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PORPHYRIN THIN FILM DIELECTRICS

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ABSTRACT

New advances in technology are creating numerous power electronic applications. These applications require a substantial amount of energy that can be produced using capacitor technologies. Novel molecular dielectrics are now being incorporated in capacitors to achieve high energies, and high polarizability.

In this project, different methods of characterizing the molecular chromophore porphyrin were evaluated. The first approach was to spin cast polypropylene doped with Zinc tetraphenylporphyrin (ZnTPP) or zinc diphenylporphyrin (ZnDPP) onto gold sputtered wafers which were to be characterized using a newly constructed capacitance testing device. Analysis of the data produced by this device suggested other potential characterization methods, including the fabrication of Indium Tin Oxide (ITO) Sandwich Cells and the use of microfabrication techniques. Multi-layering porphyin thin film layers was also under experimentation. These methods have set a firm foundation such as providing experimental methods, as well as troubleshooting that will eventually lead to the proper characterization of thin film porphyrin dielectrics.

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1. INTRODUCTION

New advances in technology are generating numerous power electronic applications that require considerable amounts of energy. This unprecedented growth can be attributed to the confluence of several technologies, such as computers, wireless telecommunications, electrical vehicles, and power transmission [1, p.16]. These applications have paved the way for a revolution in capacitor technologies.

There are a wide variety of capacitors in use including ceramic and polymer film capacitors. Ceramic capacitors are largely used because of their high dielectric constants, K > 5000. However, they suffer from low breakdown strengths. Polymeric film capacitors exhibit an enormous dielectric strength, ranging up to 10,000 V, but typically exhibit a very low dielectric constant [1, p.20]. The major advantages of polymeric films are low cost, and ease of production.

Over the last couple of decades, capacitor technologies have evolved due to breakthroughs in molecular chemistry, better understanding of molecular polarizability, and the introduction of new synthesis techniques. Different dielectric media are being established and subjected to a variety of tests. The dielectric media under observation include molecular chromophores.

Several labs at the University of Pennsylvania, directed by Dr. Santiago and Dr. Therein, are evaluating methods for characterizing molecular dielectrics. The overall goal is to develop dielectric composites using ferroelectric nanoparticles and molecular chromophores for the fabrication of high energy capacitors. These various composites may eventually give rise to novel dielectrics exhibiting both high dielectric breakdown, and high dielectric strength.

The objective for the SUNFEST 2004 project is to successfully create porphyrin thin films and composites, and derive various methods for measuring the dielectric response, and other properties exhibited by the dielectric media. Zinc tetraphenylporphyrin (ZnTPP) and Zinc diphenylporphyrin (ZnDPP) are two different types of porphyrin that were explored.

2. BACKGROUND

2.1 Dielectrics

Dielectrics are electrical insulating materials that have the ability to absorb charge. They contain charges that are tightly bound to individual nuclei. These charges can move only a fraction of an atomic distance away from their equilibrium positions [2, p.132]. When dielectrics are subjected to an external electric field (polarizing field), electron clouds distort (or polarize) forming electric dipoles (as in Figure 1). This in turn generates an opposing electric field that changes the macroscopic field inside and outside the dielectric.

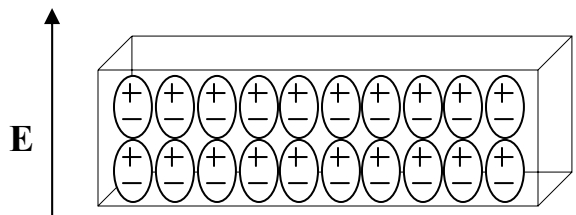


Figure 1. A uniformly polarized dielectric

Dielectrics can be classified into two categories, linear and non-linear. A dielectric is said to be linear when the relative permittivity is constant and independent of applied voltage. The relationship between the polarization vector and the Electric Field of the dielectric media is expressed mathematically through the equation:

$$\mathbf{P} = \chi_e \varepsilon_0 \mathbf{E} \quad [3]$$

where $\mathbf{P}$ = polarization vector, χ_e = electric susceptibility, ε_0 = permittivity of free space.

This equation merely demonstrates that the polarization vector is proportional to the electric field since the electric susceptibility is a unitless constant, which is the measure of ease with which dipoles can be formed into the dielectric [2, p.134].

In dielectric composites and non-homogeneous materials, the electric susceptibility, χ_e, varies with position, thus allowing different magnitudes of polarization. In nonlinear media, χ_e is a function of the magnitude of the Electric Field, $\mathbf{E}$ [2, p.134]. Since this project involves a homogeneous layer, and composites of the dielectric porphyrin, different magnitudes of the polarization vector were expected. An external electric field (polarization field) is achieved by sandwiching the dielectric between two conducting plates, forming a capacitor.

2.2 Capacitor Fundamentals

2.2.1 Theory

A capacitor is essentially an electronic device that can store electrical charge. The amount of charge a capacitor can store is equivalent to the expression: Q=CV. To calculate the capacitance of an element that consists of two or more distinct conductors, this equation can be rewritten in terms of the Electric Field generated by charges on the conductors:

$$C = \frac{\oint_{S+} \varepsilon \mathbf{E} \bullet \mathbf{ds}}{\int_{S+}^{S-} \mathbf{E} \bullet \mathbf{dl}} \quad [F] \quad [2, p.180]$$

When using a parallel plate configuration, the capacitance is defined as:

$$\mathbf{Q/V = (p_s S)/V = (\varepsilon VS)/(dV) = \varepsilon\ S/d\ [F]} \quad [2, p.181]$$

$$\varepsilon = \varepsilon_o \varepsilon_r$$

$$\varepsilon_o \sim \mathbf{8.85 \times 10^{-12}\ [F/m]}$$

where S, V, d, ε_r represent the area, Voltage, and relative permitivity respectively.

It is easily seen through this equation that the relative permittivity (dielectric constant) affects the total capacitance.

2.2.2 Capacitors Today

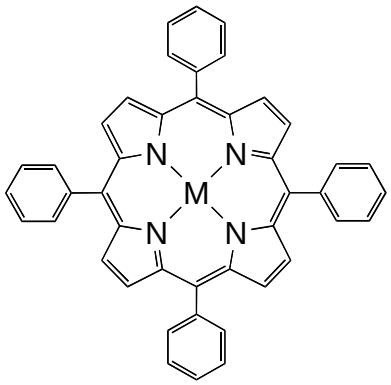
Existing capacitor technologies include the minimization of capacitor devices and the incorporation of thin film polymer dielectrics. Although these dielectrics tend to exhibit a low dielectric constant, they exhibit very large dielectric strengths, enduring up to 10,000 volts [1, p.20]. Another advantage displayed by these thin films is that they can be used in metallized film capacitors. Metallized film capacitors are advantageous because they exhibit a “self healing” phenomena. Two electrodes short-circuit through a defect in the dielectric, resulting in the current vaporizing the metallization near the short. This effectively disconnects the shorted portion from the rest of the capacitor [1, p.22].

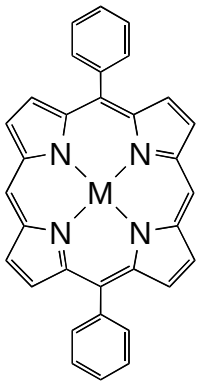
Although these capacitors constitute a mature technology, dramatic improvements in their performance can be realized through established electronic materials chemistry. Novel approaches in molecular chemistry are now creating and exposing potential dielectric substitutes and composites. One such molecular chromophore is porphyrin.

2.3 Porphyrin

Porphyrins, from the greek word *porphura* (purple), are based on 16-atom rings containing four nitrogen atoms [4]. Porphyrins occur widely in nature and play vital roles in various biological processes. One example is Heme, which contain iron porphyrins that are largely responsible for oxygen transport and storage in living tissues [5]. One unique quality of porphyrin is the ability to insert metals into their molecular structure. Metals such as iron, cobalt, copper, nickel, and zinc have been used in establishing different porphyrins.

The porphyrins in this research project contain zinc as their central metal ion. Various literature searches indicate that Zinc porphyrins are one of the easiest to prepare from free base porphyrins, as well as being the most stable. This project uses Zinc tetraphenylporphyrin (ZnTPP), and Zinc diphenylporphyrin (ZnDPP). These porphyrins have a slightly different molecular structure from one another; ZnDPP exhibits open meso positions, while ZnTPP does not, (Figure 2).





M~ Zinc

Tetraphenylporphyrin (TPP) Diphenylporphyrin (DPP)

Figure 2.
Molecular structure of porphyrins used in the research experiment.

Polarization

Porphyrins are polarizable because their ground state electronic structure has almost all pi electrons delocalized throughout the linear molecule. When external fields are introduced, the electrons/ electron density shift so that there is an overall negative charge at the positive electrode and an overall positive charge at the negative electrode. Since the electrons are delocalized and constantly moving through the pi orbitals of all the atoms, the polarized state is rather stable.

Potential Disadvantage

One potential disadvantage that porphyrins tend to display is the phenomena of photobleaching. Photobleaching, also commonly referred to as "fading," occurs when a fluorophore permanently loses the ability to fluoresce due to photon-induced chemical damage and covalent modification [6]. This changes the chemicals electrical properties, possibly making it more conductive. Since we are experimenting with porphyrin as a dielectric, this would lead to unwanted results.

To limit the "fading" of our samples, a desiccator was used with aluminum foil sides to prevent the penetration of light. Samples were also stored in small containers in the microfabrication laboratory. Although these precautions were taken, the samples were eventually exposed to light during e-beam evaporation and spin coating. This could have caused unwanted light activation as well as a greater potential to interact with oxygen, but since exposure was kept to a minimum, the porphyrin thin films were suggested to be testable up to a week.

3. EXPERIMENTAL METHODS

This section reports on efforts to create experimental setups for characterizing composites and homogeneous layers of the porphyrins Zinc tetraphenylporphyrin (ZnTPP), and Zinc diphenylporphyrin (ZnDPP).

3.1 Capacitance Device

The first method employed was the construction of a capacitance device, enabling relatively quick, precise measurements of capacitance with dielectric coated substrates. Initial designs for the device were created using AutoCAD 2000i software. The device was fabricated in the Mechanical Engineering machine shop located at Towne building (see Appendix A). Two copper contacts were also constructed using a lathe machine. After the fabrication, silver epoxy was used to attach braided copper wire to the copper contacts. The fully assembled device is displayed in Figure 3.

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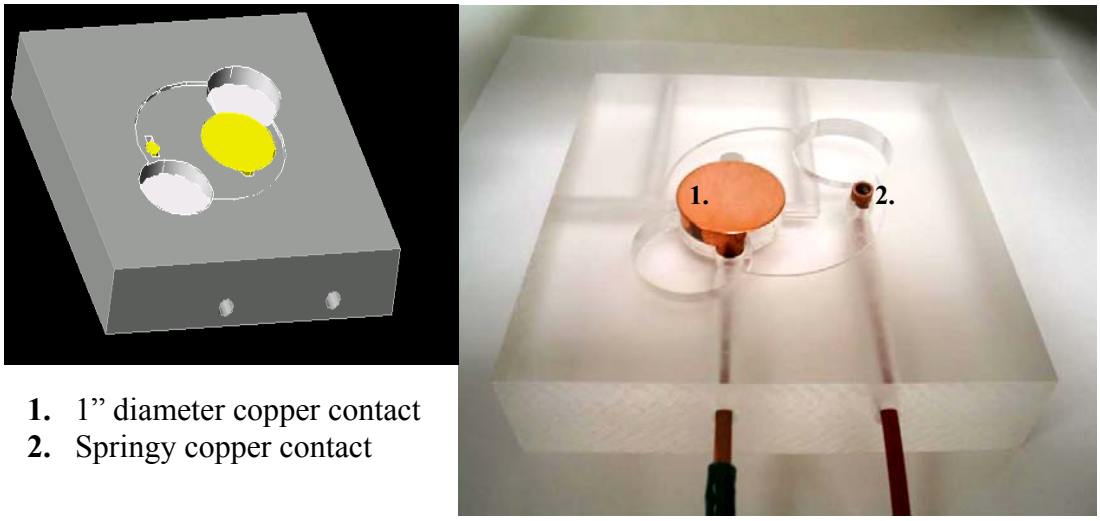


1. 1” diameter copper contact
2. Springy copper contact

Figure 3. (left) Autocad design of Capacitance Device, (right) constructed Capacitance Device

3.1.1 Substrate

The substrate in use is a silicon wafer. After the wafer was chemically cleaned and dried, a thin layer of silicon dioxide was applied to the surface of the substrate. The wafer was then placed inside an e-beam evaporator machine to deposit gold contacts. In an e-beam evaporator machine, a small amount of gold is placed inside a crucible. The crucible is bombarded by a beam of electrons evaporating gold onto the surface of the substrate. The wafers were now ready for spin coating.

3.1.2 Spin Coating

Spin coating allows the simple production of relatively thin films. The action of centrifugal forces due to the rotating substrate spreads the drop of solution as the solvent evaporates leaving a thin film on its surface [7, p.104]. Five gold coated wafers were used to spin coat different porphyrin composites. The first step was to tape an outside edge of the wafer, thus allowing a conducting edge after spinning. A solution was produced using a half a gram of polypropylene and 25ml of the solvent decalin. Two to three drops of this solution was then applied to the surface of the wafer, which was spun at 4000 rpms for approximately 60 seconds. The wafer was then placed onto a 240°C hotplate for approximately two minutes. After annealing, 5mg of ZnTPP was dissolved in a 20 M polypropylene solution, and spun onto the wafer under similar spinning conditions. This process was repeated on a total of three gold wafers, (see Figure 4). The porphyrin ZnDPP was used on the other two wafers, following the same process.

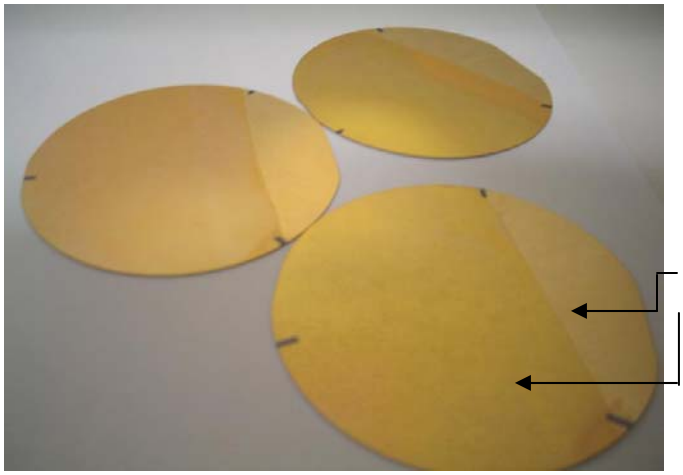


Figure 4.
Spin Coated Wafers
-Conducting Edge
-Thin film dielectric

3.1.3 Testing and Results

The dielectric coated wafers were tested using the capacitance device and an HP 4276A LCZ meter. In order to make capacitance measurements the wafer is placed dielectric face down onto the 2" dish in the capacitance device, with the conducting edge over the springy contact. A foam cushion is placed on the back of the wafer, with a 200 gram weight on top to establish pressure. The other 1" diameter copper contact completes the capacitor. The two copper wires were then connected to the LCZ meter to make appropriate measurements of capacitance versus frequency (Figure 5).

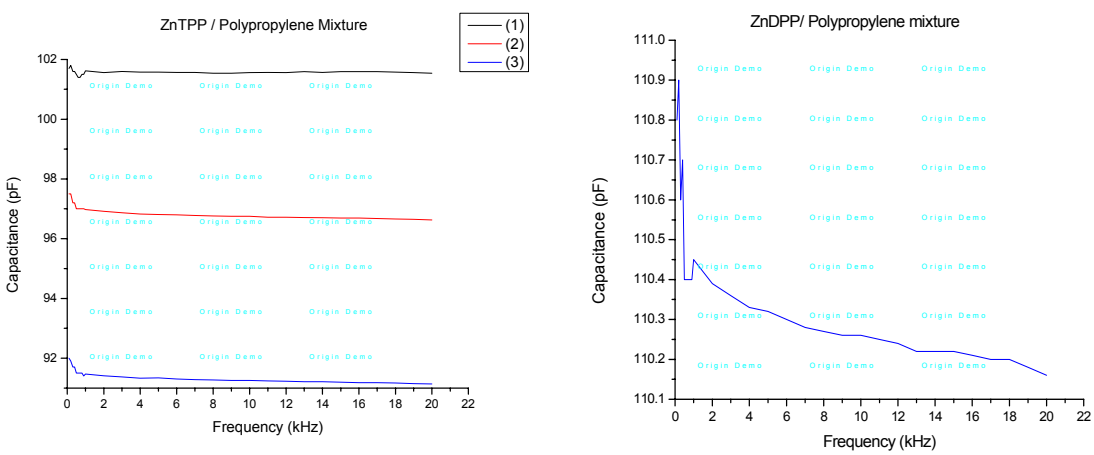


Figure 5. *capacitance vs. frequency*
(Left) ZnTPP / Polypropylene Mixture, (Right) ZnDPP / Polypropylene mixture.

Unfortunately, this method encountered a significant number of problems. Due to the malfunctioning stylus profilometer the thickness of the thin film could not be measured. Ellipsometry could not be used either because the film was not very transparent. It was assumed that the thickness was less than one micron, and using this assumption the derived result was a dielectric constant less than one. The capacitance values obtained were also

questionable, due to the oxidizing copper contacts. After the copper contacts were chemically cleaned, the device still produced similar results. Further investigation determined that the device contained internal parasitic capacitance from the copper contacts, diminishing the actual capacitance.

3.2 (ITO) Sandwich Cell Capacitor

A new method was devised allowing precise contacts to be established by creating sandwich cell capacitors. Indium Tin Oxide (ITO) was sputtered onto glass plates to create a conducting substrate. These conducting substrates were used since the supply of gold and silicon wafers were exhausted. A solution was created using 20mg of Zinc tetraphenylporphyrin (ZnTPP) with 2 ml of the solvent tetrahydrofuran (THF). Three to four drops of this solution was placed onto the substrate, and spun at 4000 rpms for approximately 60 seconds. This process was done on a total of four ITO substrates. Since ITO is transparent, a silica substrate is spun with the same solution so film thickness could be measured using the ellipsometry device.

An Infrared Laser machine (Universal Laser Systems X660) was used to create a 3mm square pattern onto clear plastic Mylar; the pattern served as a shadow mask during e-beam evaporation. Gold was evaporated through the mask and onto the dielectric, creating a gold square contact. Thin copper wire was then connected to the ITO substrate and gold square contact with silver epoxy. The final results were four sandwich cell capacitors ready for testing, Figure 6.

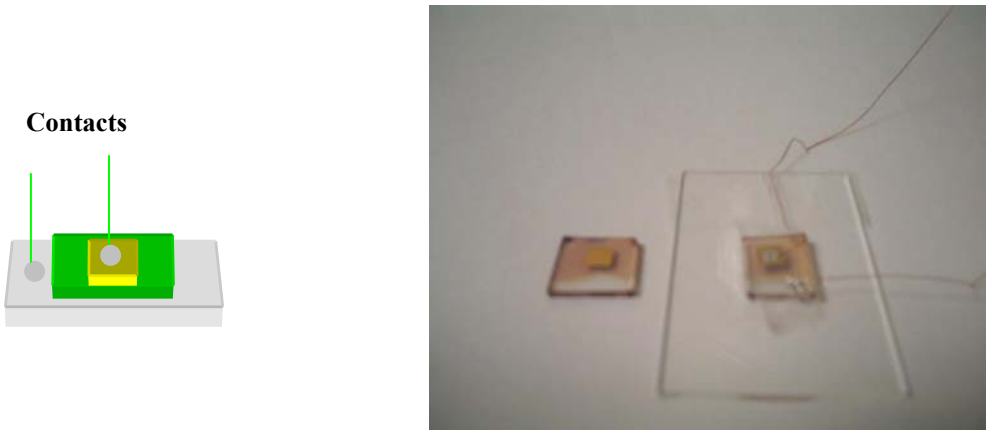


Figure 6. Indium Tin Oxide Sandwich Cell Capacitors

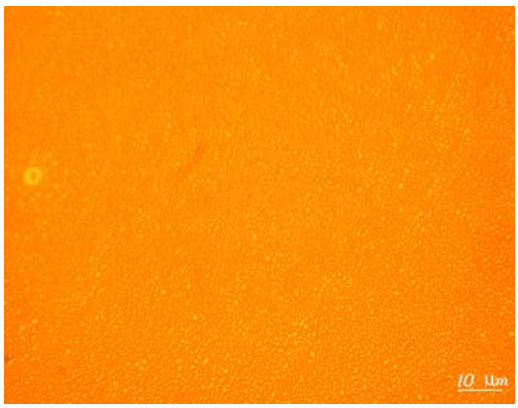
3.2.1 Testing and Results

Upon testing, it was discovered that the porphyrin thin films contained minor pinholes, creating shorts. One possible solution was to experiment with the “self healing” characteristics of porphyrin. As noted in Section 2.22, metallized capacitors exhibit a certain phenomenon that when connected to high levels of voltage, the small shorted contacts are destroyed preventing conduction. Ten volts was applied to each ITO capacitor for approximately thirty minutes. Upon inspection, it was observed that the ITO capacitors still suffered from minor shorts. Two possible explanations for this predicament are that the

dielectric thin film was burned, allowing conduction to continue, or several small pinholes remained causing shorts. The same spinning process was performed a second time, but the film still exhibited the same behavior.

Multi-layering porphyrin thin films was also tried, but did not produce the desired results. Most samples spun and hard baked displayed non-uniformity. Also, the porphyrin solutions always aggravated and disturbed the previous thin film layer.

Another method employed involved using different porphyrin samples. A trimer porphyrin (DDD) and Zinc diphenylporphyrin were exposed to similar spinning conditions. It was observed under microscope analysis that these porphyrin films suffered from the same pinhole phenomena, although the size of the pinholes varied widely, as shown in Figure 7.



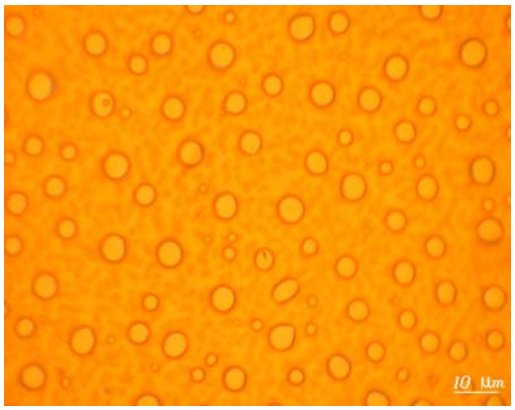


Figure 7. Zinc-diphenyl-porphyrin (ZnDPP) (DDD) Trimer porphyrin

Due to the time consuming process of e-beam evaporation and thin film layering this method was eventually abandoned.

3.3 Photolithography

A final method was then introduced involving the micro-fabrication of fixed electrodes for measuring the dielectric response of the porphyrin (ZnTPP). The electrodes were produced using a micro-fabrication technique known as photolithography.

Photolithography is an optical means for transferring patterns onto a substrate [8]. It can generally be performed using positive or negative photoresist. These two photoresists have different chemical reactions when exposed to ultra violet light. Positive photoresist becomes soluble in developer solution, while negative photoresist hardens and becomes practically insoluble. For our experiment a positive photoresist was used.

First, glass substrates were chemically cleaned to remove impurities and organic residue. The glass substrates were then placed inside the e-beam machine, evaporating a maximum gold thickness of 250 nm. A second cleaning was performed by rinsing the gold plates with acetone, isoproponal, and de-ionized water. They were then spun dry and prepared for the process of photolithography.

Positive photoresist was applied to the surface of the gold substrate, and spun at 4000 rpms for approximately 30 seconds. The gold plate was then soft baked, allowing solvent to evaporate and photoresist to harden.

After the soft bake was completed a mask was aligned with the gold substrate. Ultraviolet light was projected through the mask and onto the photoresist. As a result, the exposed

photoresist was chemically changed, becoming soluble in resist developer. After 15 seconds of UV exposure, the slide was developed in positive photoresist developer for approximately 35 seconds. The gold substrate was then submerged in deionized water for one minute, and spun dry. Hard baking was performed to harden photoresist and enhance adhesion, which was followed by gold etching with potassium iodide and iodine. The final product was a substrate of gold patterned electrodes spaced 20um apart, shown in Figure 8. Positive photoresist was then removed and the substrate was prepared for spin coating.

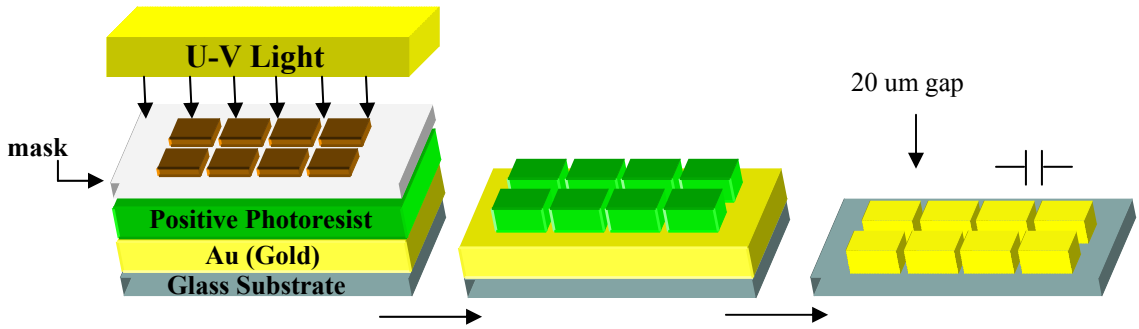


Figure 8. The photolithography process, shown in order from left to right

A 10 M solution of Zinc tetraphenylporphyrin (ZnTPP) was created with the solvent tetrahydrofuran (THF), and placed onto the gold patterned substrate. The sample was then spun at 4000 rpms for 60 seconds. Under microscope investigation it was observed that the dielectric had a slightly darker appearance within the 20um gaps, suggesting it was successfully within the gap. The electrodes were then chemically cleaned with tetrahydrofuran (THF) solvent, and connected with thin copper wire using silver paint (see Figure 8).

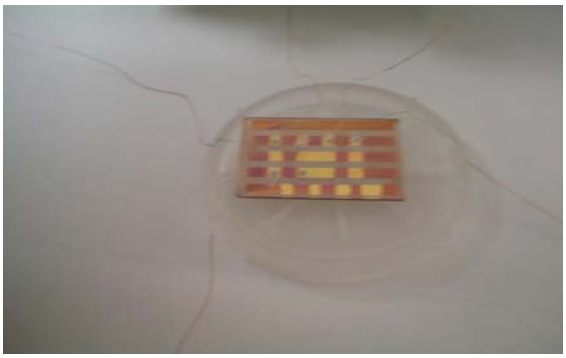


Figure 8. Final Product: Dielectric covered substrate

3.3.1 Testing and Results

The substrate was tested with an Agilent impedance analyzer 4249a. This particular equipment was used to see if the substrate behaved like a capacitor. Since the dielectric had a thickness greater than 250 nm it was expected to display fringing capacitance. A very small capacitance was also expected due to the small area of the electrodes (see Appendix B). The impedance was measured with varying frequency and a cole-cole plot (Figure 9) was produced. (Since some dielectrics tend to exhibit a small amount of leakage current, dielectric capacitors are usually modeled as a parallel combination of a resistor and capacitor. A cole-cole plot of this equivalent circuit is illustrated in the Appendix C). The measured results did not show this relationship. Certain measurements seemed to be out of range of the equipment. It was suggested that this was due to the thickness of the dielectric, causing fringing capacitance. The true capacitance could not be calculated due to the erratic pattern of the cole-cole plot. However, under ideal conditions the capacitance was calculated to be approximately 4pF. A possible explanation for this large capacitance resides in the instrument itself; it was speculated that the internal capacitance of the instrument was measured, rather than the small capacitance produced by the substrate.

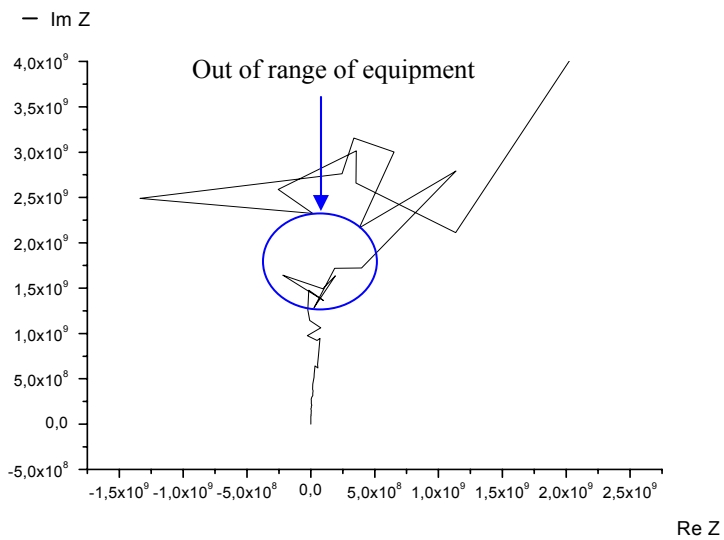
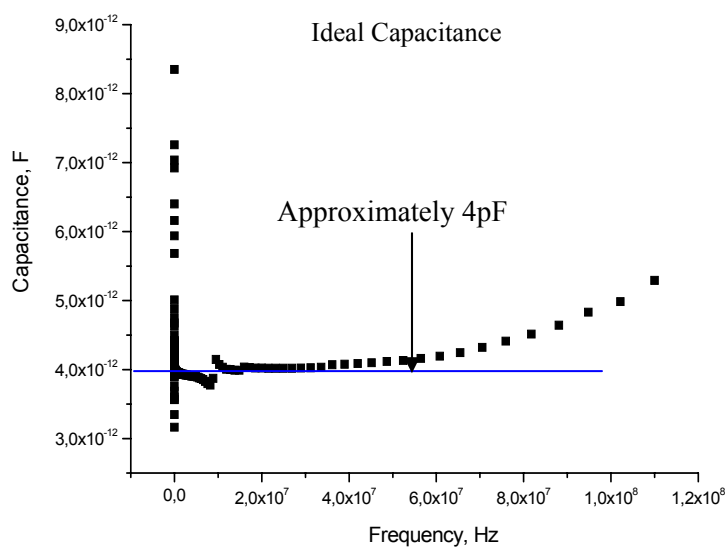


Figure 9.

Top
Cole-cole plot
Bottom
Calculated Ideal Capacitance

$$C = 1/(\omega|Z|)$$



4. DISCUSSION AND CONCLUSIONS

Although these methods did not produce the desired results, they provided a vital stepping stone toward future implementations. Various methods were investigated and compared to one another, establishing a concrete chain of steps to follow for future work. In the future, different molarities of porphyrin should be explored in establishing uniform thin films. Although this was a desired investigation in this experiment, limited amounts of porphyrins were available limiting the concentration of the solutions. For better spinning results, the spinning process should continue in the microfabrication laboratory clean room. The microfabrication clean room has different filtering systems than the chemistry laboratory, which would provide better spinning conditions, thus providing better results.

5. RECOMMENDATIONS

Spin coating is just one of the methods of film deposition. Another experimental method that could be used is vapour phase film deposition. Under high vacuum, the vapours of the solution are deposited as films which can be successfully measured by a stylus method [7, p.39]. This could provide a uniform, homogeneous thin film, enabling the proper characterization of the dielectric. Journal searches also suggest the use of a scanning probe microscopy apparatus in making successful calculations of capacitance.

Various composites, such as porphyrin mixtures with PZT can be created and studied in future work. These specific types of composites may eventually lead to novel dielectrics that have a very large dielectric breakdown, and dielectric constant.

6. ACKNOWLEDGMENTS

I would first like to extend my appreciation to Dr. Santiago for his help and guidance throughout the summer project. I would also like to take this opportunity to express my gratitude to Paul Frail, who provided me with porphyrin samples as well as valuable knowledge regarding porphyrin chemistry. I am also grateful to Dr. Scott Slavin for his guidance in the microfabrication laboratory, and other staff for all of their support throughout the duration of the project. Last, but not least, I would like to thank the National Science Foundation for supporting such a beneficial program (SUNFEST) that has greatly influenced my intention of pursuing graduate studies.

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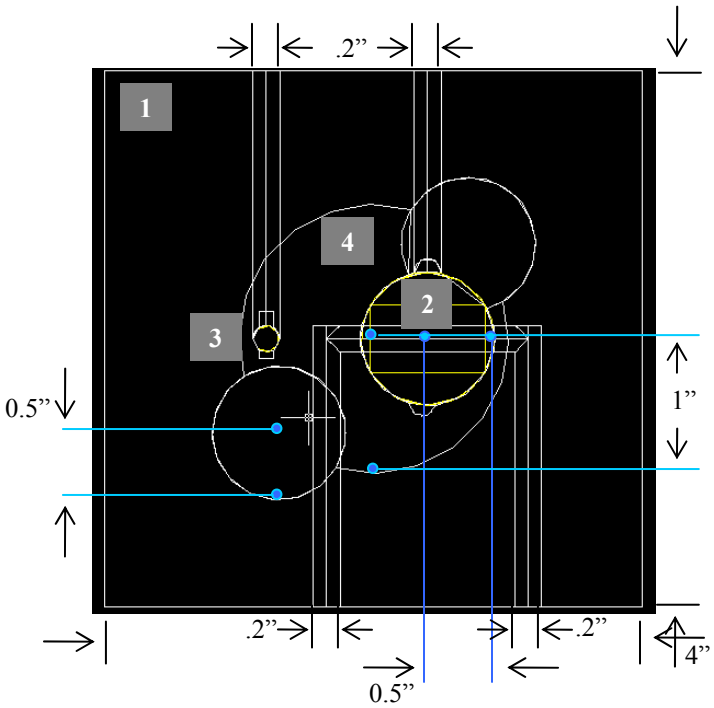
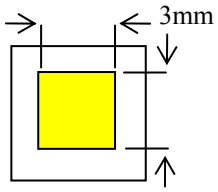
APPENDIX A:

Autocad drawing - Capacitance Device

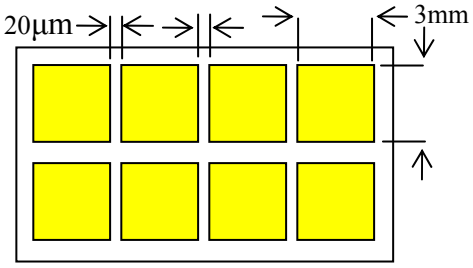


	(1) platform	(2) Large contact	(3) Small contact	(4) Circular dish
diameter	----------	1”	.2”	2”
height	.8”	.5”	.5”	---------
depth	----------	---------	---------	1mm

ITO capacitor (Top view)



Gold patterned substrate (Top view)



Height of gold contact: 250nm

APPENDIX B:

Theoretical calculations

(First method) Capacitance device

Capacitance = $(\varepsilon_r \cdot \varepsilon_0 \cdot \pi \cdot r^2)/d$ $\varepsilon_r = \varepsilon_{mixture}$

$= ((\varepsilon_r \cdot 8.85\text{EE-}12)(\pi \cdot (0.0127)^2))/d$

$= (\varepsilon_r \cdot 4.48\text{EE-}15)/d$ [F]

(d < 1μm) -----> (Capacitance > ε_r • 14.088EE-9 [F])

(Second method) ITO sandwich cell capacitor

Capacitance = $(\varepsilon_r \cdot \varepsilon_0 \cdot A)/d$

$= ((\varepsilon_r \cdot 8.85\text{EE-}12)(9\text{EE-}6))/d$

$= (\varepsilon_r \cdot 79.65\text{EE-}18)/d$ [F]

(d < 1μm) -----> (Capacitance > ε_r • 79.65EE-12 [F])

(Third method) Photolithography produced substrate

Capacitance = $(\varepsilon_r \cdot \varepsilon_0 \cdot A)/d$ A= 250EE-9 · 3EE-3

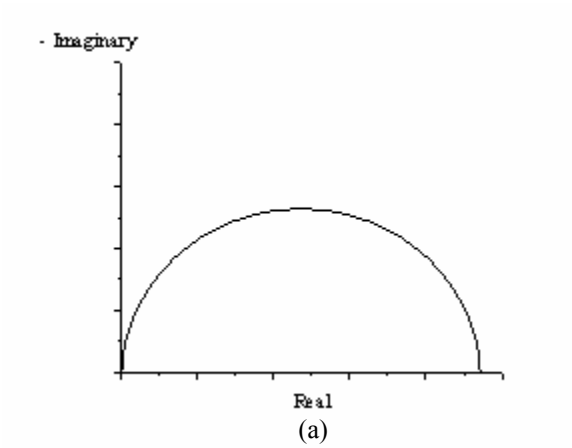
$= ((\varepsilon_r \cdot 8.85\text{EE-}12)(750\text{EE-}12))/d$

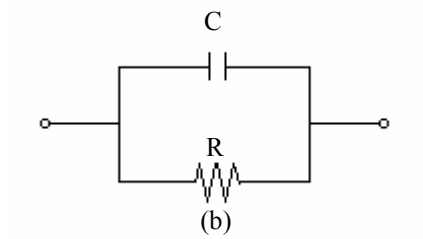
$= (\varepsilon_r \cdot 6.638\text{EE-}21)/(20\mu m)$ [F]

$= (\varepsilon_r \cdot 331.875\text{EE-}18)$ [F]

APPENDIX C:

Cole-Cole plot





(a) Cole-Cole plot for a lossy capacitor (b) Equivalent circuit

Equations:
$|Z| \cos(\theta) \rightarrow$ Real
$|Z| \sin(\theta) \rightarrow$ Imaginary