DEVELOPMENT OF BIOPOLYMER BASED
RESONANT SENSORS

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DEVELOPMENT OF BIOPOLYMER BASED RESONANT SENSORS

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DEVELOPMENT OF BIOPOLYMER BASED RESONANT SENSORS

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Currently investigation of biopolymers for electronics, photonics and sensor applications is becoming more widespread. In this work, fabrication of a resonant sensor using various biopolymers has been accomplished. Biopolymers are becoming more and more common in the fabrication of electronic and photonic devices due to their inexpensiveness or cost effectiveness, eco-friendliness and ease of processing. The resonant sensor consists of an inductor in series with a variable capacitor composed of two electrodes separated by a chemically sensitive biopolymer. The resonant sensor is a multi-parameter device as one can measure the resonance frequency, amplitude and phase of the scattering parameters. Examples of chemical testing using the resonant sensor will be presented.
Dedicated to my parents
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CHAPTER 1

INTRODUCTION

Sensors are becoming more widespread in everyday societal living. Our food for human consumption, our environment and public settings are susceptible to chemical threats. By utilizing accurate and sensitive sensors, this threat may be minimized if not eliminated. Sensors are also used in medicine. Using sensors to detect various chemicals in the human body is necessary in order to monitor different diseases and illnesses. A sensor is a device that converts a physical phenomenon into an electrical signal (1). Sensors respond to a stimulus by providing an electrical signal. Sensors are valuable measuring tools due to their ability to provide information that would otherwise be difficult to obtain. They are created many different ways depending on the application or what is being sensed.

Polymer materials are often used as the sensing layer in the fabrication of sensors. Polymers are long chain-like molecules made up of many repeating units called monomers. They are found in nature and can be made synthetically. Some examples of synthetically made polymers as the sensing layer in sensors are explained below. A report of a MEMS (MicroElectroMechanical System) capacitive chemical sensor uses poly (ethylene-vinyl acetate) (PEVA) as the sensing layer between two electrodes (2). Once a chemical is detected, the
polymer swells, increasing the distance between two electrodes and the relative permittivity increases. Kim et al. report of a customized polyimide layer in the construction of a relative humidity (RH) sensor (3). Cho and Jokerst report of using SU-8 photoresist (a viscous polymer) in the fabrication of a microdisk photonic sensor (4). Sridhar and Takahata report of a hydrogel based passive sensor with a variable inductive transducer (5). Lastly, electrochemical sensors coated with Nafion have also been reported (6). The variable inductor is coupled with a hydrogel element that makes dimensional changes in response to the target parameter to modify the inductance.

The aforementioned polymers are made synthetically. Synthetically made polymers often use harmful toxins or generate toxic byproducts that can pollute the environment (7). In an effort to preserve the environment, scientists, engineers, biologists and others search for other materials to fabricate sensors and other devices. Materials that conform to preservation of the environment are the naturally occurring polymers mentioned previously which are called biopolymers. Biopolymers are natural organic polymers found in nature in which no harmful toxins are used to create them.

1.1 What are biopolymers?

Biopolymers are polymers that are generated from renewable natural resources (7). They can be produced by biological systems such as microorganisms, animals, plants, insects and humans. Biopolymers include starches, proteins and Deoxyribonucleic Acid (DNA). Monomers are the building
blocks of these polymers. The biopolymer’s monomeric units are usually amino acids, sugars and nucleotides. Some biopolymers, like nucleic acids and proteins, have the inherent ability to carry and manipulate biological information. Other polymers such as the polysaccharides, nature’s family of sugars, provide fuel for cell activity and serve as structural elements in living systems (7).

1.1.1 Why use Biopolymers?

Biopolymers are being studied as promising materials for several reasons. Biopolymers, for example Deoxyribonucleic Acid (DNA), contain optical and electromagnetic properties that can be used in electronic and photonic devices (8). These properties include low and tunable resistivity, and ultralow optical and microwave loss (8) (9) (10). Additionally, biopolymers are inexpensive, biodegradable and easy to integrate into electronic and photonic components and devices. As a comparison, most synthetic plastic or polymer materials are not biodegradable and are derived from nonrenewable resources (7). Next, biopolymers ease of integration involves fabrication techniques that are inexpensive and simple to manipulate. Typically, biopolymers are not used as thin film polymers which make them unique materials for fabrication of devices. Some examples utilizing the biopolymer in devices include a DNA complex used as an electron blocking layer in a light emitting diode (LED) (11), a polypyrrole doped DNA electrode biosensor (12), doped DNA used as a bottom gate layer in a field effect transistor (13) and a DNA layer fabricated into nanoscale wells in a silicon substrate to demonstrate crystal photonic waveguides (14). Since they
are renewable resources, biopolymers can safely be biodegraded and thus not harm the environment.

1.1.2 Biopolymers used in this work

The biopolymers used in this thesis are salmon DNA and silk. The salmon DNA is developed by the Chitose Institute of Science and Technology in Japan, the Air Force Office of Scientific Research Asian Office of Aerospace Research and Development and the United States Air Force Research Laboratories Materials and Manufacturing Directorate. The salmon DNA is extracted from biowaste material leftover from processing the edible fish, specifically salmon milt and roe sacs (8) (9) (15).

Silk is a fibroin protein material isolated from the Bombyx mori silkworm (16). This silk protein is a biocompatible material as such; it is often used in mammalian cell proliferation.

1.2 Objectives of this research

This thesis was conducted demonstrate the effect doping has on biopolymers and the use of biopolymers as a chemically sensitive layer in the construction of a resonant sensor. Some known synthetic polymers are also used as the sensing layer in this work to compare to the biopolymers. Additionally, not only is the structure using known synthetic polymers and biopolymers as a chemically sensitive layer in the sensor, but a relative focus of introducing this concept as a viable contribution to chemical sensing techniques is of importance.
1.3 Significance of this research

The significance of this thesis is twofold. First, the discussion of doping biopolymers is significant because doping allows for changes to the inherent properties of the biopolymer. Furthermore, these changes add to the mobility in the biopolymer thus making it a possible candidate for a semiconducting layer in devices (13).

Techniques using polymers as the chemically sensitive layer in a sensor based on polymer swelling have been previously reported (2). However, this thesis presents a chemical sensor not based on polymer swelling but on changes in the resonant frequency due to changes in the capacitance or inductance in the resonant sensor. From this change in the aforementioned parameters, the chemical of interest can be deduced.

1.4 Outline of this thesis

Finally, the outline of this thesis is presented. Chapter 2 presents information on the some of the synthetic polymers and biopolymers used in this thesis. This includes some of their properties and uses in devices today.

Chapter 3 describes the sensor. First, the 3D model of the capacitive test structure is described, detailing each layer of the device. Next, the electrical model for the capacitive test structure is explained with the insertion of the equation for the parallel-plate capacitance which directly relates to the dielectric permittivity. Lastly, the S-parameter equations and the equation for the resonant frequency from which the capacitance can be retrieved are included.
Chapter 4 explains how the experimentation was carried out. It describes the steps necessary in determining electrical parameters by fitting the electrical model to the experimental results obtained from the scattering parameters.

Chapter 5 clarifies the results acquired from the scattering parameters. Initially, results are discussed for the biopolymers and polymers in which no chemical tests were administered. This includes the polymers and biopolymers that are doped with transition metals and those that are not doped. Finally, the biopolymers and polymers in which chemical tests were administered are presented and discussed.

Chapter 6 discusses final conclusions and the direction in which this experimentation is progressing in our group and possible suggestions for future work.
CHAPTER 2
BACKGROUND

As mentioned previously, the use of polymers in electronic and photonic devices is quite prevalent. Some polymer materials are discussed briefly in this section. Natural polymers or biopolymers, also known as bio-dielectrics, have been around for many years but not really utilized. However, their use in electronics and photonics is becoming more popular as the need for biodegradable components become more of a demand as a step in preserving the environment. A background of the biopolymers used in this thesis will be presented as well as synthetic polymers for comparison purposes.

2.1 A Review of Some Polymers Used in Sensors

As previously mentioned, synthetic polymers are primarily used in sensors. This section is a brief review of some of those polymers.

2.1.1 Poly (ethylene-vinyl acetate) (PEVA)

Poly (ethylene-vinyl acetate) (PEVA) possesses excellent swelling performance when exposed to certain chemicals like toluene and benzene (2). In addition, this swelling is reversible. That is, once the chemical is recognized, weak bonds occur between PEVA and the chemical or analyte resulting in the
polymer returning to its original state. Also, adsorption of chemical warfare agent simulants dimethyl-methyl-phosphonate (DMMP) and chloroethyl ether (CEE) are reported (17). PEVA is shown to be sensitive to nonpolar hydrocarbons which are sensitive to the aforementioned chemical warfare agent simulants.

2.1.2 Polyimides

Polyimides are known to be used as a flexible substrate due to its mechanical properties and fabrication compatibility (3). Additionally, polyimides are widely used as an interlayer dielectric material in relative humidity (RH) sensors and are compatible with IC processing (3) (18). They possess good hysteresis, linearity, high sensitivity to humidity and show high resistance to most chemicals (19). Polyimides are extensively investigated for use as a moisture sensing material. The sensitivity to moisture in combination with its mechanical properties further proves its usefulness in RH sensors due to swelling of the polymer in many instances. Lastly, the shrinking dimensions of microelectronics create a need for dielectric materials with low relative dielectric constants and this need is often filled by low relative dielectric constant polyimides (15).

2.2 Polymer Materials Used as the Dielectric in this Work

For comparison purposes, two polymer materials have been employed. They are poly (methyl methacrylate) or (PMMA) and Nafion.
2.2.1 Poly (methyl methacrylate) (PMMA)

Poly (methyl methacrylate) (PMMA) is a common polymer in many sensors. Just as polyimides possess sensitivities to relative humidity, PMMA does as well. Su et al. report on the effects doping has on PMMA in relative humidity sensors (20). The PMMA is doped with two different salt complexes that enhance the sensitivity, linearity and ionic conductivity of the PMMA. For optical purposes, PMMA is used in fiber optic sensors as optical waveguides or claddings (21). However, fiber optic sensors usually use PMMA in matrix form due to its optical parameters’ inability to be influenced by the environment. As an example, Hungerford et al. utilized PMMA as a strengthener with Nile red dye (22). This is done to study silica-calcite glass for a biocompatible application since PMMA is a mechanically robust and biocompatible polymer. Lastly, PMMA is used as a sensing layer in bimorph micro/nano cantilever chemical sensors (23). One side of the cantilever is coated with PMMA. Upon sensing the chemical (analyte), the PMMA detects it and thus a mechanical change occurs.

2.2.2 Nafion

Nafion is a synthetic biopolymer referred to as a perfluorosulfonate ionomer (24). Ionomers are comprised of repeat units of electrically neutral repeating units and ionized units. Nafion is composed of a backbone of Teflon made famous by the DuPont ™ Company. Although not technically a biopolymer, due to its biocompatibility, it is used in biosensors as a sensitive biological element (6).
Nafion is affected by relative humidity which affects its proton conductivity (24) (25). Many experiments with Nafion use it two ways; as a dry Nafion sensor and a wet Nafion sensor. This is due to Nafion’s response to moisture in that the signal of the sensor changes. Furthermore, due to Nafion’s response to moisture, the material is used in fuel cells to promote conductivity thus promoting current flow (25) (26).

2.3 Biopolymer Materials Used as the Dielectric in this Work

The two biopolymers used in this work are salmon DNA and Silk.

2.3.1 Salmon Deoxyribonucleic Acid (DNA) Biopolymer

The salmon DNA in this work comes from purified waste from the fishing industry in Japan. In its original state, its molecular weight is high thus making it a highly resistive material. Furthermore, it is a water soluble material (15). If desired, the DNA is sonicated to a lower molecular weight. Additionally, in order for the DNA to be deposited as a thin film, it needs to be water insoluble. Therefore, a surfactant, such as hexadecyltrimethylammonium chloride (CTMA), is mixed with the DNA (15). This surfactant makes the complex DNA-CTMA insoluble in water. In order to preserve DNA as a biopolymer, the complex must be precipitated thus removing the excess CTMA. Moreover, this complex becomes soluble in organic solvents and makes this a useful biopolymer for device fabrication. Upon processing the DNA into a useful
material, metal nanopowders can be added to enhance its electrical and optical properties for use in devices.

The double-helical structure of DNA yields unique charge transport mechanisms. Within a double stranded DNA molecule, transport occurs through a combination of thermally activated hole-hopping and standard molecular wire transport mechanisms (15). Additionally, increase in charge transport mobility has been achieved by blending the DNA molecules with conductive polymers such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) or (PEDOT:PSS) as well as conductive nanoparticles such as single wall carbon nanotubes to allow some tunability in the material (13).

2.3.2 Silk Biopolymer

Silks are generally defined as protein polymers that are spun into fibers by some lepidoptera larvae such as silkworms, spiders, scorpions, mites and flies (27). However, the most extensively characterized silks are from the domesticated silkworm, *Bombyx mori*. Historically, silkworm silk has been used commercially as biomedical sutures in repairing wound injuries for decades and in textile production for centuries (16) (27). Also, there are reports of using this biomaterial in tissue engineering due to its slow degradation, excellent mechanical properties and biocompatibility (16) (27) (28). The recent ability to fabricate silk-based materials of various geometries including films, sponges, mats, and fibers from purified silk fibroin solution, has resulted in the reemergence of silk as a biomaterial (16). From the above examples, silk finds
its largest application in tissue engineering. The silk biopolymer in this study is provided by Rajesh Naik’s Biotechnology Group at the Materials and Manufacturing Directorate of the Air Force Research Laboratory (AFRL) located at Wright Patterson Air Force Base in Ohio.

2.4 Why use a Coplanar Waveguide (CPW) Device?

As previously mentioned, there are many chemical sensors based on the premise of being either capacitive or resonant using a polymer as the sensing layer (2) (3). Additionally, many are complicated structures that require many fabrication steps as well as some external circuitry for detection. The structure of this sensor device involves simple fabrication steps with a biopolymer that is safe for the environment and abundantly available. The simple structure involves a coplanar waveguide (CPW) transmission line (29). The coplanar waveguide (CPW) consists of a center strip with two ground planes that are parallel to and in the plane of the strip (30). Coplanar waveguides and their modifications are widely used in high-speed microwave integrated circuits due to the ease of series and shunt elements integrated into the line without the need of drilling holes into the substrate as well as easier on-wafer probing (9) (30). The sensor is self resonating thus it requires no external circuitry.

2.5 Summary

This chapter has covered some background information regarding common synthetic polymers used in sensors, synthetic polymers used in this work for
comparison to the biopolymers, the biopolymers utilized for experimentation and the reasons for using the coplanar waveguide structure of this sensor work.

The next chapter describes the electrical circuit used as the sensor in this thesis. This includes its fabrication and operation as a resonant circuit.
3.1 3D Model

Illustration of the design of the resonant sensor and the electrical circuit used for testing is presented in this chapter. The resonant sensor design is based on the concept of a ferroelectric varactor shunt switch realized by Guru Subramanyam et al (31) (29). Figure 3.1 shows a 3D view of this device consisting of 4 separate layers on a high resistivity (> 6 kΩ) silicon (Si) substrate with a thin silicon dioxide (SiO₂) isolation layer. Directly on top of the SiO₂ layer is the bottom electrode, Metal 1, containing a shunt line which connects two ground lines. Notice the shape of Metal 1 is in the form of an H. Next the ferroelectric material, Barium Strontium Titanate (BST), is deposited. Finally, the top electrode is composed of a ground-signal-ground coplanar waveguide (CPW) transmission line (Metal 2) which is deposited on top of the BST.

Figure 3.1: Ferroelectric varactor shunt switch consisting of BSTO₃ sandwiched between two metal layers.
The ground lines in Metal 1 are directly below the ground lines in the Metal 2 thus creating an effective ground for the sensor. Figure 3.1 shows a parallel plate varactor is created between the signal line centered between the two ground lines in Metal 2 and the bottom conductor, the shunt line, connecting the two ground lines in Metal 1. The varactor capacitance and the large ground capacitance are in series thus creating an effective capacitance of the varactor. The shunt conductances of the large ground-pad capacitors, as well as the sensor area, eliminate any need for via holes thus resulting in a simple process (29).

The resonant sensor is similar in structure but consists of a biopolymer sandwiched between the two metal layers. Instead of just an "H" formed bottom layer (Metal 1), Metal 1 contains windings in place of the shunt line in the ferroelectric varactor that form the inductance of the LC resonator or sensor. The two ground lines in Metal 1 are shunted together by their midpoints by a 375 µm wide conductor. The length of the “windings” from each ground line to the sensor area is 125 µm. The area of the sensor itself is 125 µm². In addition, the signal line in the top layer (Metal 2) and where it overlaps the bottom metal layer (Metal 1) form the capacitance contributing to the resonant frequency. Consequently, the layer of SiO₂ has been omitted in the resonant sensor design as well. The 3D picture of the resonant sensor is shown in Figure 3.2. Also, a photograph of the resonant sensor is shown in Figure 3.3 illustrating the sensor under measurement with the Ground-Signal-Ground (GSG) probes in place.
Figure 3.2: 3D view of the resonant sensor showing the overlap of the signal conductor in the top metal layer (Metal 2) and the parallel shunt line in the bottom metal layer (Metal 1) which forms the capacitance area in the sensor device. Additionally, the biopolymer, the chemically sensitive layer, is sandwiched between the metal layers.

Figure 3.3: A photograph of the resonant sensor with the CPW probes in place in order to record a frequency sweep of the structure.


3.2 Electrical Model

The diagram of the electrical model of the resonant sensor is shown in Figure 3.4. The input port of the signal line of the CPW line is designated by “1”. Additionally, the transmission line boxes and port “2”, output port, make up the rest of the signal line. The test capacitance of the sensor area is indicated by $C(V)$. Normally, the capacitance varies with applied DC bias in the biopolymers due to the ionic charges. $C(V)$ can be represented as a parallel plate capacitor as follows,

$$C(V) = \frac{\varepsilon_0 \varepsilon_r(V) A}{t}$$  \hspace{1cm} (3.1)

where $\varepsilon_0$ is the free space permittivity, $\varepsilon_r$ is the permittivity or dielectric constant of the biopolymer, $A$ is the overlap area between the two metal conductors and $t$ is the thickness of the biopolymer. $R_d(V)$ represents the shunt resistance of the biopolymer (dielectric) modeling the leakage conductance ($G$) of the capacitor being tested (32). Next, $R_s$ indicates the parasitic series resistance and $L$ is the parasitic series inductance of the shunt line (32). From the electrical model and frequency response of the sensor area, the capacitance can be computed. By manipulating equation 3.1, the relative dielectric constant ($\varepsilon_r$) of the biopolymer can be obtained and is shown below as Equation 3.2.

$$\varepsilon_r(V) = \frac{C(V)t}{A\varepsilon_0}$$  \hspace{1cm} (3.2)
Once the frequency response is recorded, the resonant frequency can be obtained from this data. Resonant frequency occurs when the impedance of the capacitor and inductor are at a minimum or equal to zero (33). The impedance of the capacitance and leakage conductance (modeled by the shunt resistance in the electrical model) is computed as

$$Z_c = (j\omega C + G)^{-1}$$

(3.3)

where $C$ is the capacitance and $G$, the leakage conductance, is the reciprocal of $R_d$, the shunt resistance in Figure 3.4.

Equation 3.4 shows the impedance of the parasitic series inductor and the parasitic series resistance. Adding equations 3.3 and 3.4 and equating them to zero gives the conditions for resonance.
\[ Z_L = j\omega L + R_s \quad (3.4) \]

In solving the equation for the resonant frequency, the shunt resistance is very high, thus the leakage conductance or loss in the material is very low due to the low loss nature of the material so it can be ignored. Additionally, the parasitic series resistance is a very low value as well. This is due to the intrinsic property of metals being low in resistivity. Solving for \( \omega \), the radial frequency, gives the result in Equation 3.5.

\[ \omega = \frac{1}{\sqrt{LC}} \quad (3.5) \]

Substituting the radial frequency for the operating frequency in Hertz (Equation 3.6), the resonant frequency is then determined and this result is shown in Equation 3.7.

\[ \omega = 2\pi f \quad (3.6) \]

\[ f = \frac{1}{2\pi \sqrt{LC}} \quad (3.7) \]

This equation can be manipulated and solved for \( C \) to obtain the capacitance of the sensor area once a chemical has been applied or upon doping of the biopolymer. Notice that the frequency changes when the capacitance changes. There is an inverse relationship between the two. Consequently, as the capacitance increases, frequency decreases and vice versa. Moreover, the frequency changes in a non-linear fashion. This is illustrated in Figure 3.5 with a fixed inductance of 0.22 nH.
Figure 3.5: Frequency as a function of capacitance with a fixed inductance of 0.22 nH. The inverse relationship permits a sharp decrease in frequency as the capacitance increases.

 Lastly, the frequency response of a two-port network such as this also provides the S-parameters from the Vector Network Analyzer (VNA). The resonator is a reciprocal network thus, $S_{11}$ is identical to $S_{22}$ and $S_{21}$ is identical to $S_{12}$. Thus from microwave network theory, $S_{ij}$ is defined as,

$$S_{ij} = \frac{V_i^{-}}{V_j^{+}}$$

(3.3)

where $V_i^{-}$ is the amplitude reflected out of port $i$ and $V_j^{+}$ is the amplitude incident at port $j$ (34). $S_{ij}$ is found by driving port $j$ with an incident wave of voltage $V_j^{+}$ and measuring the reflected wave amplitude, $V_i^{-}$, coming out of port $i$. For this resonant sensor design, it can be shown that
\[ S_{11} = \frac{Z_{in}^1 - Z_o}{Z_{in}^1 + Z_o} \]  

and

\[ S_{21} = \frac{v_o}{v_{in}} \]  

where \( Z_{in}^1 \) is the impedance as seen looking into port 1 and \( Z_o \) is the characteristic impedance of the CPW transmission line (15). The algebraic calculation of the S parameters of the structure takes into account the loss associated with the real transmission line (15). The loss associated with each 50 Ω transmission line is 1 Ω. Using Figure 3.4 and the characteristic impedance, \( Z_o = 50 \), \( Z_{in} \) and the S parameters for the capacitive test structure can be computed as

\[ S_{11} = \frac{2R_s + 2j\omega L + 2\left(\frac{1}{R_d} + j\omega C\right)^{-1} - 2499}{102R_d + 102j\omega L + 102\left(\frac{1}{R_s} + j\omega C\right)^{-1} + 2601} \]  

and

\[ S_{21} = \frac{50[R_s + j\omega L + \left(\frac{1}{R_d} + j\omega C\right)^{-1}]}{51[51 + R_s + j\omega L + \left(\frac{1}{R_d} + j\omega C\right)^{-1}]} \]
3.3 Summary

This chapter discusses how the sensor is fabricated and the electrical equivalent circuit. In addition, the equations for the S-parameters, resonant frequency, capacitance and inductance are explained.

The next chapter describes how the experiments are performed which includes all the equipment used for probing and data acquisition.
CHAPTER 4

EXPERIMENTAL PROCEDURE

Design of an electronic device is not an arbitrary decision especially those dealing with microwave integrated circuits. Ideas must be investigated, simulations of the design must be administered and optimizations of parameters need to be established to ensure viability and promise of the concept. As a result, for this concept, specific values for the parameters in the electrical model are determined by fitting the circuit model to the experimentally obtained S-parameters. This is done by utilizing the Computer Aided Design software package by Applied Wave Research’s (AWR) Microwave Office® for simulation purposes. A Hewlett-Packard 8720 Vector Network Analyzer (VNA) along with an on-wafer microwave probe station is used to measure the S-parameters. The setup with the Ground-Signal-Ground (GSG) probes in place is shown in Figure 4.1.
Figure 4.1: Picture of the on-wafer microwave probe station with the probes connected to one of the many devices on the wafer.

Figure 4.2: The complete measurement synopsis. The probes are connected to the sensor from which a frequency sweep is rendered using the VNA. Once the VNA has completed the frequency sweep, the values of the S-parameters acquisitioned are sent to a computer through a GPIB.
The S-parameters are determined as follows: First, the VNA is calibrated over a frequency range of 0.5-18 GHz using the line-reflect-reflect-match (LRRM) method (15) (29). Next, in utilizing the device as a chemical sensor, the chemical is applied only to the capacitive area and a frequency sweep is rendered from the VNA. Next, the S-parameters are recorded and sent through a General Purpose Interface Bus (GPIB) which is connected to a computer for data manipulation. This same methodology is rendered when the humidity test is applied as well as for the analysis of the doped biopolymer. The connections to the probe station, VNA and computer are shown above in Figure 4.2. The Radiant Tester, which is used for low frequency measurements, and the Temperature controller (controls the temperature of the wafer chuck) are not used in this experiment.

Once the measured S-parameters are recorded, they are imported into AWR’s Microwave Office® simulation package. The electrical parameters are determined from the electrical model introduced in Figure 3.4. Initially, values are estimated for the electrical model. Subsequently, the electrical model is tuned manually in order to simultaneously match the experimental results of \( S_{11} \) and \( S_{21} \) across the frequency range specified. This process is repeated for each set of experimental data retrieved from each device on the wafer. Returning to the four parameters in the electrical model (Figure 3.4), \( C(V) \), \( R_d(V) \), \( R_S \) and \( L \), they must all be varied to match the experimental data. Just using \( S_{21} \) or \( S_{12} \) curves can result in several matches that appear to be exactly correct. However, using \( S_{21} \) (or \( S_{12} \)) curve and the \( S_{11} \) (or \( S_{22} \)) curve generally produces a unique
electrical model that matches both curves well (15). However, this can sometimes be a challenge due to a lossy biopolymer material meaning the dielectric constant is not purely real (34). Figure 4.3 shows a screen shot in AWR’s Microwave Office of the experimental data being matched with the electrical model. $S_{21}$ and $S_{11}$ versus frequency graphs are illustrated on the left side of the figure and the schematic and variable tuner are shown on the right of the figure.

Figure 4.3: A screen capture of AWR’s Microwave Office. This is an example of tuning the electrical parameters to match the measured S-parameters from the VNA. The graphs of $S_{21}$ and $S_{11}$ with both experimental and theoretical data from the model are on the left side of this figure. The electrical model and the variable tuner are seen on the right side of this figure.
4.1 Summary

This chapter explains how the testing is done. By obtaining experimental data from each device and then matching this data to the electrical model, determination of the parameters involved can be found through a matching method.

The next chapter presents the outcome of the experimental data and what the data represents.
CHAPTER 5
RESULTS AND DISCUSSION

This chapter describes the frequency dependent measurements for all the biopolymers used as the chemically sensitive layer in the sensor. Additionally, the well known polymer poly (methyl methacrylate) (PMMA) is measured in order to compare with the biopolymers. Initially, data is retrieved for doped PMMA and doped DNA as compared to their undoped counterparts. This is to illustrate how doping affects the resonant frequency and the amplitude. Furthermore, undoped and doped samples of PMMA are tested as chemical sensors by the application of deionized (DI) water on the film. The iron doped DNA-CTMA is also tested as a chemical sensor by applying DI water to the film. Alternatively, Nafion and Silk are not doped and are tested as chemical sensors by applying chemicals such as ethanol, isopropanol and DI water or by blowing on the sensor (Humidity test). All testing in this study is done at 0V DC bias and at room temperature. Also, deviations in measurements of the devices occur on the same substrate due to thickness variations in the biopolymer films (9) (15). Lastly, all of the undoped and doped biopolymers and PMMA films were measured using a frequency sweep of the S-parameters but only the aforementioned films resulted in conclusive data for discussion.
5.1 Undoped and Doped Biopolymers (No Chemical Test)

Undoped and doped biopolymers in which chemical tests are not performed are presented in this section. Initially, undoped PMMA is introduced and compared to its doped equivalent. Next, undoped DNA-CTMA is analyzed and compared to its doped counterpart. Both PMMA and DNA-CTMA are doped with iron, manganese and nickel but only the devices with conclusive information are included in this thesis.

5.1.1 PMMA

PMMA is the first polymer for discussion. Two different wafers with the sensor devices containing the well known polymer PMMA as the dielectric layer are measured. They are used as reference samples to compare the effect of doping.

5.1.1.1 PMMA (NO DOPANT)

The reference swept frequency response of both PMMA samples without any doping is shown in Figure 5.1 and Figure 5.2. The amplitude of $S_{21}$ of Sample 1 is located at -36 dB with a resonant frequency of 2.95 GHz. The amplitude of $S_{21}$ of Sample 2 is located at -58 dB with a resonant frequency of 6.7 GHz.
Figure 5.1: Frequency sweep of $S_{11}$ and $S_{21}$ of Sample 1 - undoped PMMA. The resonant frequency is 2.95 GHz and the amplitude is -36 dB.

Figure 5.2: Frequency sweep of $S_{11}$ and $S_{21}$ of Sample 2 – undoped PMMA. The resonant frequency is 6.7 GHz and the amplitude is at -58 dB.
5.1.1.2 PMMA Doped with 5 Wt% Iron (Fe)

In Figure 5.3, the frequency response of the undoped PMMA (Sample 1) layer compared to the 5 wt% Iron (Fe) doped PMMA layer is shown. The resonant frequency shifts from 2.95 GHz to 4.7 GHz and the amplitude increases from -36 dB to -54 dB after doping resulting in an 18 dB difference. This increase in amplitude suggests iron contributes attenuation or loss in the PMMA film. The increase in the resonant frequency is expected due to the dielectric constant of iron being less than that of PMMA. This decreases the dielectric constant and capacitance in the PMMA biopolymer thus increasing the resonant frequency. As a result, it can be concluded that it is possible to determine the effect of iron doping in PMMA.

The relative phase is shown in Figure 5.4. Note that the phase of $S_{21}$ must be adjusted to the lagging phase in order to obtain the total relative phase. Notice the 5 wt% Fe doped sample leads the undoped PMMA sample.

Figure 5.3: Comparison of the frequency response of $S_{21}$ of undoped PMMA (Sample 1) and 5 wt% Fe doped PMMA.
5.1.1.3 PMMA Doped with 5 Wt% Nickel (Ni)

Figure 5.5 shows the measured frequency response for the undoped PMMA (Sample 1) layer compared to two devices with the 5 wt% Nickel doped PMMA layer. $S_{21}$ of the first sample results in a resonant frequency of 6.6 GHz and an amplitude of -46 dB. $S_{21}$ of the second sample results in a resonant frequency of 6.4 GHz and an amplitude of -41 dB. When doped with Nickel, the frequency in both samples is greater than that of the undoped PMMA by about 3.5 GHz. This results in a smaller capacitance and thus a smaller effective permittivity. This result is expected due to the dielectric constant of the nickel nanopowder being less than that of PMMA thus lowering its dielectric constant which increases the resonant frequency. Also, the amplitude increases by 10 dB in the first sample and 5 dB in the second sample. Figure 5.6 shows the relative phase of $S_{21}$ of...
the two Nickel doped samples. Notice how the Nickel doped samples lead the undoped PMMA sample.

Figure 5.5: Frequency sweep of $S_{21}$ of the reference PMMA (Sample 1) and 5 wt% Nickel doped PMMA.

Figure 5.6: Relative phase of $S_{21}$ of the reference PMMA (Sample 1) and 5 wt% Nickel doped PMMA.
5.1.2 DNA-CTMA

Next, the complex DNA-CTMA is discussed. As mentioned previously in Chapter 1, this complex is a low loss material where doping is known to change its dielectric constant.

5.1.2.1 DNA-CTMA (NO DOPANT)

Figure 5.7 shows the frequency response $S_{21}$ of the DNA-CTMA complex without any added dopant. The resonant peak of $S_{21}$ is at 5.84 GHz and the amplitude is at -20.2 dB. The undoped DNA-CTMA is used as a reference in order to compare to the doped DNA-CTMA samples.

Figure 5.7: Measured swept frequency response of undoped DNA-CTMA at 0V DC bias and room temperature.
5.1.2.2 DOPED DNA-CTMA

Various dopants are added to the DNA-CTMA complex. The dopants used are transition metals namely iron (Fe), manganese (Mn) and nickel (Ni) in the form of nanopowders. These dopants noticeably change the swept frequency response of the sensor devices.

5.1.2.3 DNA-CTMA Doped with 2 Wt% Iron (Fe)

Figure 5.8 shows how doping creates a frequency shift of the resonant frequency in comparison to the undoped DNA-CTMA reference layer. In addition, doping contributes to an increase in the amplitude of the sensor. While the undoped DNA-CTMA’s resonant frequency is at 5.84 GHz, the 2 wt% Fe doped samples are at 4.35 GHz. The amplitude of the DNA-CTMA is at -20 dB while the 2 wt% Fe doped samples are at -28.2 and -28.9 dB, respectively. The dielectric constant of iron is less than that of the DNA-CTMA complex which should result in a lower dielectric constant of the material, a lower capacitance and a resonant frequency shift to a higher value. However, this did not occur. Apparently, due to the nature of iron being a ferromagnetic material, the inductance seems to be increasing instead of the capacitance. The relative phase of $S_{21}$ for both the reference sample and the 2 wt% Fe doped samples are shown in Figure 5.9. Notice the phase of the doped samples lag behind the undoped DNA-CTMA reference sample as does the magnitude as mentioned previously in Figure 5.8.
Figure 5.8: Measured swept frequency response of the amplitude of the reference sample and the 2 wt% Fe doped DNA-CTMA.

Figure 5.9: Relative phase of $S_{21}$ in degrees for the reference sample and the 2 wt% Fe doped DNA-CTMA.
5.1.2.4 DNA-CTMA Doped with 10 Wt% Manganese (Mn)

Figure 5.10 shows the effect of doping DNA-CTMA with 10 wt% of manganese (Mn). Using the undoped DNA-CTMA as a reference and looking at the first resonant frequency peak of the 10 wt% Mn doped DNA sample, a frequency shift of the resonant frequency occurs. The resonant frequency shifts from 5.84 GHz in the undoped DNA-CTMA sample to 2.25 GHz in the Mn doped sample. This direction of the shift is not expected due to the dielectric constant of the DNA-CTMA being greater than that of manganese. This shift causes an increase in the capacitance thus an increase in the dielectric constant of the material. However, due to the nature of the material it is possible that the inductance is increasing as opposed to the capacitance. The amplitude remains primarily the same.

Figure 5.10: Measured swept frequency response of the amplitude of the reference sample and the 10 wt% Mn doped DNA-CTMA.
In figure 5.11, the relative phase of $S_{21}$ for both the reference sample and the 10 wt% Mn doped DNA-CTMA are shown. Notice the phase difference of the doped sample compared to the reference sample.

![Figure 5.11: Relative phase of $S_{21}$ in degrees for the reference sample and the 10 wt% Mn doped DNA-CTMA.](image)

5.1.2.5 DNA-CTMA Doped with 5 and 10 wt% Nickel (Ni)

Figure 5.12 also shows how doping DNA-CTMA with 5 wt% and 10 wt% Nickel (Ni) affects the resonant frequency and amplitude. The frequency response of the 5 wt% Nickel doped DNA-CTMA shows a resonant frequency of 7.25 GHz which is 1.4 GHz greater than that of the reference sample.

The 10 wt% Nickel doped DNA-CTMA shows two different results. This is due to the measurements taken on the same substrate but at different locations. The variability is due to possible non-uniformity of the film on the substrate. On the first sample with 10 wt% Ni doped DNA-CTMA, the amplitude is only about
10 dB more than the reference sample and the frequency is less than that of the reference sample. Since nickel is a ferromagnetic material like iron, the reason for this shift is due to the increase in inductance. In contrast, on the second sample, the amplitude is about 20 dB greater than the reference sample and the frequency is more than that of the reference sample. This frequency shift results in a lowered dielectric constant and smaller capacitance. Figure 5.13 shows the relative phase of $S_{21}$ of the reference sample and the Ni doped samples.

Figure 5.12: Measured swept frequency response of the amplitude of the reference sample of the undoped DNA-CTMA and the 5 and 10 wt% Nickel doped samples of DNA-CTMA.
5.2 Undoped and Doped Biopolymers (Chemical Tests)

In order to test the effect chemicals have on the dielectric layer in the sensor, various chemicals are applied. The data is recorded and analyzed.

5.2.1 PMMA (DI Water)

Once more PMMA is presented as the reference polymer in this study. Figure 5.14 shows the reaction of DI water applied to the undoped PMMA layer (Sample 2) in the capacitive area/sensor. Recalling the resonant frequency of the undoped PMMA occurs at 6.7 GHz and the amplitude is at -58.7 dB, the resonant frequency of the undoped PMMA with water applied occurs at 7 GHz and its amplitude is at -62.4 dB. This results in a 300 MHz shift in resonant frequency and a 3.7 dB increase in amplitude. PMMA is sensitive to water; as a result, the
expectation is for resonant frequency to shift to a lower value. The dielectric constant of water is greater than that of the PMMA material thus a higher capacitance and dielectric constant and a shift to a lower resonant frequency. However, this was not the case.

When the water is suctioned from the effective area, the resonant frequency shifts to 7.15 GHz and the amplitude shifts to -55 dB. Notice how the amplitude proceeds back to its original position in which no water had been applied. Alternatively, the resonant frequency increases slightly.

Figure 5.14: Measured frequency sweep of $S_{21}$ of undoped PMMA (Sample 2), water added and water removed from the sensor area.

Further chemical tests are done on the 5 wt% Fe and 5 wt% Ni doped PMMA films. The swept frequency response of the effect of the 5 wt% Fe doped PMMA film (reference), 5 wt% Fe doped film with water applied and the 5 wt% Fe doped film with the water removed is shown in Figure 5.15. Observe the reference
resonant frequency at 4.8 GHz and the amplitude at -57.3 dB. Once the water is applied to the sensor, a frequency shift occurs to 4.26 GHz and an 8.7 dB increase of the amplitude occurs as well. This decrease in frequency means the dielectric constant and the capacitance of the material increased. This is due to the dielectric constant of water being greater than that of the 5 wt% Fe doped PMMA. But when the water is removed, it is observed that the resonant frequency and amplitude values appear to slowly return to their initial position.

![Graph showing frequency response of 5 wt% Fe doped PMMA](image)

Figure 5.15: Frequency response of 5 wt% iron doped PMMA (reference), 5 wt% iron doped PMMA with water applied and with water suctioned off of the sensor area.

The next measured frequency response is that of 5 wt% Ni doped PMMA. In Figure 5.16, notice the frequency shift from 6.62 GHz to 8.11 GHz and the amplitude from 50.4 dB to 51.8 dB upon application of water to the sensor area. Since the dielectric constant of water is much higher than that of the material, the expectation is that the resonant frequency would shift to a lower value due to the
increase of the dielectric constant. However, this is not the case. Once the water is removed from the sensor, notice the how the resonant frequency returns to its initial position at 6.62 GHz but the amplitude increases slightly to -54 dB. Figure 5.17 shows the relative phase of $S_{21}$ originally with no water applied, application of water and removal of water.

Figure 5.16: Frequency sweep of $S_{21}$ of the 5 wt% Nickel doped PMMA (reference), 5 wt% Nickel doped PMMA with water applied to and water removed from the capacitive area.
5.2.2 DNA-CTMA Doped with 2 wt% Iron (Humidity Test)

The humidity test done on the 2 wt% Fe doped samples is shown in Figure 5.18. The reference data, 2 wt% Fe doped DNA, shows a resonant frequency of 4.35 GHz and amplitude of -28.9 dB. There is a decrease in the frequency and an amplitude decrease when humidity is introduced to the sensor. The water from the blowing permits the shift in frequency thus increasing the dielectric constant and capacitance of the material. The relative phase in degrees of the reference sample and the 2 wt% Fe doped DNA-CTMA with blowing is shown in Figure 5.19.
Figure 5.18: Measured swept frequency response of the amplitude of the reference sample, 2 wt% Fe doped DNA-CTMA, and the 2 wt% Fe Doped DNA-CTMA with Humidity test done.

Figure 5.19: Relative phase of $S_{21}$ in degrees of the reference sample and the 2 wt% Fe doped DNA-CTMA with Humidity test done.
5.2.3 Silk (Two Testing Methods)

Silk is another material used as a biopolymer in this study. Although the silk films were not doped with any metals, changes were discovered once a chemical of interest was introduced to the sensor.

Two methods were employed in order to test the effect of the chemicals on the sensors. In the first method, the chemical was initially applied and the experimental data was immediately recorded. After recording the data, we waited for the chemical to evaporate. Upon what appeared to be total evaporation, the chemical was applied to the sensor again and experimental data was recorded. In the second method, the chemical was applied and the experimental data was again immediately recorded by the data acquisition program. However, in this method, opening and closing of the program was rendered consecutively about 4-6 times for each chemical application. Following the introduction of the reference data, results from both methods will be introduced.

5.2.3.1 Process 1: Evaporation of Chemical on the Sensor

A frequency sweep of the silk film without any chemical added is shown in Figure 5.20. The resonant frequency is measured at 5.58 GHz with an amplitude of -49.1 dB.
5.2.3.1.1 Silk Chemical Test (Ethanol)

The first chemical of discussion is Ethanol that was introduced on the sample. Figure 5.21 shows the frequency swept response of the application of ethanol on the sensor. Notice how $S_{21}$ decreases in magnitude (amplitude) once the ethanol is applied in both instances. The Ethanol 1 application shows how $S_{21}$ decreases in magnitude but the resonant frequency remains the same. From the decrease in magnitude, the attenuation constant can be obtained. Since the resonant frequency remains the same in this application, it can be concluded that the capacitance remains the same. The Ethanol 2 application shows how $S_{21}$ decreases in magnitude and also the resonant frequency decreases. From the decrease in magnitude and the decrease in resonant frequency, the attenuation
constant and the capacitance can be obtained, respectively. Figure 5.22 shows the relative phase of $S_{21}$ in degrees.

![Graph showing measured swept frequency of $S_{21}$](image)

**Figure 5.21:** Measured swept frequency of $S_{21}$ of the reference sample and two applications of Ethanol.

![Graph showing relative phase of $S_{21}$](image)

**Figure 5.22:** Relative phase of $S_{21}$ of the reference sample and two applications of Ethanol.
5.2.3.1.2 Silk Chemical Test (Isopropanol)

Figure 5.23 shows the frequency response from applying Isopropanol to the sensor area. Notice how the resonant peak of $S_{21}$ increases in magnitude in the first application of isopropanol. Upon applying isopropanol the second time (Isopropanol 2), $S_{21}$ decreases in magnitude. In both instances, the resonant frequency does not change. The increase and decrease in magnitude reflect the losses in the biopolymer layer and the conductor. In applying isopropanol initially, it was allowed to air dry before applying isopropanol the second time. This application may not have evaporated completely which results in a decrease in the loss the second time around. The relative phase is shown in Figure 5.24.

![Figure 5.23: Measured swept frequency of $S_{21}$ of the reference sample and two applications of Isopropanol.](image-url)
5.2.3.1.3 Silk Chemical Test (DI Water)

DI water illustrates the most dramatic change in frequency shift and amplitude compared to ethanol and isopropanol. Reverting back to the dielectric constant, DI water has a dielectric constant greater than both ethanol and isopropanol. As a result, a more prominent change in the response is expected. In addition, silk’s dielectric constant is less than that of water so an increase in the material dielectric constant and capacitance is expected once the water is applied to the silk film. Hence, the frequency sweep of $S_{21}$ is shown in Figure 5.25. Notice the shift in resonant frequency peaks. The resonant frequency shifts to about 0.5 GHz less than its original position and the amplitude decreases by 20 dB once the DI water is applied to the sensor initially. In the second application, again the resonant frequency shifts to about 0.5 GHz less than the previous position but
the amplitude only decreases by about 10 dB compared to the first application.

As expected, the dielectric constant increased, accordingly, the capacitance increased. Figure 5.26 shows the relative phase of $S_{21}$.

![Figure 5.25: Measured swept frequency response of $S_{21}$ of the reference data and the sensor with DI water applied.](image-url)
5.2.3.2 Process 2: Repetitive Inquiry of Sensor as Chemical Evaporates

A second analysis was done for the silk biopolymer. This analysis consists of applying the chemical to the sensor and doing a frequency sweep then immediately shutting down the program and re-opening it. This process is done 4-6 times for each chemical mentioned previously in Process 1.

The reference data for this process is shown in Figure 5.27. The resonant frequency of $S_{21}$ is at 4.7GHz and the amplitude is at -29.6 dB.
5.2.3.2.1 Silk Chemical Test (Ethanol)

Figure 5.28 shows the effect of ethanol being applied to the sensor. Notice how the first sample (Ethanol1) initially shows how the resonant frequency at 4.7GHz and amplitude at 29 dB of $S_{21}$ change. As continuous acquisition of the sample is recorded, the frequency and amplitude of $S_{21}$ eventually return to the initial value which is that of the reference data. This occurred because ethanol's dielectric constant and silk's dielectric constant are close in value. Therefore, there is a small decrease in the resonant frequency and a small increase in the dielectric constant of the material. Additionally, since ethanol has a high evaporation rate, $S_{21}$ returned to its initial value. Figure 5.29 is a magnified viewpoint between 4 and 6 GHz of this point. The relative phase is shown in Figure 5.30.
Figure 5.28: Measured swept frequency response of $S_{21}$ of the reference data and 6 continuous data acquisition samples of ethanol.

Figure 5.29: Magnification of Figure 5.28.
5.2.3.2.2 Silk Chemical Test (Isopropanol)

The next chemical test performed is that of isopropanol. Figure 5.31 shows the frequency sweep of $S_{21}$ of the reference data and 4 consecutive data acquisitions of isopropanol. Notice the closeness in value of each of the data. This indicates the fast evaporation rate of isopropanol. Furthermore, its dielectric constant is even closer in value to silk’s dielectric constant than the ethanol had been. Therefore, to detect this chemical, a sensor having a quick response time is desirable. Nevertheless, the resonant frequency does shift to a lower value thereby increasing the dielectric constant and the capacitance. Figure 5.33 shows the relative phase of $S_{21}$ of the reference data with no isopropanol applied to the sensor and 4 consecutive data acquisitions of isopropanol. Since the data
is so close, Figure 5.32 shows a magnified view of Figure 5.31 and Figure 5.34 shows a magnified view of Figure 5.33.

Figure 5.31: Measured frequency sweep of $S_{21}$ of the reference data and 4 inquiries of the sensor with isopropanol applied.

Figure 5.32: Amplified view of Figure 5.31.
Figure 5.33: Relative phase of $S_{21}$ of the reference data and 4 inquiries of the sensor with isopropanol applied.

Figure 5.34: Magnified view of Figure 5.33 representing the relative phase of $S_{21}$ of the reference data and 4 inquiries of the sensor with isopropanol applied.
5.2.3.2.3 Silk Chemical Test (DI Water)

The final test data for the silk includes the application of DI water to the sensor. Figure 5.35 displays the frequency sweep of $S_{21}$. DI water shows the slowest evaporation rate of all the chemicals. Notice the sample of Water1 is the result of water being applied initially and the sensors’ response. Water2 through Water5 samples are the result of the water evaporating thus allowing the sensor to return to its initial state before the water was applied. As expected, a lowered resonant frequency occurred and the dielectric constant and capacitance increased. Figure 5.36 illustrates the relative phase of $S_{21}$ of the reference data and the 5 data acquisition results of applying DI water.

![Figure 5.35: Measured frequency sweep of $S_{21}$ of the reference data without DI water and 5 runs of the DI water application.](image)
5.2.4 Nafion

The last material tested is Nafion. Figure 5.37 shows the frequency response of $S_{11}$ and $S_{21}$ of the Nafion film with no chemical test done. The resonant frequency is at about 7.4 GHz with an amplitude of about -21 dB. Comparison of the Nafion film without blowing and with blowing is shown in Figure 5.38. Note that blowing represents a relative humidity of 100%. Observe the frequency change as well as the decrease in the amplitude. The frequency decreases from 7.4 GHz to about 7 GHz in the first sample and from 7.4 GHz to 7.25 GHz in the second sample. Thus the capacitance is increased and the effective dielectric constant is also increased. These measurements agree with those determined by Paddison et al. They demonstrated that the dielectric constant increases with increasing water content. However, above about 14 GHz this is not the case.
Additionally, the amplitude decreases from -21 dB originally to -16.7 dB in the first sample and from -21 dB to -17.2 in the second sample.

Figure 5.37: Frequency sweep of $S_{11}$ and $S_{21}$ of the Nafion film with no chemical test applied.

Figure 5.38: Frequency sweep of $S_{21}$ of the Nafion film without blowing (reference) and the Nafion film with blowing two times.
5.3 Summary

This chapter describes the effect of doping in the well known polymer PMMA and also the uses of the DNA-CTMA and Silk biopolymers as the chemically sensitive dielectric layer in a resonant sensor application. In order to quantify this effect, a frequency sweep of all the materials is performed. The first section begins with well known polymer PMMA. The undoped and doped PMMA films are compared. Additionally, the undoped and doped DNA-CTMA films are compared. The second section reveals the effect of various chemicals on some of the undoped and doped biopolymer films as well as the well known polymer, PMMA. First, undoped and doped PMMA films are tested with DI water applied. Next, a Humidity test by blowing on the film is performed on the 2 wt% Fe doped DNA-CTMA complex. Thirdly, three chemicals (ethanol, isopropanol and DI water) are tested on undoped silk films. Two different processes are utilized to measure the effect of the aforementioned chemicals and to show the devices’ use as a possible sensing platform. Finally, a Humidity test is rendered by blowing on the Nafion polymer material. From the measured frequency responses, each of the above tests reveals either a frequency shift or an amplitude increase or decrease or both.

The last chapter presents an overall conclusion of this work and future efforts this work is generating.
CHAPTER 6
CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

This section concludes the work done measuring the effect doping has in biopolymers as well as using biopolymers as a sensing layer in a resonant chemical sensor. Doping PMMA with the metals, nickel and iron, shows an increase in the resonant frequency thus a decrease in the dielectric constant and capacitance. This is due to the low dielectric constant of the metals. In contrast, doping DNA-CTMA with the metals, manganese and iron, shows a decrease in the resonant frequency. Instead of a change in capacitance, a change in inductance may have occurred. However, when DNA-CTMA is doped with nickel both a shift lowering the resonant frequency and increasing the resonant frequency occurs.

The chemical test using DI water applied to the sensor with undoped PMMA as the sensing layer showed an increase in the resonant frequency and thus a decrease in capacitance and relative permittivity. Next, the iron doped PMMA material was tested with DI water applied to the sensing area. When applying the water, the shift to a lower resonant frequency is very evident thereby increasing the dielectric constant of the PMMA. This is due to the high dielectric constant of DI water changing the dielectric constant of the material to a higher
value. Once the water was removed, the resonant frequency proceeded to its original position. This shows the sensor could possibly be used at least more than one time. Doping PMMA with nickel showed promising results as well. Its resonant frequency shifted to a higher frequency resulting in a lower dielectric constant and lower capacitance.

Iron doped DNA-CTMA as the chemically sensing layer is also tested as a chemical sensor. When blowing on the sensor, resembling 100% relative humidity, the resonant frequency shifted thus concluding that this material could be used as a relative humidity sensor.

In using silk as the chemically sensitive dielectric in the sensor, changes occurred in the resonant frequency as well. Two methods are initiated. In the first method, solvents are used as the chemical or analyte. In applying ethanol and isopropanol to the sensor area and allowing them to air dry between the first and second applications, changes in the magnitude occurs. Conversely, when applying DI water, the resonant frequency shifts and magnitude decreases. Again, the higher relative permittivity or dielectric constant of water is the contributor of this result. In all three instances, each solvent is individually detected by the first method of testing using the silk biopolymer.

In the second method, an even more profound outcome occurs. In sensors, obtaining rapid results is desired. In testing both the ethanol and isopropanol, an immediate shift is detected. Additionally, both responses approach their original position. Due to the amount of time that transpired in testing, it is apparent that the sensor responded promptly especially since both solvents evaporate quickly.
in air. Also, because the dielectric constants of both solvents are near that of silk, the changes were small. Alternatively, since water possesses a slower evaporation rate than both ethanol and isopropanol, it returns to its initial position at a slower rate.

Lastly, the Nafion biopolymer is tested by blowing on the sensor area. Nafion is known to be sensitive to water. Accordingly, a resonant frequency shift occurs resulting in the effect of relative humidity on the dielectric constant of the Nafion film.

This experimentation has shown that using a biopolymer as the dielectric layer in this device is a promising platform for sensing chemicals. This is done by utilizing resonant frequency shifts obtained due to the change in the capacitance of the sensor area. The change in the capacitance is in turn due to the changing effective permittivity of the biopolymer layer in the presence of analytes.

6.2 Future Work
In an attempt to make the device more robust and measure selectivity, an environmental chamber is in the development stage. This chamber would ideally be under vacuum in order to obtain more succinct and precise measurements. In addition to testing chemicals applied on the sensor in this chamber, testing the sensor using gases is also in the making.
Since polymers have been well known to vary with temperature and voltage, thereby using it as a tunable material, the same is possible with biopolymers. This testing is presently being done in our group for future applications.

Presently, GSG probes connected to the device via CPW transmission lines measure the frequency response of the device. In the future, it is possible to connect an antenna to the device which is connected to network analyzer in order to utilize the sensor wirelessly.

Food science may be an area the sensor can be utilized. Humidity is a factor in the growth of mold on foods. With more testing, the sensor could be a promising tool for this application.

Lastly, our intent is to use this design as a Radio Frequency Identification Device (RFID). By using the resonant peaks as signatures, objects can be identified easily as each one will have a unique signature.


