THE DEVELOPMENT OF DNA-BASED BIO-POLYMER HYBRID THIN FILMS
FOR CAPACITOR APPLICATIONS

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THE DEVELOPMENT OF DNA-BASED BIO-POLYMER HYBRID THIN FILMS
FOR CAPACITOR APPLICATIONS

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ABSTRACT

THE DEVELOPMENT OF DNA-BASED BIO-POLYMER HYBRID THIN FILMS FOR CAPACITOR APPLICATIONS

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Polymer materials are widely used as insulation materials in electric circuits, power generation and energy storage applications. Deoxyribonucleic acid (DNA) based bio-polymer hybrids described in this research have been found to display interesting electrical characteristics, such as a relatively high dielectric constant, good electrical resistivity and high voltage dielectric breakdown behavior. These characteristics are comparable to current state of the art polymer materials and have been shown to be promising as insulating dielectrics for capacitor applications. This investigation describes the processing, test structure design and fabrication, and electrical characterization of DNA based hybrids for dielectric applications. Salmon DNA hybrid films incorporating sol-gel derived ceramic materials have relatively high dielectric constants and higher environmental stability compared to DNA-only films.
Thin film devices were fabricated and an in-depth dielectric characterization was performed, demonstrating stability in measured dielectric values, \(k>5\) (1kHz) and reliability in voltage breakdown measurements, attaining values consistently > 300V/µm. This research is focused on the processing, fabrication and characterization of a new DNA-based bio-polymer hybrid material for dielectric applications. This material has been processed and optimized specifically for capacitor applications. Capacitor test structures have been fabricated using the DNA-hybrid material. Layered devices have also been designed, fabricated and characterized. Several device architectures have been characterized for dielectric properties, investigating frequency and temperature dependence, leakage current, voltage breakdown, and polarization measurements for energy storage and efficiency. Dielectric applications of DNA bio-polymer hybrid materials have been investigated and their unique fabrication challenges have been addressed.
For future generations of engineers and scientists:

May you find that new, novel and sustainable energy source.

The world is depending on it!
ACKNOWLEDGMENTS

This dissertation has been a process and a life changing experience. I started by wanting to understand materials better. Coming from an electrical engineering background, I realized that everything begins with the materials. I have found these two disciplines, materials and electrical engineering, to be a great combination. Our world is currently in an electronics boom, especially mobile devices. It seems like even 10 year olds have cell phones these days. So when studying electronic materials-what is the real need? Specifically, what is the one thing that every electronic device needs? The answer- POWER/ENERGY SOURCES. New/novel energy sources are of great interest to me as well as a great need for most of society including personal, commercial and government needs. Along with this need is the intense striving for the development of a novel “green” energy source as fossil fuels are diminishing and the projection of energy needs in the future outweighs the current resources.

I started to work in electrical engineering in 2005 after several years out of the field. I realized that all things electronic came down to the materials. I returned to school and had classes with Terry Murray, Andrew Sarangan, Kladi Lafdi, Andrey Voevodin, Elena Guliants, Liming Dai and with the advisement of Danny Eylon and Tony Saliba started on a Materials Engineering path. While taking a polymer class with Liming Dai I did research on energy storage, batteries and capacitors, using conducting
polymers and nanomaterials. I hoped to continue research in this area and I cross referenced Liming Dai’s work, energy sources and the Air Force Research Laboratory (AFRL). I discovered Jim Grote, from AFRL, and Liming Dai had recently co-published a paper using a new bio-polymer material, salmon DNA. It was shortly after that I joined Jim Grote’s Biotronics Research Group at AFRL, and started learning about the DNA material. Research dissertations by Emily Heckman, Josh Hagen and Carrie Bartsch were great starting points for my research. Collaborations with the University of Arizona, Case Western Reserve University (CWRU), University of Cincinnati, and Pennsylvania State University (PSU) have also helped develop and broaden my research. For the last few years I have learned to process the DNA material, fabricate test structures and characterize capacitor devices made from a DNA-hybrid material. I want to thank everyone in the Biotronics Research Group for their support, knowledge and encouragement over the years. I want to thank Perry Yaney, Steve Smith, Kristi Singh, Jerry Landis, Jennifer Decerbo, Vic McNier, Marlene Houtz, Eliot Gomez and Chris Grabowski for their help with fabrication and measurement. I especially want to thank Narayanan Venkat and Fahima Ouchen for their daily involvement in my project and Jim Grote, my research advisor, for always being positive and looking for new/novel ways to push the research to the next level. I also want to thank my faculty committee Terry Murray, James Snide, Guru Subramanyam and Elena Guliants for their guidance and direction. I want to thank my home office in the Sensors Directorate, AFRL/RYWA, for their understanding and support of this research and the many days I worked away from the office.
I grew up in a large family that encouraged education. We learned we could achieve anything we put our minds to. We were expected to work hard and do good work. I thank my Mom and Dad and siblings for those great lessons. I also want to thank my immediate family Paul, Paul Ryan, Joe and Tera who always remind me there is a reason to keep learning and working hard. I have learned so much from this project; both the science and engineering of processing, fabricating and characterizing a new material for energy storage applications and also the journey of starting down a new, unfamiliar path and processing new knowledge, fabricating great friendships, and characterizing my place in the greater scientific community.
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CHAPTER 1

INTRODUCTION

1.1 Overview of Research

This research is an interdisciplinary project combining electrical and materials engineering as well as scientific study of physics, chemistry and biology. It is the study of electronic materials, specifically dielectrics. Dielectric materials are commonly used in electronic devices. Dielectrics are insulators that have the capacity to store energy. This research targets dielectrics for use in energy storage and generation. Batteries and capacitors are two well-known electrical energy generation/storage devices. Batteries generate energy (electro-chemical energy generation) by changing chemical energy into electrical energy and power many devices such as cell phones, computers, toys, and cars. They are good at producing a small charge over a long period of time. Capacitors on the other hand store energy. They store energy under the influence of an electric field. They can produce a large charge over a short time, as in the form of lightning. In a parallel plate capacitor, charge is stored on conducting plates (electrodes). If a dielectric insulation material is placed between the two conducting plates of the capacitor, charge will be stored on the plates as long as the insulation material resists the electric field as shown in Figure 1.
Figure 1. Charge separation in a parallel plate capacitor

The capacitor stores energy and can be discharged quickly and used for applications such as powering flash cameras. The dielectric material is defined by its strength: the minimum field at which it can no longer resist conduction of charges. Dielectrics also have a dielectric constant or relative permittivity which is the ability of the material to store electrical energy in an electric field. Energy stored in a parallel plate capacitor, as shown in Figure 2, is defined by the volumetric energy density (J/cc), and is calculated as follows [1]:

\[ u = \frac{1}{2} k \varepsilon_0 E^2, \]

where \( u \) is the energy density in J/cc, \( k \) is the dielectric constant of the material, \( \varepsilon_0 \) is the permittivity of free space (\( \varepsilon_0 = 8.85 \times 10^{-14} \text{F/cm} \)), and \( E \) is the dielectric strength of the material expressed in V/cm. Energy density increases linearly with the increase in dielectric constant \( k \) and quadratically with dielectric strength, \( E \). Dielectric materials in this study are investigated for improvements to both \( k \) and \( E \).
1.2 Overview of Dielectrics

The term dielectric is used to indicate the energy storing capacity of the material. A dielectric is a material that has a resistance to an electric field which makes it a good insulation material in a capacitor. In this research dielectric is used in reference to the nonconducting-insulation layer of a capacitor.

1.2.1 Dielectric Materials

The most common dielectrics are ceramics, polymer films, and oxide layers on metal. Natural materials such as mica, glass, air, and paper are also dielectric materials. Dielectrics are great materials for capacitors. When used in capacitors these materials store electrical charge statically in an electric field between two electrodes. Introducing a dielectric layer into a capacitor decreases the electric field, E, which decreases the voltage, V, where $E = \frac{V}{d}$, and d is the distance between electrodes. An electric field is the gradient of electric potential or voltage that is applied to the material. Capacitors with a dielectric can store charge at a lower voltage.
Materials typically used for high energy density applications include polymer films such as biaxially oriented polypropylene (BOPP), which has remained the state-of-the-art polymer film capacitor for the past few decades because of its exceptionally high electrical breakdown strength measured between 600-700V/µm.[2] It is limited, however, by its low dielectric constant $k = 2.2$ (1kHz). Alternate to polymer dielectrics, ceramic dielectrics are known for their high $k$ but have lower electric field strength. A suitably designed hybrid dielectric encompassing both polymer and ceramic components can, in principle, combine the advantages of a high dielectric strength as well as an enhanced relative permittivity to potentially function in high energy density capacitor systems.[3-5] The utilization of a bio-polymer material such as DNA as a dielectric has advantages such as low cost, low weight, and amenability to a variety of low temperature film fabrication processes including drop casting, spin-coating, and inkjet printing. Recent studies by Norwood et al.,[6,7] suggest that DNA in the form of a complex such as DNA-CTMA (CTMA=hexadecyl trimethyl ammonium group), can be blended with alcohol-based inorganic sol-gel materials to provide promising hybrid thin film dielectrics with potential for capacitor applications. This research has shown DNA-CTMA/sol-gel ceramic hybrid thin films to have a relatively high dielectric constant $k \sim 5.0$ (1kHz), which is higher than that of most synthetic polymers[8,9], and they also have high dielectric strength values consistently in the 300 to 350V/µm range[8,9], pointing to their potential utilization in high energy density capacitors applications.

1.2.2 Dielectric Properties
Dielectric materials have important material and electrical properties. Characterization of these materials to determine the dielectric constant and strength, and the energy storage
capabilities is vital to determining if the material is suitable as a high energy density dielectric.

1.2.2.1 Material Properties

Material properties such as dielectric constant, dielectric loss factor (tan δ) and dielectric strength are addressed. Polarization mechanisms operating within the material are also reviewed.

1.2.2.1.1 Dielectric Constant

The dielectric constant $k$ or relative permittivity is an important parameter to dielectric materials and is essential to designing capacitors. The dielectric constant is the extent that a material can store electrical energy in an electric field. The dielectric constant measurement is dependent on several variables such as temperature and frequency. For instance the dielectric constant in air changes with temperature, humidity and pressure. When a material with high $k$ is placed in an electric field the field in the dielectric is reduced, this increases the capacitance. The capacitance created by the presence of the material is directly related to the dielectric constant $k$ of the material as follows [1]:

$$k = \frac{Cd}{\varepsilon_o A},$$

where $C$ is the Capacitance (F), $d$ is the film thickness (cm), $\varepsilon_o$ is the permittivity of free space ($\varepsilon_o = 8.85 \times 10^{-14}$F/cm ), and $A$ is the area (cm$^2$). Changes in relative permittivity cause a change in capacitance. Generally speaking polymers have low $k$, ceramics have moderate values and metal oxides have high $k$. Table 1 shows dielectric constants of a variety of materials. [10]
<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>1</td>
</tr>
<tr>
<td>Glass</td>
<td>5-10</td>
</tr>
<tr>
<td>Mica</td>
<td>3-6</td>
</tr>
<tr>
<td>Mylar</td>
<td>3.1</td>
</tr>
<tr>
<td>Neoprene</td>
<td>6.70</td>
</tr>
<tr>
<td>Plexiglas</td>
<td>3.40</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>2.25</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>3.18</td>
</tr>
<tr>
<td>Teflon</td>
<td>2.1</td>
</tr>
<tr>
<td>Germanium</td>
<td>16</td>
</tr>
<tr>
<td>Strontium titanate</td>
<td>310</td>
</tr>
<tr>
<td>Titanium dioxide (rutile)</td>
<td>173 perp, 86 para</td>
</tr>
<tr>
<td>Water</td>
<td>80.4</td>
</tr>
<tr>
<td>Glycerin</td>
<td>42.5</td>
</tr>
<tr>
<td>Liquid ammonia(-78°C)</td>
<td>25</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.284</td>
</tr>
<tr>
<td>Air(1 atm)</td>
<td>1.00059</td>
</tr>
<tr>
<td>Air(100 atm)</td>
<td>1.0548</td>
</tr>
</tbody>
</table>

Table 1. Dielectric constants at 20°C
1.2.2.1.2  Dielectric Loss

Another important property of dielectric materials is the dielectric loss factor (tan δ). The dielectric loss is the material’s inherent dissipation of electromagnetic energy; the ability of the dielectric to support an electrostatic field while dissipating minimal energy. The lower the dielectric loss the more effective the dielectric material.

1.2.2.1.3  Dielectric Strength

The dielectric strength or electric field strength is the maximum electric field that a material can withstand without experiencing a failure of its insulating properties, for a specific configuration of dielectric material and electrodes. The electric field strength is expressed as \( E = \frac{V}{d} \), where the applied field \( E \) = the applied voltage \( V \)/electrode separation or dielectric thickness \( d \). The breakdown voltage is the maximum applied voltage that results in breakdown of the material. At breakdown the electric field frees bound electrons. For solid materials a breakdown severely degrades or destroys its insulating capability, and breakdown is permanent. Factors affecting dielectric strength include: sample thickness, temperature, frequency, and humidity.

1.2.2.1.4  Polarization Mechanisms

The three main mechanisms of polarization are electronic (distortion of electron cloud), ionic (ion movement) and orientational (rotation of permanent dipoles). Each polarization mechanism has characteristic relaxation/resonance frequencies. Polarization mechanisms are dependent on temperature and frequency. The larger the dielectric constant of a material the more available the polarization mechanisms.
1.2.2.2 Electrical Properties

The electrical properties of a dielectric material help determine the application most suited for the material. Electrical characterization includes capacitance/dielectric, voltage breakdown, leakage current and polarization measurements. Conduction and charge injection mechanisms are also considered as they directly influence the operation of the dielectric in a capacitor application.

1.2.2.2.1 Capacitance

Capacitance is the ability of a material to store electrical charge and is measured in Farads. It is the ratio of the electric charge on each conductor to the potential difference between them, \( C = \frac{Q}{V} \). Capacitance is defined as [1]:

\[
C = k \varepsilon_0 \frac{A}{d},
\]

where \( k \) is the dielectric constant, \( \varepsilon_0 \) is the permittivity of free space \( (\varepsilon_0 = 8.85 \times 10^{-14} \text{F/cm}) \), \( A \) is the area \( (\text{cm}^2) \), and \( d \) is the film thickness \( (\text{cm}) \). Capacitance measurements change with time, frequency and temperature. Dielectric constant and dielectric loss factor (\( \tan \delta \)) are derived from the capacitance measurement, taken over a range of temperature and frequency. Dielectric constant and dielectric loss vary with temperature and frequency due to the polarization mechanisms present in a material. Both temperature variation and temperature cycling are observed to show environmental stability and determine operating parameters of the material.

1.2.2.2 Voltage Breakdown

Every insulator can be forced to conduct electricity. This is known as the voltage breakdown or dielectric breakdown. Voltage ramp studies are used to determine intrinsic
material breakdown characteristics. The breakdown voltage is measured to determine the electric field strength, $E=V/d$. A ramped voltage is applied across the dielectric material until breakdown occurs. Thicker films will require higher voltage sources for measurement.

1.2.2.2.3 Leakage Current

Leakage current is the gradual loss of energy from a charged capacitor. It is important at low frequencies and becomes negligible at higher frequencies. Temperature and humidity have a significant effect on leakage current. Measurement of leakage current through a sample will determine the sample’s insulation resistance.

1.2.2.2.4 Polarization

Polarization is the dipole moment per unit volume. The electric dipole moment is the product of charge and separation. The three polarization mechanisms: electronic, ionic and orientational can be present in the material. Polarization can be induced by either stretching or rotating a material. All materials stretch in an electric field. Non-polar materials stretch and polar materials stretch and rotate. Stretching creates an induced dipole moment, and rotation occurs in polar molecules, those with a permanent dipole moment. Polar molecules polarize more strongly than non-polar molecules. Variables of polarization are material and electric field. For most materials the stronger the electric field the greater the polarization. Some insulators remain in a polarized state after the field is removed. Polarization measurements provide information on energy storage and efficiency. Energy storage is the measurement to determine the amount of energy the capacitor material can store up to the point of breakdown.
1.2.2.5 Charge Transport and Injection Mechanisms

In a polymer, charge transport occurs via thermally activated hopping, with a mobility that typically increases with electric field and temperature. Charge injection is effected by the electrode/dielectric interface. Charge injection can be limited by charge hopping and material thickness. Factors influencing charge injection at the metal/organic interface include energy distribution at interface, chemistry at interface and physical origins of interface dipoles. The barrier height and width are also affected in the process, potentially influencing charge injection.

1.2.3 Dielectric Applications

Dielectrics are used in many electrical applications. Layers beneath conductors in printed circuit boards act as dielectrics. Dielectrics are also used in transmission lines, shielding, and in waveguides. In this research dielectrics are investigated as gate insulators in thin film transistors (TFTs) and as insulation materials in capacitors.

1.2.3.1 Gate Dielectrics

Gate dielectrics are the dielectrics used between the gate and substrate of a field effect transistor (FET). Gate dielectrics require an electrically clean interface and high capacitance. Polymer gate dielectrics have low capacitance and require high operating voltages. Materials with high dielectric constants are of interest to increase the capacitance and lower the operating voltage of the device.

1.2.3.2 Capacitors

A capacitor is a passive electrical component used to store energy in an electric field. The first capacitor dates back to the Leyden Jar. Michael Faraday is known for the first
useable capacitors and the delivery of electric power that we all enjoy today. The unit of measurement is fittingly the Farad. A parallel plate capacitor is an energy storage device made up of two parallel plates separated by an insulating dielectric material. When a voltage is applied across the plates, the electric field in the dielectric displaces electric charges and stores energy. There are many electronic applications for capacitors in tuning circuits, filters and power systems. Vital capacitor parameters can determine a potential application. Capacitors are not ideal. External leads and internal paths create inductive and resistive parasitic components, such as leakage current, effective series inductance (ESL), and effective series resistance (ESR). Figure 3 shows an electrical model of a capacitor. Previously we discussed several important material and electrical properties of the dielectrics used in capacitors. Capacitance measurements vary with frequency, temperature and time. The limit of the device is measured as the voltage breakdown, the voltage at which the dielectric breaks down and allows current to flow freely. The electric field strength or dielectric strength, is defined as $E = \frac{V}{d}$. Capacitors are operated below their breakdown voltage. They can be charged at high voltages and quickly discharged in $\leq$ ms. The energy density of the capacitor is determined by the equation: $u = \frac{1}{2} k \varepsilon_0 E^2$, with the dielectric constant $k$, and the electric field strength $E$, being variables that can be influenced to improve the performance of the capacitor.

![Figure 3. An electrical model of a capacitor](image)
1.2.3.2.1 Types of Capacitors

There are several types of capacitors. Capacitors can be polymer films, ceramic, or electrolytic. Each has their advantages and disadvantages. Capacitor types are matched to applications based on their characteristics. Film capacitors can have an inherently higher voltage breakdown, low leakage and slow aging, yet have low dielectric constants. Ceramics have moderately high dielectric constants, yet they are large and expensive and have low breakdown voltages. Electrolytics have lots of capacitance in a small space yet have leakage and lifetime limitations. Current commercial electrostatic capacitors are divided into three subgroups based on the dielectric: ceramics, electrolytic (aluminum and tantalum), and polymer. Performance was reviewed by the Department of Energy (DOE) Freedom Car program. Table 2 summarizes the review results.[12]

<table>
<thead>
<tr>
<th>Capacitor Properties</th>
<th>Polymer Film</th>
<th>Ceramic</th>
<th>Electrolytic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Density</td>
<td>Excellent</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>ESR*</td>
<td>Poor</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Temp. Stability</td>
<td>Poor</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Reliability</td>
<td>Poor</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Ripple Current</td>
<td>Poor</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Failure Mode</td>
<td>Good</td>
<td>Excellent</td>
<td>Marginal</td>
</tr>
<tr>
<td>Cost</td>
<td>Excellent</td>
<td>Good</td>
<td>Marginal</td>
</tr>
</tbody>
</table>

Table 2. Comparison of capacitor performance of different dielectric materials

1.2.3.2.2 Standards for Testing

Commercial standards for capacitor testing provide a long list of important parameters to analyze. Important parameters include capacitance, leakage current/insulation resistance,
breakdown voltage, ESR, ESL, and thermal stability. A temperature test chamber ranging from -55C to 125C and highly accelerated life tests (HALT) can be used to characterize the devices. Electrical characteristics as well as environmental and lifetime testing is vital for reliable operation.

1.3 Problem Statement

There is a need for high energy density materials for many current electronic applications, both commercial and within the government. Mobile devices and power systems are some examples of the current need. Smaller form factors and embedded components push the need for higher energy density materials. This research has shown that DNA-based bio-polymer hybrids, have demonstrated potential as an insulating dielectric material for capacitors. Relative to many organic polymers with dielectric constants in the range of 2.0-3.0, DNA-based bio-polymers have a higher dielectric constant \( \geq 5.0 \) (1kHz), and show stability over frequency and temperature. Electrical characterization has shown consistent breakdown voltage measurements \( >300V/\mu m \) for single layer and \( >600V/\mu m \) for multilayered films. These breakdown measurements are comparable to the current state of the art polymer capacitor BOPP, with voltage breakdown 600-700V/\( \mu m \).[2] The DNA-based bio-polymer also has the potential to be combined with ceramic additives for advantages of high environmental stability, mechanical strength and increase in dielectric constant. A systematic, in-depth investigation of DNA-CTMA/sol-gel ceramic hybrid films for energy storage applications is described in this research. Single and multilayered film test structures were designed and devices fabricated for dielectric testing. Temperature-dependent dielectric constant and dielectric loss factor (\( \tan \delta \)), as well as the frequency-dependent
behavior of the DNA-CTMA/sol-gel ceramic hybrid films, were examined. Breakdown voltage measurements were performed to determine electric field strength and potential energy density. Leakage current and polarization measurements were also performed to determine the energy storage capability and efficiency of the devices. The goal of this work is to develop new materials for capacitor applications that merge the processability and potentially high breakdown strength of bio-polymers with the inherently high permittivity of ceramics. This research is focused on investigating the development and optimization of such DNA-based bio-polymer hybrid thin films for high energy density capacitor applications.

1.4 Significance

1) DNA-hybrid thin films show promising properties as a capacitive insulation material. Blending the DNA bio-polymer with ceramic additives has shown to produce robust thin films that have stable and reproducible characteristics suitable as insulation materials for capacitors. This research has shown DNA hybrid thin films to have higher dielectric constants, $k > 5$ (1kHz), than common synthetic polymers and compete with existing polymers in regards to electric field strength, 300-600V/µm for single and multilayer films.

2) Layered devices show increased electric field strengths, increasing the potential energy density of the material. Appropriately chosen Electron Blocking Layers (EBL) and Hole Blocking Layers (HBL) in the layered DNA hybrid devices have shown evidence of potentially acting as barrier layers to charge injection into the insulation material of the capacitor, thereby delaying dielectric breakdown of the material and providing for a substantial increase in electric field strength and device energy density.
1.5 Dissertation Overview

This research investigates a new bio-polymer, deoxyribonucleic acid (DNA) from salmon, as a dielectric material. This DNA material has shown interesting electrical and optical properties which have been investigated for use in OLEDS, OFETS, and optical modulators. The current research focuses on using the material as the insulation material in a capacitor. The following sections describe why this material is being investigated, specific material and electrical properties, the current state of the art, and the advantages of the new material. The experimental process and results are reported as well as the design and characterization of an optimized layered device. Summary/conclusions and the way ahead conclude this dissertation.
CHAPTER 2

BACKGROUND

2.1 State of the Art Polymer Capacitors

Biaxially oriented polypropylene (BOPP) has remained as the state-of-the-art polymer film capacitor for the past few decades because of its exceptionally high electric breakdown strength between 600-700V/µm.[2] It is limited, however, by its low dielectric constant \( k = 2.2 \) (1kHz). Table 3 shows significant parameters of this benchmark material.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>2.2 @1kHz</td>
</tr>
<tr>
<td>Loss tangent</td>
<td>0.0005@1kHz</td>
</tr>
<tr>
<td>Dielectric strength</td>
<td>600 V/µm</td>
</tr>
<tr>
<td>Film thickness</td>
<td>7-12 um</td>
</tr>
<tr>
<td>Capacitance range</td>
<td>picofarads to microfarads</td>
</tr>
<tr>
<td>Operating range</td>
<td>-55 to 65 C</td>
</tr>
</tbody>
</table>

Table 3. BOPP polymer capacitor properties
Alternate to polymer dielectrics, ceramic dielectrics are known for their high $k$ yet lower electric field strength. Research into high energy density materials has revealed that high $k$ materials as well as high electric field strength measurements, while key to increasing potential energy density, have interesting limitations at high fields. Studies by Chen et al., at PSU show that at very high electric fields the leakage current sharply increases with field due to tunneling, reducing the efficiency of the device.[13] Increasing the maximum field may not increase the energy density of the device. High fields also induce large hysteresis loops as investigated by Zhu et al at CWRU, showing that the efficiency of devices is dropping off at high fields.[14] While high energy density materials can be influenced by increasing dielectric constant and dielectric strength, performance limitations exist at high fields and will need to be addressed to increase device efficiency.

2.2 DNA Bio-Polymer Devices

Bio-polymers are particularly attractive building-block materials for device application due to the ease of processing as host matrices in a variety of functional composites and their ability to attain unique electrical and optical properties. In addition, biomaterials impart specificity and selectivity when introduced into device platforms. Biopolymers, including salmon DNA-based materials, have shown promise in electronic and photonic device architectures. Research into the use of salmon DNA as an electronic/photonic material began in 2001 with Professor Naoya Ogata, Ogata Labs of Japan and the Chitose Institute of Science and Technology (CIST), and the purification of the DNA material.[15,16] Processing procedures were optimized to make the material optical/electrical grade for use in photonic and electronic devices by blending DNA with
CTMA (CTMA=hexadecyl trimethyl ammonium group).[17] The DNA-CTMA complex is solvent soluble and can easily be used for thin film fabrication. Purification of DNA-CTMA has been performed and reported on showing improved device dielectric performance.[18] This purified material is currently being used in all research test devices using DNA-CTMA. DNA-based bio-polymers possess interesting optical and electromagnetic properties, including tunable electrical resistivity, ultra-low optical and microwave loss, and compatibility when blending with ceramics. Several research dissertations have been completed using the DNA bio-polymer. Organic field effect transistors (OFETS)[19], organic light emitting diodes (OLEDs)[20], and nonlinear optical (NLO) polymer electro-optic modulators[21] fabricated from DNA bio-polymer as passive layers have demonstrated performances that compete with state-of-the-art devices using currently available organic-based materials. Ease of processability and abundance (a throw out of the Japanese fishing industry) make DNA-based biopolymer a good choice for many device applications. The utilization of a bio-polymer material such as DNA as a dielectric has some natural advantages. Bio-capacitors are inherently capable of reducing environmental footprint since they stem from ‘green’ materials. DNA is low cost, low weight, and is amenable to a variety of low temperature film fabrication processes including drop casting, spin-coating, and inkjet printing. DNA films have been reported to have a dielectric constant in the range of 7.0-8.0 (1kHz) and DNA-CTMA dielectric constant is >5 (1kHz).[22] which is higher than most synthetic polymers. Further investigation into the dielectric and electrical properties of the DNA-based bio-polymer has shown potential for its use as an insulation material in a capacitor,
specifically due to its relatively high dielectric constant as compared with other organic polymers and comparable dielectric strength.

2.3 DNA Hybrid Devices

The significance and potential of DNA bio-polymer hybrid dielectric properties were borne out in earlier studies in OFETs and as cladding layers in NLO devices.[23-29] Many baseline studies have been performed on DNA, DNA-CTMA, and DNA-hybrids including electrical resistivity and dielectric measurements.[6,22,30,31,32,33,34] AFRL has been involved extensively in this research and continues to investigate the DNA bio-polymer material as a dielectric for both capacitor and gate insulator applications.[7,8,9,31,35,36] The structural complexity and unique self-assembly property inherent and unique to DNA also allow it to be heavily doped by both organic and inorganic dopants via specific binding modes such as intercalation and groove binding, providing the potential for high levels of incorporations of the fillers without phase separation. This bio-polymer has the ability to be combined specifically with ceramics to enhance its dielectric properties. A suitably designed hybrid dielectric encompassing both polymer and ceramic components can, in principle, combine the advantages of the high dielectric strength of the polymer as well as an enhanced relative permittivity of the ceramic to potentially function in high energy density capacitor systems.[3-5] Recent literature reports[7,8] suggest that DNA, in the form of a DNA-surfactant complex such as DNA-CTMA, can be blended with alcohol-based inorganic sol-gel materials to provide hybrid thin film dielectrics with a relatively high dielectric constant as well as a high dielectric strength. Early successes at the University of Arizona with a DNA-sol-gel hybrid built a foundation for this material to be thoroughly
investigated in the current work as a potential insulator dielectric in energy storage applications. By virtue of its relatively high dielectric constant relative to many organic polymers, the DNA hybrid dielectric can also serve as a more efficient gate dielectric to help reduce drive voltage for the operational enhancement of field effect transistors (FETs) in electronic applications.[23,24,31,35,37,38,39] In the context of the current study, a homogeneous blend of the DNA-CTMA bio-polymer with an in situ sol-gel-derived ceramic will combine the advantages of the high field strength of the bio-polymer and its ease of processability with the high dielectric constant and environmental stability of the ceramic, enabling the fabrication of robust thin film devices with potentially high energy density for capacitor applications. Prior dielectric baseline results on DNA and DNA-CTMA films[22,37] were found to be useful to help design DNA-based hybrid dielectric systems by blending the bio-polymer with various ceramic materials. Based on the above premise, a sol-gel derived ceramic in combination with the DNA bio-polymer is being investigated for potential dielectric applications. Such applications include embedded and pulsed power capacitors as well as use as gate insulating dielectrics in thin film transistors.

A systematic investigation of the DNA-CTMA/sol-gel dielectric system for energy storage applications is described by Joyce et al.[36]. Single film test structures were designed and devices fabricated for dielectric testing. Breakdown voltage measurements were performed to determine electric field strength and potential energy density. Temperature-dependent dielectric constant and dielectric loss factor (tan δ) as well as the frequency-dependent behavior of the DNA-CTMA/sol-gel films were also examined. Advances in state-of-the-art polymer capacitors have set the bar for
performance metrics. Current benchmark polypropylene capacitors have a dielectric constant of 2.2 (1kHz) and electric field strength of \(~600\text{V/µm}\). AFRL research to date has shown the DNA-sol-gel hybrid to have a dielectric constant of 5.5 (1kHz) and electric field strength of 330V/µm.[36] The DNA bio-polymer/ceramic hybrid films, take advantage of the positive attributes of both polymer and ceramic materials. Material optimization and purification continues as early results show promise for the DNA-sol-gel hybrid as the dielectric in a capacitor.
CHAPTER 3

EXPERIMENTAL PROCESS

3.1 Materials Processing

A thorough investigation of the properties of the DNA material was conducted. Many areas were investigated to understand the DNA bio-polymer material including DNA-CTMA processing, hybrid synthesis, thin film fabrication and dielectric/electrical characterization. Material study included: gel electrophoresis, optical surface study, sonication, soxhlet rinse, dialysis, resistivity and temperature stability measurements.

3.1.1 DNA and DNA-CTMA

The salmon DNA utilized in this study, obtained from the Ogata Labs of Japan[15], has high purity (96%) and high molecular weight (600-800Mda) and was used as received for capacitor applications. As received purified salmon DNA is freeze dried and water soluble. DNA is easily processed, low cost and available. To process the DNA to make it usable in electronics it is dissolved in deionized (Di) water at a concentration of 4 mg/ml. For this research 2g of DNA is dissolved into 500 ml DiH₂O. This solution is stirred for approximately 6 hours until dissolved. As DNA becomes more viscous, the stirring rate is increased. The DNA is then mixed with a surfactant hexecyltrimethyl ammonium chloride (CTMA). First 500ml Di H₂O is added to 1.95g of CTMA. CTMA is very water
soluble. It is stirred for only 5-10 minutes, then put in the refrigerator overnight. The corresponding DNA-CTMA complex is synthesized from known procedures by mixing the aqueous solutions of both DNA and CTMA to provide a water-insoluble complex which could be solubilized in n-butanol.[17,18] This complex will be solvent soluble. The molecular weight of DNA can be altered before it is combined with CTMA, by sonication. Using sonication, the longer the sonication cycles the lower the molecular weight. To reduce the molecular weight from 600-800 Mdalton to 200 kdalton, 10 sonication cycles are needed.[17] Sonication is separating DNA strands. Between cycles they recombine, however some base pairs remain open. Sonication for 2 cycles will achieve 1000 kdalton, 5 cycles-500 kdalton, and 10 cycles-200 kdalton. DNA resistivity varies with molecular weight. The lower the molecular weight, the lower the resistivity.[33,34] The research application drives the needed resistivity/molecular weight. For insulation materials, high molecular weight DNA, as received at 600-800 Mdalton, is most advantageous. Higher molecular weight provides higher resistivity, lower conductivity, and better insulation. Small samples of the DNA solution are used to measure the molecular weight using Gel Electrophoresis. Gel Electrophoresis, 1% agarose gel, is used to determine the size of the DNA particles in solution. DNA base pairs relate to molecular weight and there are more base pairs when unsonicated. One base pair equals 620 dalton, 250-350 dalton per nucleotide. Sonicated DNA is compared to known ladders to determine the new molecular weight before use. Sonicated DNA is stable for up to 3 weeks in the refrigerator. Sonicated DNA is filtered to remove impurities from the sonication by performing two filtration cycles using a 1.45 µm and then a 0.65 µm filter. After choosing
the molecular weight of the DNA (DNA is sonicated as desired), the solution is now ready for titration with the CTMA.

DNA is added to the CTMA mixture with a long glass pipette. The DNA-CTMA mixture is left overnight or for at least 6 hours, to spin/blend. It is then refrigerated overnight to separate. The next day the liquid is on top. This liquid is filtered to catch all DNA-CTMA. The bottom more dense blend is put in a cellulose extraction thimble along with what was filtered from the liquid. The DNA-CTMA then goes through a soxhlet rinse to remove the excess CTMA from the solution. This takes about 6 hours. The DNA-CTMA is then vacuum oven dried in a Teflon beaker for 1-2 days. When the DNA-CTMA is completely dried, it is stored in a nitrogen glove box until it is ready to use. Ouchen et al., optimized a procedure to further purify the DNA-CTMA with an ethanol dialysis rinse.[18] This optimized DNA-CTMA showed enhanced characteristics and is now used for all DNA-CTMA experiments.

3.1.2 DNA-CTMA/Ceramic Hybrid Films

A typical procedure, similar to Norwood et al., [6,7] is utilized for the fabrication of DNA-CTMA/sol-gel hybrid films. Sol-gel precursors utilized for the fabrication of DNA hybrid films were purchased from Aldrich Chemicals and consisted of Zirconium n-propoxide 70 wt% in n-propanol and a crosslinkable organosilicon alkoxide monomer, methacryloxypropyl-trimethoxysilane (MAPTMS). Zirconium n-propoxide complexed with methacrylic acid was mixed with MAPTMS in the presence of 0.1 N HCl to provide the sol-gel formulation.[40] DNA-CTMA derived from unsonicated DNA was solubilized in n-butanol and the viscous 6wt% solution was blended with the Zr/Si sol-gel
solution. After vigorous stirring, the DNA-CTMA/sol-gel ceramic solution was filtered through a 1.0µm syringe filter and spin coated on appropriate substrates for film fabrication. Spin parameters were adjusted to control film thickness. Films used in this study have thicknesses varying between 2.5 and 3µm, as measured on a Veeco DEKTAK 6M stylus profiler. Films were cured overnight under nitrogen at 130°C. DNA-CTMA/sol-gel is thermally crosslinked. A densely crosslinked system should enhance breakdown strength since it is relatively free of defects. Too high a concentration of crosslinks renders material brittle. AFM studies using a Dimension 3100 AFM with NanoScope V Controller were performed on the DNA-CTMA/sol-gel and the Zr/Si sol-gel films to determine surface roughness. The DNA-CTMA/sol-gel material was also tested for temperature stability using Thermogravimetric Analysis (TGA). TGA measurements show changes in the physical and chemical properties of the material as a function of temperature. Results are used for high temperature material selection.

Due to material characteristics of high dielectric constant and low gate leakage current, the DNA-CTMA/sol-gel material was also investigated for use as a gate insulator in ZnO TFT. The sol-gel recipe was altered, changing spin rate and concentration of the DNA-CTMA/sol-gel in butanol and isopropanol to get thinner films. The objective for a gate insulator layer is thin (~50nm), smooth films for coating a substrate to grow ZnO. Lower viscosity, therefore lower molecular weight DNA is used for this application, while higher molecular weight DNA is used for capacitive work. Highly p doped Si substrates were used (low resistivity 1-20 ohms) and low molecular weight, low concentration DNA-CTMA/sol-gel solution was spun onto the substrate. Spin rate and solvents were varied for desired film thickness. Films were cured at 120°C.
Surface roughness study was performed with AFM. AFM showed < 10nm surface roughness, however ripples were present across films. Thin films were deposited onto Si substrates using spin parameters 4000rpm, 5 sec ramp, and 45 sec spin duration, achieving 50-100nm films. This gate dielectric research encompassed fabricating a thin film for the gate dielectric of a ZnO based FET. Samples were used for growth of the ZnO layer at room temperature. Other gate dielectrics used are polyimide or SiO₂. This research showed that DNA-CTMA can potentially be an alternative to SiO₂ as the gate insulator.

3.2 Device Fabrication

The material properties of the DNA-CTMA/sol-gel hybrid showed strong potential for capacitive applications. A test structure was designed and fabricated for further investigation of dielectric and electrical characteristics. Fabrication areas addressed include design of test structure, masking and electrode metallization, and film deposition by spin coating.

3.2.1 Test Structure Design

A capacitive test structure was fabricated using a metal-insulator-metal (MIM) design as shown in Figure 4. Indium Tin Oxide (ITO), sheet resistance 7-10Ω/sq, was used as the bottom electrode on a glass substrate. The DNA-CTMA ceramic hybrid film was spun onto the ITO coated glass substrate, and then 100nm Al top electrodes were deposited by evaporation through a shadow mask to define the area of the individual devices. The area of each top circular electrode was designed to be 3mm in diameter (0.0707 cm²),
allowing for twelve devices on each test structure. Electrode size, material and thickness were all varied to determine the optimum test structure design.

![Diagram](image)

**Figure 4. MIM device incorporating a spin-coated DNA-CTMA/sol-gel ceramic hybrid film**

Several materials were considered for top and bottom electrodes. Al was first used as the bottom electrode, however to remove the variable of oxidation prior to completing device fabrication ITO was chosen for the test structure bottom electrode. Au, Pt, Ag and Al were all considered for top electrode metallization. Initial testing did not result in any noticeable material advantage. Al was chosen as the top electrode due to cost, availability, work function and use of Al in the literature for similar capacitor research. The work function of Al, ~4.3eV is close to that of ITO, ~4.7eV, therefore suitable for this test structure. The contacts for electrical measurements were made on the bottom ITO electrode and on the top Al electrode. There were twelve devices on each substrate/test structure. The average film thickness of the MIM devices was measured using a Veeco DEKTAK 6M stylus profiler. The DNA-CTMA/sol-gel hybrid films typically varied in thickness from 2.5-3.0 µm. Actual capacitive devices with spin-coated DNA-CTMA/sol-gel films are shown in Figure 5.
Figure 5. Actual MIM devices incorporating spin-coated DNA-CTMA/sol-gel ceramic hybrid films

Electrode size and thickness were also considered. Devices were fabricated with larger, 6mm diameter, top electrodes. Initial results did not show any enhancement to voltage breakdown measurements. The 3mm design was chosen to provide adequate spacing between devices to prevent interference from or damage to adjacent devices during testing. Electrode thickness was varied between 100 and 300nm. Increased metal evaporation time resulted in degradation of devices. The thickness of 100nm was found to be optimum for consistent device fabrication.

3.2.2 Film Fabrication

DNA-CTMA is insoluble in water and solvents are used to prepare thin films. For this research DNA-CTMA was dissolved in several solvents for testing, such as butanol and isopropanol. Different weight % solutions of DNA-CTMA can be prepared. The concentration of the DNA-CTMA affects the viscosity of the solution. Depending on the application, thickness desired, and uniformity of the film, different solvents, concentration and spin parameters can be chosen. When spin coating films, thickness variables include solvent, molecular weight, concentration and spin speed.[19] Butanol (1-butanol anhydrous) is known to produce very uniform films. For a 5g sample of 10wt% DNT-CTMA in solution, 0.5g of DNA-CTMA is used and butanol is added to
reach 5g total solution. Using a rotomixer in the oven at 60°C, the DNA-CTMA solution is mixed until dissolved, approximately 3-4 hours. Heating the mixture reduces the viscosity. With higher molecular weight and higher concentrations, heat is needed to dissolve the DNA-CTMA fully and filter the solution. The solution is filtered through a 0.2µm syringe filter using the new era pump system in the oven at 60°C. Higher concentrations are especially hard to filter through a 0.2µm filter without the oven. For a 20wt% solution, filter sizes of 1µm and then 0.45µm were used. Filter size depends on the size of DNA molecules and wt% of solution. The solution can sit at room temperature until ready to spin thin films. Samples of higher molecular weight or higher concentration have higher viscosity and need heating. When spin coating high concentration or higher molecular weight DNA-CTMA, the sample is warmed before spinning in a 60-70°C oven. Films are spun onto cleaned glass or ITO coated glass substrates and cured in a vacuum oven for 2-3 hours at 90°C. After the films are dried, the DEKTEK 6M stylus profilometer is used to measure film thickness. DEKTEK limitations are at thicknesses < 10nm. Spin parameters can determine the thickness of the film.[19] Changing spin coating parameters, changes the thickness. For a 1µm film from a 200kda, 10wt% DNA-CTMA in butanol, the spin parameters would be 2000rpm, 5 sec ramp, 35 sec spin duration. A 200kda, 2wt%, 4000 rpm spin speed results in a 70-80nm film. Factors affecting film thickness include: concentration, molecule weight (sonication) and spin speed. These parameters affect the thickness as follows: higher concentration-thicker film, higher molecular weight-thicker film and higher speed-thinner film. For very thin films~10 nm, MAPLE deposited DNA is used. This becomes very hard to distinguish the substrate from the film. When spin coating, as the spin speed
increases, thinner films are produced. To get 2-4µm films for resistivity and other electrical measurements one recipe would be: 200kda, 20wt% DNA-CTMA, at 2000rpm. Some guideline for attaining the thickness desired:

10 wt%  200kda  2000rpm-----1um

20 wt%  200kda  2000rpm-----6um

20 wt%  200kda  1000rpm-----10um

Films need to be uniform with even thickness and free of pinholes. This will lessen the chance of shorting. Top and bottom electrodes are also needed for electrical measurements.

For the DNA-CTMA/sol-gel films, discussed in this research, the solution consisted of 6wt% DNA-CTMA and the ratio of DNA to sol-gel is 1.66/1. After combining the DNA-CTMA and the sol-gel, the solution was filtered with a 1.0µm filter just prior to spin coating. ITO substrates were cleaned using a solvent ultrasonic bath, 15 minutes each Acetone (CH3COCH3), Methanol (CH3OH), and Isopropanol (CH3CHOHCH3). Reactive Ion Etching (RIE) was then used to clean the surface. Films were spun onto the ITO substrates. Several film thickness were considered. Initial testing showed voltage breakdown to be similar for ~1.5 to 5um films. Spin parameters of 500rpm, 5s, 20s; 1000rpm, 5s, 30s were used to achieve 2.5-3µm films. This thickness was ideal for the capacitive test structure films. The films were thick enough to prevent shorting and thin enough to be tested with lower voltage equipment. Devices were made for full dielectric and electrical study. Cure parameters of the films were also investigated. Cures ranging from two hours to overnight, at temperatures from 90 to
130°C were explored. Optimized curing of the DNA-CMTA/sol-gel films was determined to be 130°C overnight in a nitrogen oven.

3.3 Electrical Characterization

Dielectric and electrical measurements including capacitance, voltage breakdown, leakage current, and polarization were conducted to determine potential capacitor operating characteristics.

3.3.1 Dielectric Measurements

Capacitance is the amount of electrically charged carriers a capacitor can store per unit of voltage. Capacitance measurements, to determine dielectric constant and dielectric loss factor (tan δ), on the film capacitors were performed using a Solartron 1260 wide-band Impedance/Gain-Phase Analyzer operating in the frequency range of 0.1Hz to 10MHz. A 50mV AC signal was applied in all these measurements. The effective area of the capacitor for measurement was defined by the area under the 3 mm circular top electrodes. Measurements are made using the high performance LCR meter, which has the ability to measure capacitance at multiple frequencies with the aid of an internal, variable AC source. The AC signal of known frequency is applied through an internal low value resistor and the capacitor under test in a series configuration. The current flowing through the capacitor also flows through the resistor, creating an AC voltage across the resistor. The magnitude and phase of this voltage can be measured and compared to the original AC signal, and the capacitance can be computed.

Variable temperature dielectric measurements were conducted in the 20-130°C range in 10°C steps to determine how thermal fluctuations during device operation
would affect their dielectric stability. The upper limit of 130°C was chosen to ascertain the chemical stability of the DNA-CTMA/sol-gel film which was cured overnight at 130°C during the fabrication process. The frequency and the temperature dependence of both dielectric constant and the dielectric loss factor (tan δ) were investigated. The film dielectric constant was calculated from the measured capacitance as follows[1]:

\[ k = \frac{C d}{\varepsilon_0 A}, \]

Where \( C \) = capacitance (F), \( d \) = film thickness (m), \( \varepsilon_0 = 8.85 \times 10^{-12} \) F/m and \( A \) = electrode area (m²). Temperature cycling measurements, to 80°C and to 130°C, were also conducted. Films were heated and held at 80°C and 130° for approximately 1 hour and then returned to room temperature for dielectric measurements. Results obtained from the temperature and frequency dependence and temperature cycling experiments are important parameters when determining optimum capacitor operation.

### 3.3.2 Voltage Breakdown Measurements

Voltage breakdown measurements were conducted to determine electric field strength, \( E = V/d \), where \( d \) is the film thickness (µm). Breakdown voltages were converted to breakdown strength by measuring film thickness near each test device. The typical measured film thickness was 2.5-3µm. DC breakdown voltage measurements on the film capacitors were performed using a Keithley Model 6517A, Electrometer/High Resistance Meter, with a 1kV voltage source. The test sample allowed probe contact to the ITO bottom electrode and to each of the 12 devices on the test structure. Some breakdown measurements were taken directly onto the films using a copper probe. Both measurement techniques are shown in Figure 6.
Measurements were taken every 10 V until breakdown or upon reaching the 1kV limit of the instrument. Current was monitored during testing and when mA was reached, the device was considered to have reached breakdown. The voltage outputs through the test sample, a series resistance of 100kΩ then returns to the Keithley through a low noise triax cable. The overall system incorporates a Safety Interlock System, that is PC or Manual controlled, that disables the HV (1000V max.) before sample access. For thicker films or for materials with a higher breakdown voltage, a higher voltage source is needed and the Spellman SL300 High Voltage Power supply can be used. Dielectric breakdown studies were performed using a custom-built setup that features a 10 kV Spellman SL300 High Voltage Supply. The power supply is coupled to a ramping circuit set to 25V/s for all measurements. This corresponds to a breakdown event occurring at 20-30 seconds, which is an acceptable value under the ASTM D149 standard protocol for short-term dielectric strength tests.[41] Measurements were taken on multiple test structures and Weibull plots were used to show device reliability. Weibull plots show voltage breakdown trends and the probability of failure vs. electric field strength for dielectric

Figure 6. Breakdown measurements on Al top electrode (left) and directly onto film using a copper probe (right)
materials. Weibull distributions are widely used for reliability analysis.[42] The breakdown field where there is 63.2% probability for failure is referred to as the characteristic or Weibull breakdown.

### 3.3.3 Leakage Current Measurements

Leakage current measurements on the DNA-CTMA/sol-gel ceramic hybrid films were performed using a Bertan, series 225, High Voltage Power Supply, with a 1kV voltage source. The test sample allowed probe contact to the ITO bottom electrode and to each of the 12 devices. Measurements were taken with an applied stress of -400 to 400 V, staying below the breakdown limit of the device. Measurements were conducted in air, under nitrogen, and with post-nitrogen cure, showing decreased leakage current when humidity is eliminated under nitrogen. Capacitor leakage can also be measured with a Keithley Model 6517A Electrometer, and is referred to as leakage current when leakage is high (Electrolytics) and known as insulation resistance when leakage is low (Films). The 6517A Electrometer has a variable 1kV voltage source and is also used for making high resistance measurements.

### 3.3.4 Polarization Measurements

Polarization measurements were performed using a Radiant Technologies, Premier II, Ferroelectric Tester. The resulting electric displacement–electric field (D–E) hysteresis loops show polarization responding to applied voltage. Hysteresis loops and energy density plots for the DNA-CTMA/sol-gel ceramic hybrid devices were generated for several devices. Dielectric hysteresis directly affects the discharged energy density and efficiency of the device, and is determined by integrating the D-E hysteresis loop.
CHAPTER 4

EXPERIMENTAL RESULTS AND ANALYSIS

4.1 Material Characterization

The materials used in this research were studied for optimum capacitor characteristics. Gel Electrophoresis was performed to determine the molecular weight of the DNA. A 10 cycle sonicated DNA sample was measured at 450 base pairs (compared to known ladder) which is 279 kda, as shown in Figure 7.

![Image of Gel Electrophoresis](image)

*Figure 7. Gel Electrophoresis-example of 10 sonication cycles*

*B1 identifies samples from batch 1 and B3 identifies samples from batch 3. The numbers under B1 and B3 identify the number of sonication cycles that sample has been through. Sample P10 is the previous 10-cycle sonicated DNA*
Applications of the material determine the optimum molecular weight required. Resistivity measurements were then performed on the DNA-CTMA/sol-gel. Figure 8 shows DNA-CTMA/sol-gel to have a higher resistivity than DNA-CTMA only. The higher resistivity makes the DNA-CTMA/sol-gel hybrid film desirable for capacitor applications. Resistivity measurements reported by Yaney et al.,[33,34] also show higher molecular weight DNA to have a higher resistivity. It was determined that high molecule weight DNA was desired for capacitor applications, and would be used for this research.

![Resistivity measurements comparing DNA-CTMA and DNA-CTMA/sol-gel films](image)

**Figure 8.** Resistivity measurements comparing DNA-CTMA and DNA-CTMA/sol-gel films

AFM studies were performed on the DNA-CTMA/sol-gel and the sol-gel only and are shown in Figure 9. Surface roughness for the DNA-CTMA/sol-gel is slightly higher than the Zr/Si sol-gel samples.
The DNA-CTMA/sol-gel material was tested for temperature stability and compared to DNA-CTMA, and Zr/Si sol-gel. TGA analysis, shown in Figure 10, shows DNA-CTMA stable at >200°C and both Zr/Si sol-gel and the DNA-CTMA/sol-gel film to have even higher temperature stability, showing improvements over synthetic polymer dielectrics.

Figure 9. AFM of Zr/Si sol-gel film (left) and DNA-CTMA/sol-gel (right)

Figure 10. TGA of DNA-CTMA, DNA-CTMA/sol-gel, and Zr/Si sol-gel
4.2 Electrical Characterization

Electrical characterization included dielectric, voltage breakdown, leakage current and polarization measurements.

4.2.1 Dielectric Measurements

Dielectric measurements were conducted and compared for DNA, DNA-CTMA, Zr/Si sol-gel and DNA-CTMA/sol-gel hybrid films.

4.2.1.1 Baseline Measurements

Figure 11 shows the dielectric characteristics for DNA and DNA-CTMA. DNA-CTMA does have a lower dielectric constant than DNA only. The losses for both materials are nearly the same. The presence of water in the DNA material is likely a contributor to the higher dielectric constant of the DNA only films.

![Figure 11. Dielectric properties of DNA vs DNA-CTMA](image)

Figure 11. Dielectric properties of DNA vs DNA-CTMA
Measurements were also taken for the Zr/Si sol-gel films. Several devices reveal a dielectric constant and loss similar to the DNA-CTMA films, shown in Figure 12.

Figure 12. Dielectric properties of Zr/Si sol-gel

### 4.2.1.2 DNA-CTMA/Sol-Gel Dielectric Measurements

Dielectric measurements were then taken on the DNA-CTMA/sol-gel films. Frequency and temperature-dependent dielectric measurements are shown in Figure 13. The temperature range was 20-80°C, and the frequency varied from 1kHz to 1MHz.

Figure 13. Temperature and frequency dependent dielectric constant (left) and dielectric loss factor (tan δ) (right) for DNA-CTMA/sol-gel hybrid films

There is some variation in both dielectric constant and dielectric loss with temperature and frequency. Polarization mechanisms present in this dielectric material may be
responsible for this variation. Each polarization mechanism has characteristic relaxation/resonance frequencies and the dielectric constant decreases at each of these relaxation responses. Polar dielectrics also show a decrease in dielectric constant with increase in temperature. Dielectric loss however increases with frequency and temperature and tends to be higher in materials with higher dielectric constant. There is a loss of polarization mechanisms due to an increase in temperature and frequency. At higher frequencies, the relaxation frequency of the polarization mechanism is slower than the electric field. Heating is caused by an interaction of the electric field in the dielectric with the polarization. This results in higher dielectric loss due to heat dissipation.

Temperature cycling was conducted on the samples to show stability during operation. Room temperature dielectric data measured initially and after cooling from first and second heating cycles up to 80ºC are shown in Figure 14. The DNA-CTMA/sol-gel system showed remarkable stability as evidenced by the reproducibility of the dielectric data. The dielectric constant varied in the range of 5.05-5.15 at 1 kHz while the dielectric loss factor (tan δ) was measured to be in the 0.02-0.025 range at 1 kHz. While a decreased dielectric constant and an increased tan δ were observed at the higher frequencies up to 1 MHz, variations in both properties as a function of thermal cycling were negligible at these frequencies. Results for the temperature-dependent dielectric properties of DNA-CTMA/sol-gel hybrid films at specified frequencies in the frequency range of 1kHz to 1MHz are shown as composite plots in Figure 15. While the thermally-driven enhancements in dielectric constant and dielectric loss factor (tan δ) in 20-80ºC range were most pronounced at 1 kHz, measured changes in the film dielectric properties at 1 MHz were found to be the least temperature-sensitive. The repeatability of the
temperature-dependent dielectric data was also clearly evident, as demonstrated by the identical trends obtained during the two heating cycles.

![Figure 14. Room temperature dielectric constant (left) and dielectric loss factor (tan δ) (right) for DNA-CTMA/sol-gel hybrid films](image)

Material composition and the presence of impurities can also affect dielectric measurements. Purified DNA-CTMA by ethanol dialysis, reported by Ouchen et al., was investigated for its effect on dielectric parameters.[18] Dielectric measurements of the DNA-CTMA/sol-gel using soxhlet rinse, and the purified DNA-CTMA/sol-gel using ethanol dialysis are shown in Figure 16. The purification leads to an increase in dielectric

![Figure 15. Temperature-dependent dielectric constant (left) and dielectric loss factor (tan δ) (right) for DNA-CTMA/sol-gel hybrid films](image)
constant to >5.5 (1kHz), while losses remain nearly the same. This optimized material was used for all experiments incorporating DNA-CTMA.

Figure 16. Dielectric properties of DNA-CTMA/sol-gel hybrid films

Dielectric measurements were repeated for the new purified (ethanol dialysis) DNA-CTMA/sol-gel films. Variable temperature dielectric measurements were conducted in the 20-130ºC range in 10ºC steps to determine how thermal fluctuations during device operation would affect their dielectric stability. The upper limit of 130ºC was chosen to ascertain the chemical stability of the DNA-CTMA/sol-gel film which was cured overnight at 130ºC during the fabrication process. The frequency and the temperature dependence of both dielectric constant and the dielectric loss factor (\(\tan \delta\)) were investigated. Figure 17 shows results of room temperature (RT) dielectric data after repeated thermal cycles.
The DNA-CTMA ceramic system showed remarkable stability and repeatability as evidenced by the reproducibility of the room temperature (RT) dielectric data even after repeated thermal cycles. Current polypropylene (PP) film capacitors have a dielectric constant $k$ of 2.2 and temperature stability lower than 105°C.[43] Temperature-dependent dielectric properties up to 130°C, of DNA-CTMA/sol-gel hybrid films at specified frequencies in the frequency range of 1kHz to 1MHz, are shown as composite plots in Figure 18.

Figure 17. Room temperature dielectric constant (left) and dielectric loss factor (tan $\delta$) (right) for DNA-CTMA/sol-gel hybrid films after temperature cycling

Figure 18. Temperature-dependent dielectric constant (left) and dielectric loss factor (tan $\delta$) (right) for DNA-CTMA/sol-gel hybrid films
Temperature-dependent dielectric stability is a function of the frequency; these properties vary the most at 1 kHz but very little at 1MHz. Results obtained from the temperature and frequency dependence and temperature cycling experiments are important parameters when selecting optimum capacitor operation.

4.2.2 Voltage Breakdown Measurements

Voltage breakdown measurements were conducted to determine electric field strength of several materials. Figure 19 shows breakdown result for ~3µm DNA-CTMA/sol gel films. Many devices reached breakdowns >300V/µm, showing repeatable measurements on multiple devices. Several devices did not breakdown within the limits of a 1kV source.

Figure 19. Voltage breakdown measurements for DNA-CTMA/sol-gel films (left) and several films that did not breakdown at 1kV (right)

Further testing of such test structures has continued utilizing a higher voltage source to measure higher breakdown voltages. Results for the electric field strength of multiple devices of DNA-CTMA, Zr/Si sol-gel, and DNA-CTMA/sol-gel ceramic hybrid film test structures are shown representatively as Weibull plots in Figure 20.
Figure 20. Weibull plots showing voltage breakdown trends and the probability of failure vs. electric field strength for DNA-CTMA, Zr/Si sol-gel and DNA-CTMA/sol-gel hybrid films

These plots show consistent breakdown measurements between 300-350V/µm for DNA-CTMA/sol-gel ceramic hybrid films, with the characteristic breakdown strength, $E_{BD}$ at 315V/µm (the breakdown field where there is 63.2% probability for failure). DNA-CTMA/sol-gel films show a higher and more consistent breakdown than the DNA-CTMA and sol-gel films respectively. The crosslinking of the DNA-CTMA with the Zr/Si sol-gel creates a denser, more mechanically robust, film and is likely to be responsible for the increase in electric field strength. DNA-CTMA/sol-gel hybrid films show a narrower distribution, resulting in more stable, consistent breakdown compared to Zr/Si sol-gel films. Breakdown measurements were also taken on polystyrene films in the same test structure for comparison as shown in Figure 21. Polystyrene shows similar breakdown measurements to the DNA-CTMA/sol-gel hybrid film. The DNA film however has a dielectric constant near twice that of polystyrene, resulting in the DNA hybrid having potential energy density twice that of polystyrene.
Figure 21. Polystyrene voltage breakdown measurements

4.2.3 Leakage Current Measurements

The dielectric layer in a capacitor is not a perfect insulator resulting in a small current “leaking” through the dielectric. This current flow is called the capacitor’s leakage current and is in the range of nano-amps (nA). When leakage is low it sometimes referred to as insulation resistance. In general, the lower the dielectric constant of the material, the higher the insulation resistance. Leakage current measurements were taken on DNA-CTMA/sol-gel devices in air, nitrogen and post-nitrogen cure at 120°C showing the effects of the environment on the devices, as shown in Figure 22. Results show stability and performance up to an applied stress of 400V. It is evident that the environment and cure under an inert atmosphere can have a profound effect on leakage current characteristics of the device. Under nitrogen environment, the leakage current profile shows stability over a longer range of the applied bias compared to device
behavior under air, while the device cured under nitrogen demonstrates the highest stability, with significantly lower variations in leakage current even at relatively high voltages. Leakage current decreases when humidity is eliminated under nitrogen. As leakage current increases, resistivity decreases. Yaney et al.[33,34] showed that resistivity decreased in samples containing water, which would explain the increased leakage current in the samples tested at ambient conditions. Future work needs to focus on increasing the environmental stability and the resistivity of the films, and thus decreasing the leakage current.

Figure 22. Leakage current characteristics for DNA-CTMA/sol-gel hybrid films

4.2.4 Polarization Measurements

Polarization measurements were performed and the resulting electric displacement–electric field (D–E) hysteresis loops show polarization responding to applied voltage. Hysteresis loops for DNA-CTMA/sol-gel ceramic hybrid devices are shown in Figure 23.
Dielectric hysteresis directly affects the discharged energy density and efficiency of the device, which were determined by integrating the D-E hysteresis loop. Discharged energy density and efficiency are shown in Figure 24. DNA-CTMA/sol-gel ceramic hybrid devices show energy density >3J/cc and high efficiencies >95% at 100V/μm and ~80% at 225V/μm. As shown in the graphs, hysteresis loss increases at higher fields. These losses may be due to ionic impurities in the dielectric material. It can also be attributed to some ionic polarization effects potentially inherent to the DNA-CTMA surfactant complex especially at the higher applied DC fields. Further studies will investigate efficiency losses at even higher fields. Studies by Zhu et al., suggest that removal of impurity ions in polar crystalline polymers can further reduce the hysteresis loss at high electric fields.[14]
Figure 24. Energy density (left) and device efficiency (right) for DNA-CTMA/sol-gel hybrid films

Summarizing experimental results on the DNA-CTMA/sol-gel films (~3μm films at RT and 1kHz) we find a dielectric constant of 5.5, dielectric loss of 0.02, and dielectric strength of 300-350V/μm, yielding a potential energy density of near 3J/cc. Energy density improves linearly with increasing dielectric constant and grows quadratically with the electric field strength. Table 4 shows a comparison of potential energy density, based on characteristic electric field strengths from Weibull analysis, for several materials. Further research will focus on improving the energy density by enhancing the electric field strength and dielectric constant of new hybrid materials.

<table>
<thead>
<tr>
<th>Device</th>
<th>Dielectric Constant $\varepsilon$ (1 kHz)</th>
<th>Electric Field Strength $E$ (V/cm) *</th>
<th>Calculated Volumetric Energy Density $(k\varepsilon_0E^2/2, \text{J/cc})^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNA-CTMA/Sol-Gel</td>
<td>5.5</td>
<td>$315 \times 10^4$</td>
<td>2.41</td>
</tr>
<tr>
<td>Sol-Gel</td>
<td>5.0</td>
<td>$300 \times 10^4$</td>
<td>1.99</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>2.6</td>
<td>$315 \times 10^4$</td>
<td>1.14</td>
</tr>
<tr>
<td>BOPP</td>
<td>2.2</td>
<td>$600 \times 10^4$</td>
<td>3.50</td>
</tr>
</tbody>
</table>

* Based on Weibull analysis  ** $\varepsilon_0 = 8.85 \times 10^{-14}$ F/cm

Table 4. Dielectric Constant, Electric Field Strength and Calculated Volumetric Energy Density for DNA-CTMA/sol-gel, sol-gel, polystyrene and BOPP for comparison
CHAPTER 5

BIO-POLYMER HYBRID LAYERED THIN FILMS

5.1 Layered Film Approach

After thorough investigation of the DNA-CTMA/sol-gel single layer device; multi layered devices were considered. Thin buffer/barrier layers could potentially increase device performance and eliminate inconsistencies at the electrode interfaces. Inconsistencies were experienced when measuring electrical properties on the electrodes in previous experiments. A thin layer could be a buffer layer at the electrode interface. Additionally, investigation of hole blocking layers (HBL) and electron blocking layers (EBL) in previous research on OLEDs laid foundation for the use of these layers in the capacitor device. DNA-CTMA was found to act as an EBL in OLEDs [20,44]. For polymer based devices, conduction is due to a carrier hopping mechanism and not charge transport like that found in inorganic devices. Therefore, it becomes necessary to introduce charge transport and blocking layers to direct the charges through the devices in order to improve performance. In a capacitor application the HBL and EBL would act as barriers to charge injection into the dielectric region. The effect would be delaying charge injection into the dielectric and preventing premature breakdown. The additional thin film polymer layers sandwiching the DNA bio-polymer hybrid dielectric will provide a buffer/barrier to charge injection under high voltage conditions into the active dielectric region thereby increasing the electric field strength of the device.
5.2 Material Selection

Materials selected for layered devices need to be compatible with DNA-CTMA/sol-gel, have high temperature stability, and be solvent insoluble. Several materials were considered and characterized in the following sections.

5.2.1 Charge Injection Mechanisms

There are two charge injection mechanisms considered in this research as related to polymer insulation materials, layered devices and the metal/polymer interface. The barrier height and the barrier width of the thin film at the electrode/polymer interface require investigation. Literature reports the Schottky injection mechanism effecting barrier height and the Fowler Nordeim injection mechanism describing tunneling through very thin layers.[45] These mechanisms ultimately influence charge injection across/through the barrier.

5.2.2 Electron Blocking Layers (EBL)

Several nucleobases were considered for these layers. They are the building blocks of DNA and RNA, and exhibit many characteristics desirable for dielectric layers. Nucleobases were considered based on availability, high temperature stability and being solvent insoluble. Figure 25 shows TGA results of the nucleobases and DNA-CTMA, showing high temperature stability with Guanine stable >400ºC.[46,47]
Figure 25. TGA of nucleobases and DNA

Literature shows DNA-CTMA to be an EBL based on its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO).[20] It was suspected that nucleobases could also have this same effect. Occupied molecular orbitals are separated from unoccupied orbitals by an energy gap called the HOMO-LUMO gap (HLG). Literature shows some variance in the HLG for all nucleobases, with references stating the gap is ~5eV[48,49,50], with Guanine having the lowest LUMO between 1.8 and 0.3eV[49,50], as shown in Figure 26. Guanine having the lowest LUMO makes it well suited as an EBL. Guanine was also chosen as a layer due to its compatibility with DNA-CTMA/sol-gel, being solvent insoluble, its ability to be deposited as a very thin layer, and its temperature stability >400ºC. Guanine was deposited in 60nm layers by physical vapor deposition.
Variance in the HLG is due to the difficulty in obtaining experimental measurements and also the variety of measurement techniques used. In a capacitor, proper placement of EBL and HBL can prevent charge injection into the dielectric region. Literature shows the thickness of the layer to be a factor, with thinner films acting as the recombination layer in layered devices.[51,52] When the layer is too thin tunneling can occur. The effects of tunneling have been reported on by Chen et al.[13]. Several configurations of Guanine layered devices were fabricated for testing, using 60nm layers to avoid the effects of tunneling due to layer thickness. A suggested band diagram is shown in Figure 27.
Figure 27. Suggested band diagram for Guanine layered devices

5.2.3 Hole Blocking Layers (HBL)

Another material considered is Bathocuprione (BCP). BCP is an organic electronic material useful in OLEDs as an electron transport and hole blocker. HLG, thermal stability and layer thickness were all considered. BCP was chosen as a layer for the capacitor structure based on literature showing BCP effective as a HBL, with a HOMO of 7eV[53]. Temperature stability of BCP is shown to be near 400ºC in the TGA plot in Figure 28. Wang et al., investigated the influence of different thicknesses of the BCP layer on the performance of OLEDs and states that the BCP layer acts as a recombination region of the charge carriers when the layer is >3nm. When the layer is <3nm tunneling occurs.[53]. In an LED electron transport is needed. BCP provides an HBL while allowing electron transport. For the capacitor structure in this experiment, a vapor deposited 60 nm BCP layer would be placed as a HBL to delay/prevent charge injection.
into the dielectric region. Figure 29 shows a suggested band diagram for such layered devices incorporating BCP as a HBL.

Figure 28. TGA of BCP and Guanine

Figure 29. Suggested band diagram for layered devices
5.3 Layered Design and Fabrication

The same MIM test structure used for the previous experiments on single layered devices was again used for experiments with multilayered devices, Figure 30 shows the additional layers in the device.

![Diagram of a MIM device incorporating a spin-coated DNA-CTMA/sol-gel ceramic hybrid film dielectric with additional layers]

**Figure 30. MIM device incorporating a spin-coated DNA-CTMA/sol-gel ceramic hybrid film dielectric with additional layers**

Thin layers, 60nm, were deposited by physical vapor deposition onto ITO coated glass substrates. These layers were chosen to be thick enough to delay tunneling yet thin enough to not affect the overall dimension of the device. DNA-CTMA/sol-gel was then spin-coated onto the thin film. The need for a solvent insoluble material was to avoid any compromise to the layers, since DNA-CTMA/sol-gel is prepared with solvents. Both Guanine and BCP met this requirement as well as being able to be vapor deposited with thickness accuracy. The second barrier thin film was vapor deposited on top of the DNA-CTMA/sol-gel and then Al top electrodes were deposited through a mask by evaporation. Several layered designs were considered. Guanine was deposited on both sides of the DNA film and also on either side of the DNA film to determine the effect of the
placement of the additional layers. After analysis of the breakdown measurements on these devices, Guanine was found to have the greatest benefit on both sides or on the Al side of the device. These results led to the determination that Guanine may be acting as an EBL on the Al side of the device, and the reason for the enhanced results. BCP was then chosen as a HBL and used on the ITO side of the device, to further develop this theory. The following characterization section reports results of the layered devices.

5.4 Layered Device Characterization

Several designs of layered devices were characterized and reported on in the next section. Electrical characterization revealed enhancements using an EBL and HBL in the device architecture.

5.4.1 Guanine Layered Devices

Guanine was used in several layered devices and shows improvements as compared to single layer dielectrics.

5.4.1.1 Dielectric Measurements

Dielectric characterization was conducted on the Guanine layered devices. Dielectric constant and dielectric loss are shown for a Guanine layered device, Guanine/DNA-CTMA-sol-gel/Guanine, in Figure 31, showing very similar results to the single layered DNA-CTMA/sol-gel hybrid, with dielectric constant ~5.5 to 5, over a frequency range of 1kHz to 1MHz.
Figure 31. Dielectric constant (left) and dielectric loss factor (tan δ) (right) for Guanine/DNA-CTMA-sol-gel/Guanine layered films

5.4.1.2 Voltage Breakdown Measurements

Voltage breakdown measurements were taken on several configurations of Guanine layered devices. Initial results of the Guanine/DNA-CTMA sol-gel/Guanine (G/DS/G) device show improved electric field strengths of >50V/µm for the Guanine layered devices as compared to the single layered DNA-CTMA/sol-gel film. This comparison is shown in the Weibull plots in Figure 32. To better understand the layered devices, several configurations of guanine layers were explored. The effect on breakdown strength of varying the layer position of Guanine is shown in Figure 33. Guanine deposited on both sides of the DNA layer had the greatest enhancement in electric field strength. Guanine deposited on the Al electrode side had only a small increase and guanine on the ITO side showed minimal enhancement as compared to the single layer DNA-CTMA/sol-gel films.
Figure 32. Weibull plots for DNA-CTMA/sol-gel and Guanine/DNA-CTMA-sol-gel/Guanine layered devices

Figure 33. Weibull plots for DNA-CTMA/sol-gel and Guanine layered devices
5.4.1.3 Leakage Current Measurements

Leakage current measurements of a layered Guanine device, Guanine/DNA-CTMA-sol-gel/Guanine, in comparison to a DNA-CTMA/sol-gel single layer device are shown in Figure 34. The layered device shows improvement in leakage current.

![Leakage current for DNA-CTMA/sol-gel and Guanine layered devices](image.png)

**Figure 34. Leakage current for DNA-CTMA/sol-gel and Guanine layered devices**

5.4.2 BCP Layered Devices

The breakdown results on the Guanine devices led to the approach of using HBL and EBL, appropriately designed, to improve the electric field strength of the layered devices. Test structures were designed using BCP as a HBL on the ITO side of the device and Guanine as an EBL on the Al side of the device. BCP was deposited in a 60 nm layer by vapor deposition, onto ITO coated glass substrates. The DNA-CTMA/sol-gel layer has spin coated onto the BCP, then the Guanine was deposited in a 60 nm layer by vapor deposition. Al, 100nm, electrodes were deposited through the device mask by evaporation. A schematic and suggested energy band diagram of the layered device are shown respectively in Figure 35 and 36.
5.4.2.1 Dielectric Measurements

Dielectric characterization was conducted on the layered films incorporating BCP as a HBL and Guanine as an EBL, showing similar results for dielectric constant ~5.5 (1kHz) as obtained from previous devices. Results for the BCP/DNA-CTMA-sol-gel/Guanine as films are shown in Figure 37.
5.4.2.2 Voltage Breakdown Measurements

Breakdown measurements were performed on the BCP/DNA-CTMA-sol-gel/Guanine devices. Results show a significant improvement in electric field strength, with values >600V/μm. Figure 38 shows the results of the BCP/DNA-CTMA-sol-gel/Guanine films as well as comparisons to DNA-CTMA/sol-gel films and other layered configurations. The breakdown measurements for the BCP/DNA-CTMA-sol-gel/Guanine devices now rival the high breakdown strengths of state-of-the-art BOPP, leading to the potential for a new high energy density material configuration for capacitor applications.
The BCP/Guanine layered structure was then recreated with polystyrene (PS) as the dielectric material. This device, BCP/PS/Guanine was tested to confirm the action of the BCP-HBL and the Guanine-EBL for another common dielectric material. This device also showed a significant increase in electric field strength and results of these breakdown measurements are shown in the Weibull plots below. Figure 39 shows BCP/PS/Guanine films compared to polystyrene as a single layer, confirming significant increase in dielectric breakdown strength for the HBL/EBL dielectric layered configuration. Continued study of these layered devices can reveal alternative HBL and EBL that may work in a similar way to BCP and Guanine, showing significant enhancements to electric field strength for layered capacitive devices.
5.4.2.3 Polarization Measurements

Polarization measurements were taken on the layered devices. Hysteresis loops were run for DNA-CTMA/sol-gel, Guanine/DNA-CTMA-sol-gel/Guanine, and the BCP/DNA-CTMA-sol-gel/Guanine layered devices and are shown in Figure 40, 41 and 42.

Figure 39. Weibull plots for BCP/Polystyrene/Guanine layered devices
Figure 40. D-E hysteresis loops for DNA-CTMA/sol-gel

Figure 41. D-E hysteresis loops for Guanine/DNA-CTMA-sol-gel/Guanine
Figure 42. D-E hysteresis loops for BCP/DNA-CTMA-sol-gel/Guanine

Figure 43 shows results for energy density and efficiency of DNA-CTMA/sol-gel, and layered devices with Guanine/DNA-CTMA-sol-gel /Guanine, and BCP/DNA-CTMA-sol-gel/Guanine. Results show similar behavior in energy storage potential and efficiency for all three devices. Measured energy density is near to calculated values. Efficiency for all devices begins to degrade at higher fields.
Figure 43. Energy density (left) and efficiency (right) for single and multilayer devices

These layered films may minimize ion motion and charge buildup at the interface and block movement of the charge from one layer to the next as illustrated in Figure 44.

Figure 44. Suggested electron/hole transport mechanisms in EBL/HBL layered films
The effect of layered films on output energy density and hysteresis loss has been reported by Mackey et al., stating that in multilayer devices, layer thickness affects ion movement, dielectric loss, and hysteresis.[54] Layered film devices will need to be further studied and optimized to reduce hysteresis while maintaining or enhancing breakdown strength/energy density.
CHAPTER 6

SUMMARY AND FUTURE WORK

6.1 Summary and Conclusions

In the current work, DNA hybrid films were successfully fabricated from 6wt% DNA-CTMA and a Zr/Si sol-gel precursor. Dielectric characterization revealed the stability and reproducibility of frequency-dependent dielectric constant and dielectric loss factor (tan δ) of these devices as a function of thermal cycling. Breakdown voltage measurements for the DNA hybrid films revealed electric field strengths comparable to that of polystyrene films recently tested under the same conditions, with a measured dielectric constant twice as large as that of polystyrene (5.5 vs. 2.6), providing for an 2X increase in volumetric energy density, \( U = \frac{1}{2} k \varepsilon_0 E^2 \). Breakdown voltage measurements for the DNA hybrid films revealed electric field strengths consistently at 300-350V/µm, potentially providing for a calculated volumetric energy density >3 J/cc. Polarization measurements revealed the measured energy density of the films to have >95% efficiency at 150V/µm (applied voltage of ~450V) and 80% efficiency at 225V/µm (applied voltage of ~600V). Optimization and characterization of hybrid films has continued with variations in material composition and purity, as well as layer thickness, and device design, to enhance the dielectric constant \( k \), electric field strength \( E \), the energy density and efficiency of DNA-based hybrid film devices.
In this context, layered devices have also been investigated as initial results incorporating thin layers of vapor-deposited Guanine, a nucleobase, show increased breakdown voltage measurements and increased energy density relative to that of the DNA bio-polymer hybrid single layer dielectric device. It is thought that the additional thin film polymer layers sandwiching the DNA bio-polymer hybrid dielectric provide a buffer/barrier to charge injection under high voltage conditions into the active dielectric region thereby increasing the electric field strength of the device. Layered devices have been fabricated and characterized to better understand these results and confirm preliminary findings. Experimental results show evidence that properly chosen Hole Blocking Layers (HBL) and Electron Blocking Layers (EBL) can prevent/delay charge injection into the dielectric region. Literature shows barrier height and width changes being two of the major design considerations.[45] The current research has shown BCP as a HBL, and Guanine as an EBL, can effectively delay charge injection and prevent premature breakdown in the material. A representative band diagram of this optimized HBL/EBL layered device is shown in Figure 45.

Figure 45. Suggested band diagram for the BCP/DNA-CTMA-sol-gel/Guanine layered device
Electric field strengths for the BCP/DNA-CTMA-sol-gel/Guanine layered hybrid have been measured at >600V/µm, potentially providing for a volumetric energy density >9J/cc. This is a 100% increase in electric field strength over a single layer device, and ~300% increase in energy density. This increase is evident for both polymer and bio-polymer based capacitors as shown when HBL and EBL were used with a typical polymer dielectric layer, polystyrene. Results of the layered devices show exciting potential for the HBL/EBL architecture to provide enhancements to any dielectric system. Further studies will continue to demonstrate this potential. Table 5 shows a comparison of several devices exhibiting significant improvements made with the HBL/EBL devices over the single layer device and also their comparison to benchmark BOPP capacitors.

<table>
<thead>
<tr>
<th>Device</th>
<th>Dielectric Constant $\varepsilon$ (1 kHz)</th>
<th>Electric Field Strength $E$ (V/cm)*</th>
<th>Calculated Volumetric Energy Density $(\varepsilon\varepsilon_0 E^2/2,J/cc)$**</th>
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<td>Polystyrene</td>
<td>2.6</td>
<td>$315 \times 10^4$</td>
<td>1.14</td>
</tr>
<tr>
<td>Guanine/DNA-CTMA-Sol-Gel/Guanine Multilayer</td>
<td>5.5</td>
<td>$370 \times 10^4$</td>
<td>3.33</td>
</tr>
<tr>
<td>BCP/DNA-CTMA-sol-gel/Guanine Multilayer</td>
<td>5.5</td>
<td>$610 \times 10^4$</td>
<td>9.05</td>
</tr>
<tr>
<td>BCP/Polystyrene/Guanine Multilayer</td>
<td>2.6</td>
<td>$570 \times 10^4$</td>
<td>3.74</td>
</tr>
<tr>
<td>BOPP</td>
<td>2.2</td>
<td>$600 \times 10^4$</td>
<td>3.50</td>
</tr>
</tbody>
</table>

* Based on Weibull analysis  ** $\varepsilon_0 = 8.85 \times 10^{-14}$ F/cm

Table 5. Dielectric Constant, Electric Field Strength and Calculated Volumetric Energy Density for single and multilayer devices
6.2 Future Work

The next steps for this research are the continued optimization and characterization of hybrid high energy density films. Device design considerations will include material composition and purity, layer thickness, and selection of HBL and EBL to enhance the dielectric constant $k$, electric field strength $E$, and the energy density and efficiency of hybrid film devices. Experiments using HBL and EBL with state-of-the-art BOPP as well as high temperature dielectrics, can further enhance polymer film performance and open doors to new areas of film capacitor operation. Temperature-dependent energy density and electric field strength measurements will be helpful in determining device efficiency and operating parameters. High field efficiency degradation needs further investigation as well as the transport mechanisms to determine if high field tunneling can be prevented. Lifetime testing, low temperature testing and discharge time analysis are also areas that require further study and are important to capacitor operation. The effect of additional selective layering in the device architecture will be studied as well as the basic mechanism for charge injection and conduction at the metal/polymer interfaces. [55,56,57] The electrode/polymer interface plays an important role in charge injection, conduction and breakdown. Further work is needed to understand the interface between the metal and polymer to reduce loss and improve breakdown. The results and analysis of this research suggest that suitably designed HBL and EBL, both organic and polymer, can provide a barrier to charge injection into the active dielectric region, both polymer and bio-polymer, increasing the electric field strength, and thereby increasing the overall energy density of the device.


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List of Publications and Presentations from this Research


Presentations


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