessary to use co-planar interdigital electrodes (Bieberle-Hutter, Hertz, &
Tuller, 2008; Kidner, Homrighaus, Mason, & Garboczi, 2006; Kotani, Kawayama, & Tonouchi, 2002).

Since impedance measurement results on films had been inconsistent at best, it was decided that this project would also be best served by the incorporation of an interdigital electrode array. Preliminary testing of interdigital electrodes on larger sample films was promising, so the design was applied to the materials library in order to measure each sample pad. For each 2 mm diameter pad, electrode arrays with 18 fingers, each 50 µm wide and 700 µm long (Figure 3.15) were fabricated. Wafers were patterned using photolithography and a lift off process was used after deposition of the trace material.

Figure 3.15: Final design of electrical trace arrangement with interdigital electrodes. Also shown is an optical micrograph of sputtered TiN traces in this configuration.
As can be seen in comparison with Figure 3.14, this design has undergone a number of changes in addition to the incorporation of the interdigital electrode array. The contact pads around the edges were enlarged in order to provide a larger allowance for error when making contact for testing. The trace lines themselves could no longer criss-cross as in the original design since they are now co-planar and would short circuit. The electrical switching equipment was also a consideration in the design, since the two contacts on a single pad must be connected to different multiplexers in order to obtain a measurement. As a result, the sample pads associated with each trace line were carefully chosen, as was the final wiring and pin out of the device, which will be detailed in Chapter 4. Additionally, due to the questionable quality of the silver films being produced in the PLD, namely the problems with agglomeration and particulates, the trace material was changed to sputtered TiN. This was chosen because this group has used it in the past as an electrical trace material, and sputtering yields very smooth films. While the issue of silver and other metal deposition in the PLD may be revisited in future work, using a well known material such as TiN was the best way to ensure the reliability of the impedance testing for this work.

3.5 Conclusions

The library design detailed here went through many iterations and was complicated by the fact that the design choices that were made were dependent on each other. Ultimately, the need for the fabrication of quality films and the physical dimensions of our laboratory equipment led to a functional wafer design for testing a combinatorial library of 40 discrete samples. The following chapter will detail the design
of the device created to use impedance spectroscopy to test libraries fabricated in the fashion.
CHAPTER 4:
TEST CELL DESIGN

A thin film library is of no use if a suitable method and associated equipment are not available to test the samples. Given the geometry of the combinatorial library generated by the PLD system, an appropriate system for testing the sample was designed and built. This high throughput impedance test cell required temperature control, atmospheric control, electrical contacts, and the ability to isolate each circuit. Additionally, testing had to be automated through the use of a computer program. This chapter will address the logistics of the hardware, while the software will be discussed in Chapter 5.

4.1 Electrical Contacts

4.1.1 Material

The first issue that had to be considered was how to make contact with the electrical traces on the wafer in order to test each sample pad. Choice of material was dictated by the requirements of the system. The material had to be a good electrical conductor with the ability to handle temperatures of up to 500 °C, and relatively soft such
that when a load was applied, it would make good contact with the wafer without damaging the film. Additionally, the amount of relaxation that might occur with repeated thermal cycling was a concern.

Testing of this type is often achieved with the use of a spring-type “pogo” contact, very often a Be/Cu alloy. Unfortunately, the spring material used in these contacts is not compatible with the temperature range in which we are interested, and is therefore not well-suited for this application. Pogo probes with a spring material suited for higher temperature use are available from a German company, but are prohibitively expensive. When considering alternative materials, silver was found to be a material that could meet these needs. It is a good conductor, and sufficiently soft to make a good contact without applying a large amount of force. The question of relaxation and its performance in response to thermal cycling is still potentially an issue. However, due to its availability and relatively low cost, the overall cell will be designed such that the silver contacts may be easily replaced should such a decline in performance be observed.

The viability of this choice was first tested on a single sample deposited on a 1.5 cm square piece of quartz. Ag/Pd thin film contacts and an approximately 300nm thick BaZr$_{0.9}$Y$_{0.1}$O$_{2.95}$ (BYZ10) film were deposited in the configuration shown in Figure 4.1. Impedance tests were conducted in a tube furnace with flowing wet N$_2$. Wet nitrogen was achieved by bubbling the gas through DI water.

![Figure 4.1: Example of a sample for preliminary testing](image)
Unfortunately, as discussed in the previous chapter, impedance data in this configuration on this material was impossible to get. However, it was observed that the same electrode impedance data was recorded for silver wires held on by force as was recorded for silver wires which were attached to the sample with silver paste. This was a promising result since this contact change did not affect this part of the impedance response. Research in our group occurring concurrently with this work involved impedance testing for materials that might be used in Li-ion batteries. Using the configuration shown in Figure 4.1, testing on Si-doped Li₃VO₄ (LVSO) electrolyte yielded impedance data from films much more easily than the zirconates on which the motivation for this work is based. As a result, it was determined that all preliminary testing within the cell be done with LVSO materials so as to eliminate any problems encountered with the high-capacitance properties of proton conducting oxides. After confirmation of any technical questions involving the cell, BYZ10, or other materials, could be tested with the knowledge that any poor data is due to the sample or material itself and not the testing apparatus.

Once the testing apparatus was in a more complete form, the choice of silver wire as a contact material was revisited. Testing on full libraries demonstrated that the need for good quality contact between the wires and the thin film electrical traces was essential for collection of reliable data. Preliminary testing was done using common tinned copper wire to connect with the wafer. This material was used instead of the silver due to its robustness and relative ease of incorporation into the test cell, properties which facilitated multiple test configurations and contact replacements when determining the final design. Although the wafer libraries used during this stage consisted of a blanket film where all
forty sample pads were theoretically the same, they were observed to have different responses under EIS testing. The scale of the differences (a few orders of magnitude) could not be explained by small variations in the sample pads and merited further examination. The wafer was then removed from the test cell and single pads were tested individually using both silver and tinned copper wire with varying amounts of force holding the wire against the thin film TiN. It was found that silver wire was capable of giving more consistent contact given a specific applied force. It was also found that more downward force was required than the cell was originally designed to provide in order to make a good contact that yielded reliable EIS results. This served to validate the original choice of silver as the contact material due to the fact that it is softer than copper and more malleable, thus making it easier to press down onto the wafer in order to make good contact. As a result, a thicker sterling silver (approximately 92.5% by weight silver, AWG 20) wire was chosen for the contacts. This wire was purchased from a jewelry supply vendor (Beadaholique), and the exact composition is not guaranteed. The lower purity, and larger diameter (0.812 mm versus 0.50 mm diameter of the original wires used) of the silver would serve to give the contact wire a bit more strength while preserving its conductivity and ability to make good contact with the conductive traces on the wafer.

4.1.2 Configuration

The silver wire contacts were arranged radially. This configuration was chosen so as to facilitate good contact with the electrical traces on the wafer, while minimizing the impact of the heater on the wires themselves. By avoiding wires that extend normal to
the wafer surface, there is space to apply a load to the wire ends, and they are not sitting directly above the localized heat source.

4.2 Inner structure

The core inner structure of the test cell consists of a holder for the wires that will contact the wafer, and a platform to hold the substrate during testing. Machinable glass ceramic (Macor, from Cotronics, Inc) was chosen as the material to be used to hold the silver contacts. It was chosen for its insulating qualities and its ability to withstand temperatures in the range of interest. A preliminary schematic of the inner structure of the testing apparatus may be seen in Figure 4.2, and photos of the finished product may be found in Figure 4.3.

Figure 4.2: Schematic of testing apparatus inner structure
4.2.1 Ring Contact Holder

The Macor glass-ceramic was fashioned into a ring structure with 45 equally spaced holes running along the outside, with set screws placed above each hole in order to hold wires in place and ensure their position during testing. The original concept for the contact assembly consisted of a piece of silver wire, which would make contact at the wafer surface, with stainless steel tubing crimped onto the wire for enhanced strength. Upon incorporation of thicker sterling silver wires, the need for stainless steel tubing was negated and this design was abandoned. Figure 4.4 shows the ring structure sitting on a sample wafer. This entire ring will be raised during sample loading/unloading, and lowered in order to make contact with the sample for testing.
The wires exit the ring parallel to the wafer and are bent over the contact pads such that they hang down lower than the ring holding them and can make contact with the pads (Figure 4.5). Each wire has a crimped on “pin-and-socket” type connector which then connects to standard electrical wire to connect with the testing equipment. This setup allows for the ring to be disconnected and the wires to be serviced when needed.
4.2.2 Substrate Holder/Heater

A spiral micro heater was used to test the libraries at elevated temperatures. This required the incorporation of a platform to hold the heater. The heater itself is seated in a recessed holder fabricated out of Macor, which is attached on top of an aluminum platform. Holes in the Macor and an open area under the heater were provided for connecting it to a power supply. A stainless steel disc was placed on top of the heater and it is upon this disc that wafers under testing will be situated (Figure 4.6). This disc serves the dual purposes of providing a flat surface for the wafer, as well as ensuring even heating across the sample.

![Image of spiral micro heater in ceramic holder with and without stainless steel disc](image1.jpg)

Figure 4.6: Spiral micro heater seated in ceramic holder without (left) and with (center) stainless steel disc. Photo at right shows heater platform and connections

4.3 Sample Loading and Unloading

The ring contact holder is attached to an aluminum base, which is in turn attached to a linear motion slide. A knob situated at the top of the assembly can be turned which will lower the ring contact holder onto the wafer during testing, and lift it off of the wafer during sample loading and unloading. By using the slide, the contacts are assured to contact the same location every time, and, if desired, the ring can be lowered into the
same vertical position every time, thus eliminating variations that could occur between samples.

4.3.1 Applied Load

A Macor ring was fabricated that could aid in ensuring good physical contact between the silver wires and the thin film conductive traces on the wafer. The ring was made from Macor so that it can be in contact with all of the wires yet not cause shorting, and may be seen in Figure 4.7. This ring was created such that it fits easily inside the ring contact holder and has a diameter such that it can be used to push the silver wires down onto the contact pads around the outside of the wafer. When first fabricated, the amount of force required to make measurements in this configuration was unknown. It was found that the mass of the ring itself was not sufficient to obtain consistent and reliable data from the test cell. As a result, the ring was used in conjunction with a heavier piece of stainless steel to better compress the wires against the wafer and obtain good quality contact.

Figure 4.7: Macor ring used to apply load to contact wires
4.4 Outer structure

The outer structure of the testing apparatus is relatively simple. The inner structure described above needed to be enclosed such that samples may be tested under controlled atmospheres. It is necessary to control the atmosphere during testing of some samples due to the nature of impedance spectroscopy. Impedance results are indicative of overall conductivity within the material being tested, and there is nothing in the data that directly indicates which species (electrons, protons, or other ions) are traversing the electrolyte. Therefore, in samples such as proton conducting oxides, it is desirable to provide an oxygen deficient atmosphere to ensure that one is not measuring oxygen ion conductivity, since they are known to be mixed ionic conductors.

Given the need to place the entire inner structure within an air tight box, allowances had to be made for access to the box, power inputs and signal input/output. The chamber was made from aluminum which was fashioned in the shape of a box around the inner test structure. Electrical lines that carry the test AC signal to and from the sample being tested enter the box through three hermetic D-subminiature connectors (Positronic, model number XAVAC15M/FI.0). These serve to consolidate all of the interior wires and feed them through the chamber wall without compromising the air tight specification. The power supply lines to and from the heater enter through the lower back corner of the box. They are fed through ceramic tubes which are held in place with epoxy. Once the power lines were connected to the heater, the opening of these tubes was also sealed with epoxy. This location was also used as a convenient entry point for the thermocouple. Two through-wall tube couplings were used to create a gas inlet/outlet for atmosphere control. A hole in the top was provided for access to the linear motion
slide used to move the contacts onto and off of the test sample, and is closed with a polymer cap fitted with an o-ring. Finally, the box is also equipped with a door at the front for sample loading and unloading and general maintenance.

![Figure 4.8: Impedance test cell outer structure and connections.](image)

### 4.5 Associated equipment

Aside from the parts which were fabricated in-house, there are also some other pieces of equipment associated with the test cell which are essential for its operation.
4.5.1 Heater and power supply

The spiral microheater shown in Figure 4.5 was purchased from MHI (Micropyretics Heaters International, Inc.). Model number MC-GAXP-130 is a 2-inch spiral heater, rated for 130 Watts and 1400 °C. It is powered by a Kepco power supply model ATE 15-15M. Since this power supply is an analog instrument, and temperature control will be incorporated into the software, these items are accompanied by a programmer (Kepco model SN 488-122) which serves to convert the digital signal from the software to an analog signal suitable for the power supply.

4.5.2 Electrical switching

The use of an electrical switch is essential to carry out the sequential testing of each sample pad in the library, and is achieved through the use of a Keithley Model 7002-HD high density switch system. Each pad can be uniquely identified by the choice of two electrical traces. When a pad is to be tested, the two channels which are associated with that pad are closed, creating electrical continuity to the selected pad only. The wires inside the box come through the three d-sub connectors to three lengths of shielded cable with 15 wires each. It is necessary that this cable be shielded for as much of its length as possible to avoid any stray impedance. At both the d-sub connector and the terminal block (Wieland interface terminal block, model number 87.210.2208.3) for the switch, the wires are attached by screw connections. This was chosen instead of soldering in order to allow changes if necessary. Once the wires reach the switch, they must be attached to one of two multiplexers. A sample pad cannot be tested if both of its
contacts are connected to the same multiplexer, so this affected the design of the leads on the wafer, and which pads were connected to which samples (Figure 4.9).

![Diagram](image)

Figure 4.9: Example of one quadrant’s connections to multiplexer 3 (MUX 3) and multiplexer 4 (MUX 4)

4.5.3 Impedance measurements

Impedance measurements were taken using a Solartron 1260 FRA and a dielectric interface, necessary for measuring high-impedance samples. The input and output of the machine were connected by BNC cables to the two multiplexers in use in the electrical switch.

4.6 Summary

Based on the configuration of the combinatorial libraries that were designed in this work, an associated test cell had to be designed and built to process them. Such a cell was built that is capable of testing each member of the 40-sample libraries rapidly in series. This cell may be used to test the impedance of various materials for a number of applications, and may even be altered to accommodate different library configurations. It allows for temperature and atmosphere control and satisfies all the requirements to perform its desired function.
CHAPTER 5:
SOFTWARE CONTROL

The biggest advantage of combinatorial methods lies in its ability to test all of the samples that make up a library quickly and easily. In this way, candidate materials may be identified for a given application while wasting a minimal amount of time and resources. In order to accomplish this, automation is often employed so that each sample is tested in succession without user intervention. To that end, a program to control and coordinate the test cell and associated equipment that was described in Chapter 4 was developed.

5.1 Overview

The high throughput impedance test cell and associated equipment are controlled by an in-house developed LabVIEW virtual instrument. LabVIEW (Laboratory Virtual Instrumentation Engineering Workbench) is a National Instruments product which is currently in wide use in the scientific community due to its ease of operation and ability to interface with a vast range of hardware. A main advantage of LabVIEW is that it can be used with virtually any piece of hardware that is equipped with a serial communication
port. Drivers are often included or available for a large number of these instruments, making their inclusion in a virtual instrument trivial. The Keithley electrical switch, Solartron FRA, and Kepco programmer were all connected to a PC through an IEEE-488 (GPIB) connection terminating in a USB at the computer. Each instrument carries a unique address by which it may be identified in the programming. The signal from the thermocouple is connected to the computer separately through a DAQ (data acquisition system).

In addition to the ability to easily connect to and communicate with a variety of different instruments, LabVIEW has the advantage of being based on graphical programming. Instead of traditional programs which contain lines of code, a LabVIEW program, or virtual instrument (VI), consists of blocks and loops for which you can see the inputs and outputs. The flowchart-like nature of graphical programming aids the user during development by providing a visual representation of the program. Figure 5.1 is an example of what these blocks and lines look like for part of a temperature control program. A temperature reading is made at the block labeled TIn, which is in turn displayed on the front panel and sent to a PID control block. The PID block has inputs for setpoint, PID parameters, and variable range which are then applied to send a control signal to the power supply (not shown) to adjust the voltage in response to the temperature reading. Graphical programming such as this allows errors (missing inputs, or improperly formatted inputs) to be identified prior to attempting to run the program. Additionally, troubleshooting is simplified by the ability to sample data lines easily and to observe the program as it is running to find where, for example, it may be getting stuck in a loop.
Finally, LabVIEW allows the programmer to customize the user interface to provide as many variable options and displayed outputs as desired. Thus, once a VI is developed, it may be run with a variety of options without changing the code, and without needing someone who is familiar with the programming to use it. If a problem arises, sample values can be easily displayed on the front panel for monitoring and troubleshooting. The front panel of the high throughput impedance measurement VI is shown in Figure 5.2. It allows the user to choose a variety of temperature settings, provide a unique name for the sample or samples being tested, choose a channel list (switching order), and define origin and destination file paths. The program takes the wafer to these various temperatures and tests all forty library samples automatically in series at each temperature. When all testing is done, the heater is shut down.
Figure 5.2: Front panel of LabVIEW VI developed to control impedance test cell operation

A basic program flow chart can be found in figure 5.3. The program consists of two basic parts: the temperature control loop and the measurement loop. Upon initiation, the program determines what the set temperature is and drives the heater until it meets that specification. The temperature loop continues to run and control the temperature while the impedance measurements are occurring. For each sample in the library, a measurement is taken with a set of conditions defined externally from this program. Upon completion, the program moves on to test the next sample, or, if it has completed all samples, turns off the heater and ends the program. Both the temperature control and measurement loop will be discussed here in further detail.
5.2 Temperature Control

The first major component of the program developed to operate the test cell was concerned with temperature control. Refer to Figure 5.4 for a screen shot of the final version of the temperature control loop. Figure 5.5 briefly explains the VI operations being used here.
Figure 5.4: Section of LabVIEW program dedicated to temperature control in the cell

- **Tln**: Reads the temperature in degrees C
- **PID**: Controls voltage supplied to heater based on setpoint and control parameters
- **SEPROG**: Communicates set voltage to power supply
- **Delay**: Determines if a variable is in range
- **Setpoint within range**: Creates an array
- **SET**: Calculates the mean of an array

Figure 5.5: Identification of LabVIEW program components for temperature control
The temperature control components are all enclosed in a “while” loop. A desired temperature or set of temperatures may be entered by the user in the front panel, and this data enters the loop as indicated in Figure 5.4. The loop makes use of LabVIEW’s PID control VI. The temperature is measured by a thermocouple at the wafer at a rate of 5 Hz, which is sent to the PID block along with the setpoint. Additional inputs to the PID block include control parameters (proportional gain, $K_c$, integral time, $T_i$, and derivative time, $T_d$) and the output range. In this case, the range of output signal was set from 0 – 10 V, and the signal being sent to the power supply will be in that range. In order to find the PID control parameters $K_c$, $T_i$, and $T_d$, an autotuning wizard was used upon initial setup of the system in order to determine the appropriate values for the control parameters. This autotuning wizard is an optional feature of the PID VI and may be turned on or off using the T/F input shown in Figure 5.4. When used to determine the parameters for the test cell, it was found that the best control was achieved with $K_c = 1.0708$, $T_i = 1.5216$, and $T_d = 0.0343$.

Information cannot be passed into or out of the loop while it is running through the use of the conventional data wires seen in most LabVIEW programming, yet it is necessary to run the loop continuously while the measurements are taking place. For this reason, it was necessary to create two global variables to pass information to the rest of the program while it is running. Within the loop, the running average temperature of the system is kept and used as the value that triggers the beginning of the impedance measurements. The average is used instead of simply a direct measurement of the temperature for two reasons. First of all, if there is any overshoot of the temperature set point or other instability, the extra time taken for the average temperature to come within
10 degrees of the set point allows a long enough time domain for those values to stabilize. When tuned properly, this is not too much of a concern; however a short wait after reaching the set point also allows any processes happening on the wafer, especially protonation at higher temperatures when dealing with proton conducting oxides, to come to equilibrium before continuing on with testing. Once the mean temperature is within range the global variable “Setpoint within range” is changed from false to true, which triggers a true occurrence outside the loop and starts the impedance measurement portion of the program without stopping the temperature control at the current working temperature.

The temperature control loop also contains a second true/false global variable. This value, “Measurements complete”, stops the temperature control loop once testing at that specific temperature is completed. The temperature loop is then reset for the next test temperature. This is necessary such that after prolonged testing at a given set point, the average can be reset and the next set point can be reached within a reasonable amount of time.

5.3 Impedance measurement loop

Once the program receives the signal that the temperature setpoint has been reached, it moves on to execute a stacked sequence of events that will test each of the forty sample pads on a wafer library. The stacked sequence structure is necessary so that each step is taken in the proper order, and enough time is allowed for each step to complete. An overall snapshot of the program may be seen in Figure 5.6, and major program points will be discussed in more detail.
Figure 5.6: Overview of impedance measurement sequence

Once the impedance measurement section of program is set in motion, the first step is to send an “Open All” command to the Keithley switch (Figure 5.7). This resets the switch to its original configuration and ensures that there are no closed channels, as it is imperative that only the two selected for testing be closed at a given time.

Figure 5.7: Open All command sent to Keithley switch

The next step directs the program to read the channel list (whose location is defined by the user on the front panel), and to close the two channels defined for the current cycle (Figure 5.8). Channel lists must be in the form of a user defined text file that lists the two channels to be closed for each measurement on a separate line. The
program then reads the line for whatever iteration it is on and closes those channels only. The list should be in the format slot#channel,slot#channel (such as 3!1,4!2).

![Diagram of channel list and close appropriate channels for testing]

Figure 5.8: Read channel list and close appropriate channels for testing

As can be seen in the flowchart in figure 5.4, the impedance test loop consists of closing the connections to one sample pad, taking a measurement on that sample pad, and moving on to the next in a cycle that repeats until all forty measurements are taken. This portion of the program works in conjunction with Solartron software (SMaRT®) to run the FRA/1296 dielectric interface, since there is no LabVIEW driver currently available for this particular piece of equipment. In order to circumvent this problem, we used a mouse click simulation module to run this program automatically for each sample. Three mouse clicks are simulated – one to ensure the SMaRT program window is the active window, one to start an experiment, and one to choose which experiment to run. When using the Labview high throughput impedance program described here, it is first necessary to have SMaRT open with the task bar tab furthest left. Additionally, a SMaRT experiment must be created and ready to run, and that experiment must be the first experiment in the open project. It should also be noted that if this program is used
on computers other than that on which it was developed, the location of the simulated mouse clicks should be verified and adjusted for the system on which it is being run.

The impedance of each sample pad is measured according to parameters set by the user in the SMaRT software experimental set up. Typically, an AC voltage is set, along with a range of frequencies at which to test. An impedance measurement is taken at each frequency with a user set integration time. Each parameter choice will affect the quality of the data as well as the time required to get a full range of measurements for a given sample. The individual choices should be made based on the material being tested such that dependable data can be obtained in a minimum amount of time. Typically, an impedance run will take approximately five minutes. When extended to forty sample pads and short delays between samples, this works out to about 3.5 hours to test one complete wafer at one temperature. Testing at $n$ temperatures will clearly extend this time more than $n$ times once the time to reach a temperature and come to equilibrium is taken into account.

Once the program simulated mouse clicks have started an impedance run in SMaRT, the LabVIEW program must wait until the experiment is complete to move on to the next step. Although inserting a simple delay would work to accomplish this, a slight variance in the time taken from one experiment to the next made a delay inefficient since in some cases it would be waiting well past the point when the experiment had completed. Additionally, a change in experiment parameters in SMaRT would affect the time needed to complete an experiment, and the delay may have to be altered to accommodate that. Therefore, the next step in the program is simply to poll the Solartron FRA for a status byte > 0, indicating the initiation of the experiment, and subsequently
poll the FRA until a status byte = 0 is received (Figure 5.9). This condition is only satisfied when the impedance measurement is completed.

Figure 5.9: While loop polling the FRA for a status byte > 0, indicating initiation of the experiment (top), and while loop polling the FRA for a status byte = 0, indicating completion of the experiment

The final step in the switching and measurement sequence is file management. Each set of data taken for a single sample is saved in a file designated in the experimental set-up within the SMaRT software. Once a run is complete, that file is copied, renamed and relocated to a user defined location. This may be chosen on the front panel. The front panel provides the option of adding a unique name to the file being generated, and the program adds the sample number (1 – 40), and temperature at which the measurement was taken (Figure 5.10). It should be noted that if this step encounters a file in the
destination folder with the same name that the program is trying to write, LabVIEW will not overwrite it, but will generate an error and the experiment will have to be aborted.

Figure 5.10: File management after data collection

Once this file transfer step is complete, the program returns to the beginning of the stacked sequence (“Open All” command to the Keithley switch) to test the next sample. Once all forty samples have been tested, the global variable “Measurements complete” is set to true, which stops and resets the running temperature loop. After a short delay to allow the program time to read and react to this, “Measurements complete” is set to false once again, the next test temperature is chosen, and the entire process is repeated. If all testing at all temperatures is complete, the voltage output of the heater is set to 0 and the program ends. If a user wishes to abort the experiment early, an abort button is also provided on the user front panel. This also will shut down the temperature loop, shut the heater off, and end the program.
5.4 Summary

LabVIEW was used successfully to build a program that has the ability to run the high throughput impedance test cell developed in this work. The program controls temperature and coordinates multiple pieces of equipment to take measurements on each sample in a library in series. It eliminates the need for human intervention during the entire testing process and organizes the files generated so that they may be analyzed later.
CHAPTER 6:
RESULTS

This section reviews some of the impedance results obtained as a result of this work, including bulk sample and thin film measurements.

6.1 Bulk Samples – BYZ10

Electrical impedance spectroscopy was performed on bulk samples of BYZ10 (BaZr$_{0.9}$Y$_{0.1}$O$_{2.95}$) in order to provide a standard against which any thin film results could be compared. The bulk samples were prepared in the same manner as the PLD target described earlier, however the pellets were pressed into 1 cm diameter samples. Copper wire was attached to the pellets using Ag paste, and samples were tested in a tube furnace at various temperatures under a wet N$_2$ atmosphere. N$_2$ gas was bubbled through water to achieve this atmosphere. Five sets of impedance data were taken at each temperature. The data were analyzed using ZView® software, and the resultant R values were averaged.

An example and explanation of the analysis performed will be shown here for one sample, but each data set received the same treatment. Data from the impedance testing is returned in the form of a table of values. At each frequency, the equipment measures the change in amplitude and phase shift of the AC signal sent to the sample, and then
automatically calculates the impedance, admittance, and capacitance of the sample. This data is most easily processed in graphical form, and for this case a real vs. imaginary impedance plot was created for each set of data. An example of this plot may be seen in Figure 6.1.

Figure 6.1: Example of a complex impedance plot for one measurement and the fit result associated with the equivalent circuit model

The data shown here are from a bulk sample of BYZ10 3.25 mm thick and 9.95 mm in diameter. Measurements were taken at 450 °C in a tube furnace with flowing wet N₂. Data were recorded at frequencies between 1 MHz and 100 mHz, with ten data points per decade and a 5 second integration time. A 10 mV AC perturbation signal was used. This value is typical for impedance testing, and most researchers use 10 mV or a similar perturbation signal when taking data. This number originates from the requirement that the applied amplitude be small enough such that the overall material-electrode response is electrically linear for any kind of meaningful analysis to take place (Macdonald, 1987). 10 mV generally satisfies this requirement for a wide range of
materials while providing a large enough signal to take the measurements, and this was taken as a starting point for all testing in this work. For bulk samples, 10 mV was found to be sufficient. The effect of applied signal in the measurement of thin films will be addressed in the discussion of thin film impedance measurement.

The resultant data showed three identifiable arcs in the complex impedance plot. The three arc Bauerle model, with constant phase elements in place of pure capacitors, was used as the equivalent circuit model for this set of data. The results of the fit may be seen as an overlay in Figure 6.1, and are enumerated in Table 6.1. The arc of interest is the high frequency arc (furthest left on the graph), since this is the arc associated with the material that is being measured.

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>25015</td>
</tr>
<tr>
<td>CPE1-T</td>
<td>6.79E-10</td>
</tr>
<tr>
<td>CPE1-P</td>
<td>0.81951</td>
</tr>
<tr>
<td>R2</td>
<td>49018</td>
</tr>
<tr>
<td>CPE2-T</td>
<td>4.05E-07</td>
</tr>
<tr>
<td>CPE2-P</td>
<td>0.48971</td>
</tr>
<tr>
<td>R3</td>
<td>2.12E+05</td>
</tr>
<tr>
<td>CPE3-T</td>
<td>4.91E-06</td>
</tr>
<tr>
<td>CPE3-P</td>
<td>0.50048</td>
</tr>
</tbody>
</table>

The R value associated with this first arc (R1) is used to calculate the conductivity according to:

\[
\sigma = \frac{1}{\rho} = \frac{t}{AR}
\]
In the example shown above, substituting in for the sample thickness and the electrode area, \(A\), we find that \(\sigma = 1.57 \times 10^{-4} \text{ S/cm}\). In order to reduce data collection times, one can set the frequency range such that data are not taken after the first arc is resolved. While confirmation of multiple arcs is reassuring, it certainly is not necessary, and in some cases requires data at low frequencies that make the experiment time prohibitively long. Therefore, the majority of data collected in this study was confined to impedance data at higher frequencies only, and was analyzed using a simple equivalent circuit of a resistor and constant phase element in parallel. While modeling just this portion, as opposed to the whole range of frequencies, does lead to some differences in the calculated conductivity, these differences were not large enough to cause concern. For the example case above, modeling for a single arc yields \(\sigma = 1.18 \times 10^{-4} \text{ S/cm}\). Data processed in this manner typically yielded lower conductivities than analysis of the full spectrum, meaning that any error would be on the side of caution. Given that this method and the test cell developed are meant to be a screening process for candidate materials, and not a precise indicator of the ability of each sample to be incorporated into practical applications, the sacrifice in accuracy was deemed worth the advantage of saving time.

Each set of data at the various temperatures was treated to the same analysis as described above. An average R value was found from multiple runs, and the conductivity was calculated. The results for this pellet may be found in Table 6.2.
It is known that the temperature dependence of ionic conductivity follows an Arrhenius relationship according to:

\[
\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)
\]

Using the calculated conductivity values, the process activation energy may be extracted from a plot of \(\ln(\sigma T)\) versus \(1/T\). The data shown in Table 6.2 was treated in this way (Figure 6.2) and an \(E_a\) value of 0.74 was found. This value is in good agreement with published values for grain boundary conductivity in BYZ10 (Bohn & Schober, 2000)(Babilo, Uda, & Haile, 2007). This value indicates that, in the impedance data shown in Figure 6.1, along with the other data sets, the high frequency arc actually incorporates both the grain boundary and grain interior effects and that the two arcs cannot be resolved. This is a problem that many researchers have encountered, and Babilo et. al. provides a thorough treatment of the subject (Babilo et al., 2007). However, the calculated conductivity is reflective of real-life performance of this electrolyte, as any
practical application of this material would be polycrystalline. Proton transport across the electrolyte will be rate limited in the grain boundary regions.

![Figure 6.2: Arrhenius plot of impedance data for BYZ10 bulk sample](image)

Additionally, these data are in relatively good agreement with reported conductivity values for this material. There is a wide range of reported conductivity values associated with BYZ10, and the data shown here fall within that range. Due to the variety of temperatures at which testing takes place, data had to be compared at different temperatures, and in some cases extrapolated to higher temperatures from Figure 6.3. Data presented in this work showed lower conductivity values than Bohn and Schober (5.9 x 10^{-3} S/cm at 450 °C (Bohn & Schober, 2000)) and Katahira et. al. (1.1 x 10^{-3} S/cm at 600 °C (Katahira, Kohchi, Shimura, & Iwahara, 2000)) versus an extrapolated value of 8.9 x 10^{-4} S/cm in this study). However the conductivity seen here was better than that reported by Slade et. al. (1.3 x 10^{-6} S/cm at 605 °C (Slade et al., 1995)) as well as that reported by Savaniu et. al. (7.5 x 10^{-6} S/cm at 500 °C (Savaniu, Canales-Vazquez, & Irvine, 2005)). Such large differences in reported values (up to three orders of
magnitude) may possibly be attributed to sample processing conditions. Most notably for BaZrO$_3$ based materials, the high-refractory nature of the samples leads to difficulties in obtaining a dense sample. The sample studied in this work was sintered at 1500 °C. The samples which exhibited better conductivity were sintered at higher temperatures, and the samples which exhibited lower conductivity were sintered at lower temperatures. This is a solid indication that sample density may have a profound effect on proton conductivity.

The experiments above were repeated with the same pellet using same-side co-planar contacts as well. The silver paint which had been applied for the original test was polished off, and a new set of contacts was attached to one side of the pellet. The results of this testing may be seen in Figure 6.3, and it was found that the orientation of the contacts did not have a significant effect on the conductivity measurements.

6.2 Bulk Samples – LVSO

Bulk sample of LVSO were also fabricated and tested in order to get a baseline measurement against which thin film samples could be judged. LVSO samples were tested in air at temperatures up to 300 °C. Data for a 1 cm diameter pellet with a thickness of 4.73 mm is summarized in Figure 6.3

An activation energy of 0.508 eV was extracted from this plot and this is in good agreement with literature values, which have been reported to be between 0.50 eV (Ohtsuka & Yamaki, 1989) and 0.55 eV (Yu, Bates, Jellison, & Hart, 1997; S. Zhao & Qin, 2003) for thin film samples of the material. The room temperature conductivity found here (9.74 x 10^{-9} S/cm) is approximately two orders of magnitude lower than the reported values in these works. This could be due to a combination of a number of
factors, including processing conditions, bulk versus film differences, and stoichiometry issues (e.g. Li-deficiency).

6.3 Thin Film Impedance

6.3.1 Experimental considerations

Impedance measurements on thin films require modification of some of the testing conditions that are typically employed. When working with the small amount of material contained in films, a larger applied AC voltage is often required to yield data with a measurable response. Figure 6.4 shows some results from a perturbation study on a thin film of BYZ10. This film was prepared by PLD on a quartz substrate. Silver contacts were deposited both over and under the film, but did not overlap in order to ensure that there was no short circuit. Copper wire was attached to the silver film using silver paste.
It is clear that, with increasing applied AC signal, the erratic behavior of the data is reduced. Furthermore, noise is reduced earlier at higher frequencies than at lower frequencies. In order to obtain reliable data on thin films, the AC signal has been chosen such that an appropriate signal to noise ratio is achieved without losing the linearity approximation achieved with low perturbation signals. In general, this number was found by increasing the AC value until the erratic results were eliminated, and then increasing the AC voltage past that point to ensure the preservation of linearity. If it was found that the impedance response was unchanged between these voltages, it was presumed that linearity was preserved.
Another issue inherent in impedance measurement of thin films is related to the relatively small capacitances of the material under investigation. When compared to capacitances associated with electrodes and other equipment, thin film contributions are often significantly smaller and are overshadowed by data from associated equipment. This renders the film properties essentially unmeasurable (Kidner et al., 2006; Kidner et al., 2007). In order to address this issue, thin film impedance data, especially on highly resistive materials, is typically taken using an interdigital electrode configuration. Such a configuration increases the length of the electrodes, allowing for measurable film contributions. Such a configuration was applied in preliminary film testing as well as within the test cell, and will be discussed below.

6.3.2 BYZ10 films

Impedance measurements were attempted on BYZ10 thin film samples deposited on 1.5 cm quartz substrates. All films were deposited by PLD at 400 °C with 10 mTorr O₂ background pressure. Multiple attempts were made to gather data on a variety of thin film samples. The majority of these tests employed a two-electrode strip of thin silver film. Two of the samples tested had an eight finger interdigital electrode configuration on top of the film, while one had no thin silver film and was simply tested by attaching the wires directly to the film using silver paste. Testing was carried out in a tube furnace with flowing wet N₂. Despite the various attempts and electrode configurations that were tested, it was found that obtaining an impedance value for this film was not possible. Observation of the data at different temperatures in all cases revealed that there was virtually no change in the impedance. Figure 6.5 shows a typical
example of the impedance response that was observed repeatedly. Such behavior is not expected for BYZ10 and also was not demonstrated during bulk sample testing. It was concluded that, since there was no demonstrable change in impedance values over a range of temperatures, that the arc that was observed was most likely due to the electrodes and not the film itself.

![Impedance Graph]

Figure 6.5: Attempt to measure the impedance of BYZ10 films and the resultant impedance arcs at 200 °C, 350 °C and 400 °C

The reason that data on BYZ10 films was difficult to resolve is not readily apparent, and could be the result of a number of factors either individually, or in combination. There is little information in the literature regarding the impedance testing of thin BaZrO₃-based films. The majority of work done with this material is focused on thicker films, on the order of 5 – 30 µm (Serra & Meulenberg, 2007). From the literature it appears that impedance testing on thinner films has been treated only by one group (Shim, Gur, & Prinz, 2008; J. Shim et al., 2009). Shim et. al. experimented with PLD deposition as well as atomic layer deposition (ALD) as fabrication methods. ALD samples showed higher conductivities, and a correlation with film thickness was found such that performance was enhanced in films less than 60nm thick. It was speculated that
the PLD deposited films exhibited decreased conductivity due to larger intergrain spacing. While film density in this work is possibly an issue, it should not have completely prevented the acquisition of data. The use of silver as a thin film contact in this case, film thickness, substrate/film interactions and stress and strain due to lattice mismatch between the film and the substrate are all factors that have not yet been addressed in any kind of detail.

The most likely cause of these difficulties lies with the electrode fabrication and configurations, since any film-related arcs are seemingly overshadowed by the electrode response. Even though, for reasons discussed above, some of the samples were tested using interdigital electrodes, there were some flaws in those electrodes. These films were some of the first that were created in our lab using interdigital electrodes, and Mylar tape was used to mask the substrate in the desired pattern. This is problematic for a few reasons. Firstly, there could be a issue of contamination of the film from the tape. Secondly, since they were not created by photolithography and were applied by hand, the fingers were relatively large and only numbered eight in total. And finally, after deposition, some film was removed along with the tape, causing non-uniform finger thickness and jagged edges. None of these factors is conducive to making accurate impedance measurements. Data on BYZ10 films taken in the test cell, which employs 18-finger smooth TiN electrodes with 50 µm spacing deposited by photolithography under the film, indicate that either the electrodes or the substrate were in fact the problem. It was observed that these samples exhibited some variation with temperature, which will be discussed later on in this chapter.
6.3.3 LVSO films

Prior to testing wafers in the test cell, individual larger scale thin film samples of LVSO were fabricated and tested to provide another basis for comparison of test cell data in addition to the bulk data that was collected. LVSO films were deposited by PLD onto 1.5 cm quartz substrates with three different electrode configurations: interdigital electrodes, a two-electrode strip, and a “T” electrode configuration. These electrode patterns can be seen in Figure 6.6 along with an example of the impedance response in each case. Each of these samples was tested in air at various temperatures to observe the effect, if any, of the electrodes on impedance measurements. The electrode and film patterns were made by masking the quartz substrate during deposition with either aluminum foil or Mylar tape. The periodic interdigital structure was masked off using Mylar tape which had been marked by a CO$_2$ laser to create the “fingers”.

![Interdigital electrodes](image1)

![“two-electrode strip”](image2)

![“T” electrodes](image3)

Figure 6.6: Impedance response of LVSO thin films with various electrode configurations.
The impedance results for these various electrode configurations clearly show the advantages that may be gained through the incorporation of an interdigital electrode structure. Results from the interdigital sample are less noisy and exhibit a smaller impedance arc when compared to the results of the two-electrode strip sample. Data obtained from the “T” electrode configuration appear to be free of noise and displays a significantly smaller impedance arc than the interdigital electrode sample. However, the data obtained from this “T” electrode configuration are questionable and may not have their origin with the LVSO thin film. This conclusion stems from the unusual shape of the graph, and the small impedance arc which is present in a different frequency range than the other samples. Additionally, the analysis of this sample’s temperature dependence did not match well with reported data, yielding an $E_a = 0.62$ eV. This number is probably meaningless, however, as the lower limit of impedance measurements for the Solartron 1296 dielectric interface is 100 $\Omega$, which just adds to the questionable nature of the data. Testing with a multimeter did not indicate a short circuit with this sample, but it is possible that there was a continuity problem with the film or that the behavior of the silver film caused a short circuit after exposure to elevated temperatures.

In contrast, the interdigital electrode sample matched up extremely well with published data on LVSO thin films, with an $E_a = 0.56$ eV and a room temperature conductivity of $1.04 \times 10^{-7}$ S/cm. In cases where interdigital electrodes are used, the calculation of conductivity values is slightly different than described previously. Conductivity for samples of this nature was calculated according to:
\[ \sigma = \frac{1}{\rho} = \frac{1}{R \, d \times l_{\text{finger}} \times n} \]

Where \( s \) is the spacing between the fingers, \( d \) is the sample thickness, \( l_{\text{finger}} \) is the length of the electrode fingers, and \( n \) is the number of interdigital electrodes (Bieberle-Hutter et al., 2008).

6.4 Test Cell Results - LVSO

Prior to testing sample libraries in the impedance test cell, confirmation that the impedance response was not affected by the extensive wiring and interfaces that make up the apparatus. To that end, a test circuit (Figure 6.7) with known parameters was inserted into the wiring and the thin film electrical traces were intentionally short circuited. In this way, the signal had to travel through the switch, switch terminal block, d-sub connectors, silver wires and thin film TiN in order to determine if all the wiring and equipment had any measurable affect on the measured impedance response.

![Test circuit](image)

\[ \begin{align*}
R_1 &= 100 \, \text{k}\Omega \\
C_1 &= 100 \, \text{pF} \\
C_2 &= 10 \, \text{nF}
\end{align*} \]

Figure 6.7: Test circuit used to test interfacial and wiring effects within test apparatus

The resulting data from the incorporation of this test module into the high throughput test cell may be found in Figure 6.8. The response from the module does not show any significant effects due to the wiring or interfaces. Fitting to the equivalent circuit shown in Figure 6.8 yielded \( R_1 = 99.3 \, \text{k}\Omega, C_1 = 115 \, \text{pF}, \) and \( C_2 = 10.1 \, \text{nF}. \)
After confirmation of the ability to get reliable data on LVSO samples in thin film form with interdigital electrodes and confirm that minimal effects from the wiring are present in the impedance response, the next step was to attempt to replicate this LVSO data within the high throughput test cell apparatus. For preliminary testing, forty-sample wafers were fabricated by first using photolithography and sputtering to apply the TiN electrical traces. The configuration of the TiN electrodes were as shown in Figure 3.15, with interdigital electrodes at each sample pad. Once that step was complete, the LVSO was deposited by PLD in a blanket deposition such that all forty samples should have the same approximate thickness and composition. In this way, it could be shown that the test cell is capable of measuring all forty samples accurately. Films were deposited at 400 °C in 10 mTorr of O\textsubscript{2}. Due to the lack of uniform material deposition profiles in the PLD system, each quadrant of the wafer was deposited separately, with the wafer rotated 90° for each separate section. Final film thickness was 500 nm.

The samples were also subjected to an in situ anneal at 400 °C for 1 hour under 500 mTorr of O\textsubscript{2}. Preliminary testing on quartz showed that the as deposited, unannealed films were not mechanically stable in air. After removal from the PLD chamber, if the
films were allowed to sit out exposed to atmosphere, they exhibited cracking and spalling after a few days. While the exact cause of this degradation remains unknown, it was conjectured that the as-deposited films were oxygen deficient and that cracking was due to oxygen incorporation into the lattice. When LVSO was deposited quadrant by quadrant, it was observed that the pads that were deposited earlier in the routine exhibited far less cracking and stability problems (Figure 6.9). This suggested that the extended time that these early deposition pads spent at elevated temperature in an oxygen atmosphere helped to improve their stability. This was tested by depositing a thin film sample of LVSO on quartz and subjecting it to an in-situ anneal prior to removal from the PLD chamber. It was found that this low O₂ pressure in-situ anneal after deposition mitigated the stability problems that were encountered. Films treated in this manner remained stable in air up to the temperature at which the deposition and in-situ anneal was performed. This post deposition in-situ anneal step was therefore effective and necessary to avoid cracking and film degradation.

Initial testing of the apparatus proved problematic due to contact issues between the wires and pads on the wafer. This was determined by comparing results of testing a library type wafer, and a bare wafer, and no wafer (open circuit). The impedance response of testing an open circuit (wires lifted off the wafer) and the response when the wires are in contact with only the oxidized wafer are shown in figure 6.10.
Figure 6.9: Optical micrographs showing mechanical instability of LVSO films. The numbers indicated the order in which the pads were deposited.

As can be seen, the impedance response from each of these two conditions is one very large arc. There exists no smaller arc when examined more closely. Since these conditions are the two which may occur when the wires are not properly situated on the
TiN pads around the outside of the wafer or when a sample pad is discontinuous, it was concluded that any impedance arcs that differed significantly from these were a response from the thin film.

After switching the contacts from tinned copper to sterling silver and applying a larger load (as discussed in Chapter 5), the test apparatus began to yield some usable data that could be analyzed and compared to previous results. All data were analyzed in ZView and were generally treated with a one arc equivalent circuit model. Some of the data were treated with a three arc model, but as with previous experiments, the difference between the results was negligible. An example of data taken from a single sample pad may be seen in Figure 6.11.

Figure 6.11: Impedance data from high throughput test cell for a single LVSO sample pad
As with many measurement techniques, impedance spectroscopy will always give results, but the user must determine the quality of the data and how these results should be interpreted. Since the data shown here were all arcs that were significantly smaller (by at least two orders of magnitude) than arcs observed for the two failure conditions shown in Figure 6.11, it was concluded that these arcs are associated with the LVSO film that was to be measured. A temperature dependence analysis was performed on this pad consistent with the analysis performed on the test samples discussed earlier, and the results of that analysis may be seen in Figure 6.12. The slope of this line was extracted and the $E_a$ was calculated to be 0.56 eV. The room temperature conductivity was found to be $\sigma = 0.99 \times 10^{-6}$ S/cm. This value matches up very well with Ohtsuka et. al., who reported a value of $1 \times 10^{-6}$ S/cm (OHTSUKA & YAMAKI, 1989).

![Figure 6.12: Temperature dependence of LVSO thin film sample tested in high throughput impedance test cell](image)

The simple analysis of this single pad serves to show that even given all the interfaces, switching, and other potential causes for skewed results, the test cell apparatus
can be used to obtain accurate data on thin film samples. When testing a library of samples, it was found that data were more reliable for some sample pads as opposed to others. Figure 6.13 shows a graphical representation of all data collected from a blanket library (all sample pads have the same composition and approximate thickness). Ideally, impedance measurements from each sample pad should be about the same in size and shape. However, this is not the case. While it is expected, and observed, that there should be some random variation between pads, some of the data are simply too far out of range to be considered reliable. It was found that, in its current state, the rate of failure of the apparatus to yield film data was about 20% - 25% per wafer. This is most likely due to lingering issues with the wafer alignment with the sterling silver contacts and their ability to make good contact with the electrical traces on the wafer. The inability to make good contact could be due to the method used to shape the silver contacts, and possibly a lack of proper loading.

Figure 6.13: Example of impedance data for all 40 pads of a blanket library of LVSO
These conclusions are based on observations made and experiences gained during the construction and preliminary testing of the high-throughput test cell. The wire contacts are currently a problem that needs to be addressed. Since changes were made to the wafer configuration after the hardware was designed, the original tool created to bend the wires (a hollow stainless steel ring) was improperly sized. As a result, each wire was shaped and adjusted individually, leading to a lack of uniformity from wire to wire. Even with the use of a guide, wires were often difficult to keep straight during their forming. Because of this, some wires are simply askew when neighbor wires are aligned with their associated sample pad. This may also occur due to the set screw that holds the wire in place becoming loose. The metal set screws fasten into threaded ceramic and are sometimes difficult to tighten down. Such issues will not only have a bearing on alignment, but also might cause the load to be unevenly distributed. This problem was lessened during the phase of testing which involved stronger tinned copper wires. However, as discussed in the previous chapter, sterling silver wires were a better choice due to their ability to make better contact with the TiN contact pads.

Additionally, although the original design of the test cell apparatus was meant to include a way to index the wafer and orient it in the same location every time it is loaded, such an inclusion was not present in the final fabrication. As a result, it is difficult to align each test pad with the wires, and it involves a fair amount of small adjustments and rotations. It is especially difficult to see and evaluate the contact alignment in the quadrant of the wafer nearest the user.

As discussed previously, tests that were performed on wafers outside the test cell in order to evaluate contact wire materials and load demonstrated that the impedance
response was dependent on the quality of the contact between the wafer and the wires. As load, and subsequently the quality of contact, was increased, the impedance response decreased until it met what was considered its true value. This was evaluated by adding additional load and observing no change in the impedance response. The data show a wide range of impedance values, as opposed to two distinct groups indicating the two extremes of good contact and no contact. This would be explained by a varying degree of contact quality between pads. Acquisition of high quality data from this test cell in the future will depend on the ability to make and verify good contact with the wafer. This may involve a redesign of the method of contact, the material used, and the load applied. A contact configuration that employs wires situated directly above the sample pads (as opposed to the current radial design) would solve some of these problems. If such a configuration were combined with a good way to align each wafer, there is no doubt that this test cell would consistently yield reliable data.

In the case of the data shown in Figure 6.14, although it does appear to have a wide range of response, the majority of data sets pictured here yielded similar conductivity values when analyzed. If the sample pads which were quite obviously not yielding film measurements are disregarded, the average conductivity of 32 sample pads measured at room temperature in the film is $\sigma = 4.5 \times 10^{-6}$ S/cm, while the calculated activation energy of the samples was $E_a = 0.52$ eV. While these values certainly do not prove that each and every connection is yielding an accurate measurement of the film under testing, these numbers are very encouraging.
6.5 Test Cell Results – BYZ10

A final effort was made to characterize thin films of BYZ10 by depositing a blanket library in the same manner as the LVSO films above. The data generated by this sample were promising, and an example may be seen in Figure 6.14. The impedance arcs that were generated were too small to indicate one of the failure conditions, and this data revealed a temperature dependence. It was therefore concluded that the impedance data were originating from the BYZ10 films.

![Figure 6.14: BYZ10 thin film test results from one sample pad](image)

While these results are an improvement over previous attempts to generate impedance data from thin film BYZ10, many questions are unresolved. A large portion of the data sets exhibited irregularities in the impedance response for which the simple equivalent circuit models that have been used in this work do not account. Impedance arcs looping back over themselves and large portions of the arc bowing into the negative real impedance regime are especially prevalent (and may be seen in Figure 6.15 as well).

Arcs were identified as best as they could be, and a temperature dependence analysis was carried out for some of the sample pads. If the arcs were identified correctly, $E_a$ values were consistently found between 0.80 eV – 0.89 eV. These values
are higher than what is typical for grain boundary transport in BYZ10 (typically around 0.75 eV), however they are smaller than the value of 1.2 eV reported by Shim et. al. for PLD deposited BYZ10 films. In order to increase confidence in these values, more testing on this sample needs to be done and additional samples need to be fabricated and tested. In the literature, BYZ10 has always proven to be problematic, with researchers reporting significantly different results even on bulk samples (Azad et al., 2008). This appears to be largely the result of challenges in properly interpreting impedance results. Until data are sampled at a larger range of temperatures and a larger amount of data is processed, very little can be said about the results with any degree of confidence or understanding.

6.6 Summary

Impedance testing of thin films presents a difficult challenge, and is made even more difficult when one attempts to apply combinatorial methods to the testing scheme. It has been shown here that creating a forty sample library and systematically testing those samples using the high throughput impedance test cell fabricated for this work can yield a large amount of reliable data very quickly. With a few modifications, the test cell will be able to test a variety of different materials for which impedance data is desirable, paving the way for new materials discoveries.
CHAPTER 7:

FUTURE WORK AND RECOMMENDATIONS

This chapter will detail recommendations for future work which will aid in the electrical impedance testing of combinatorial libraries for new materials discoveries. If implemented, the test cell described will be able to test libraries of any class of materials for which EIS can be useful. Suggestions on how to proceed in the study of BYZ10 will also be presented here.

7.1 Test cell

As discussed in the previous chapter, contact between the wafer and the silver wires in the test cell has proven to be challenging. The original design called for contact with the wafer to be made with round wires (Figure 7.1). The point of contact may be widened with an applied load to slightly flatten the side of the wire in contact with the wafer, however there is little room for error. While this type of contact was suitable for the individual thin film samples on which it was tested initially, it proved to be significantly harder to implement in the high throughput cell. The variations from wire to wire as they were formed caused TiN pads to be contacted at different points (closer or
further from the edge of the wafer), which is not compatible with the ceramic ring which was designed to apply the load along a set diameter. As a result, the load to some wires was not applied in the optimal location, and the quality of contact in these locations was diminished.

![Diagram](Applied Load)

Figure 7.1: Representation of round wire contacting the flat wafer

Future work involving this high throughput EIS testing apparatus needs to address the reliability and quality of contacts between the wafer and the test cell. There are multiple avenues that may be pursued to address this issue and increase the probability of making good quality contact. These include creating a forming ring of the appropriate diameter such that it may be used to bend the wires uniformly. This would also involve machining a new ceramic ring of the same diameter to be used to apply load. Alternatively, the orientation of the wires may be changed such that they are held in place directly above the pads on the wafer that they are meant to contact, thereby ensuring that each pad is contacted. Both of these implementations would likely improve reliability and performance.

A third way to address the contact issue is to change the basic form of the contacts. If foil or thin sheets of some conductive material were formed into “feet” that could lie flat against the TiN contacts on the wafer, it would allow for a wide area of potential contact. This may also be accomplished by modifying the existing wires such
that they lay flat against the wafer (e.g. hammering them flat). This approach is recommended over the others due to its ease of implementation and potential for success. Although the increased width of the contacts will require extra care to keep them from contacting each other, this approach does not require any shop work on difficult to machine ceramics and may be incorporated into the existing hardware. In contrast to wire-based contact methods, application of a load on flat contacts would simply serve to push them flush against the wafer even when they are not perfectly formed.

7.2 BYZ10

Doped barium zirconate and other proton conducting oxides remain materials of interest due to their potential applications in gas sensors, fuel cells, and other fields. In the case of Y-doped BaZrO₃, many factors which contribute to its proton conductivity are not well understood. There exist very few published reports of data for this material in thin film form, and this work has only begun to gather data on them. Before any combinatorial work can be done that is based on this material, it is imperative that a good standard be developed against which any new materials may be measured.

More impedance data needs to be taken on these thin films at multiple temperatures in order to get an accurate picture of the processes taking place. These tests need to be repeated in order to demonstrate repeatability. Questions about what may or may not be affecting measured conductivity values must also be addressed. The stoichiometry of the films much be confirmed. Studies on the effect of the substrate or the thin film contacts on the material properties must also be studied. Stress, strain, and interdiffusion could all play a part in enhancing or diminishing the conductivity of the
sample. For similar reasons, the effect of co-planar electrodes on top of the film (as opposed to underneath the film as was presented here) should be examined.

Once the issues with the test cell are addressed and a thorough study of BYZ10 is completed, the masking scheme developed to create ternary libraries by PLD should be employed to create libraries suitable for testing. These can then be screened in the high-throughput test cell and evaluated for potential candidate materials for intermediate temperature fuel cells. Additionally, testing on ternary systems for other applications, such as Li-ion batteries, may be carried out in the test cell.
APPENDIX A:

TEST CELL

A.1 Pinouts

Table A.1 shows the pinout for the impedance test cell

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Figure A.1: Contact numbering for reference in Table A.1 References
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