The Effects of Spin Coating on PVDF Films

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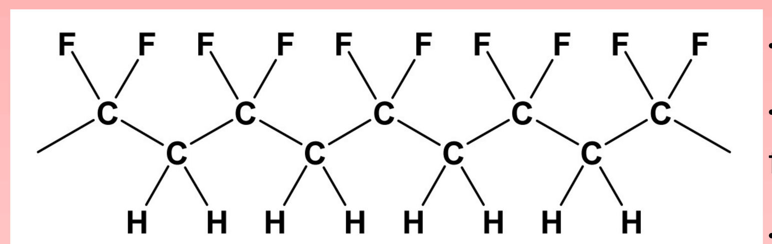
Introduction

Our research is focused on finding ways to create thin, high quality samples of the polymer Polyvinlidene fluoride (PVDF) through the method of spin coating. Spin coating is a common technique used for creating thin polymer films such as in the case of photolithography. It is an ideal technique due its quickness and ability to be used on a mass scale. We used PVDF because it is a known ferroelectric material. Ferroelectrics are currently being investigated for their potential use as random access memory (RAM) in computers. Ideally , we would like to discover what parameters of spin coating most optimally produce the thinnest and most uniform films of PVDF.

Spin Coating Theory

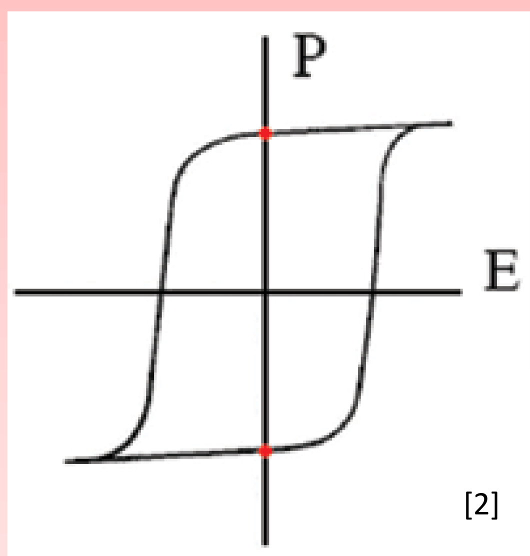
- Spin coating is a process by which thin uniform films of polymer are created
- Benefits of spin coating are that is a fast effective means of depositing film
- To spin coat a film a desired polymer is dissolved into a suitable solvent , in our case usually Dimethylformamide (DMF), Dimethyl Sulfoxide (DMSO) or Butanone
- A prepared substrate is placed on a chuck of a spin coater which can be accelerated to a given speed
- The solution is then dispensed onto the substrate either before or during spinning
- Centripetal forces cause the liquid to spread across the sample and eventually be thrown off
- As it spreads the solvent evaporates causing the polymer to be deposited
- If performed successfully a uniform layer of film is left on the substrate
- Spin coating is dependent on many parameters such as viscosity, drying rate, percent solid, surface tension , spin speed, solvent used, concentration, atmospheric conditions and more
- Our research sought to determine how specific parameters effect spin coating and what is required to create the optimal sample

PVDF



[1] Polyvinylidene fluoride (PVDF)

- PVDF is known ferroelectric material
- Ferroelectric polymers hold polarization even after external electric field is removed
- They do this by having a built in dipole, in this case caused by the fluorine's of PVDF

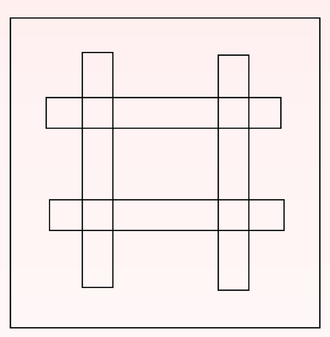


[2]

- As an external field is applied, the chains of polymer align their dipoles with the field
- When the field is removed the chains maintain their aligned position
- In order to switch the dipoles a negative external field is required, this produces a hysteresis type graph as shown
- Our research worked primarily with a hybrid of PVDF called Poly(vinylidene fluoride trifluoroethylene) P(VDF-TrPE) which replaces some of the hydrogen atoms with additional fluorine's
- The ratio of this substitution used was 65% VDF and 35% TrFE
- Though this weakened the dipole it improves crystallization and thus a creates more optimal ferroelectric.

Sample Preparation

- Samples were made on glass slides
- The glass slides had aluminum electrodes deposited on them with an evaporator

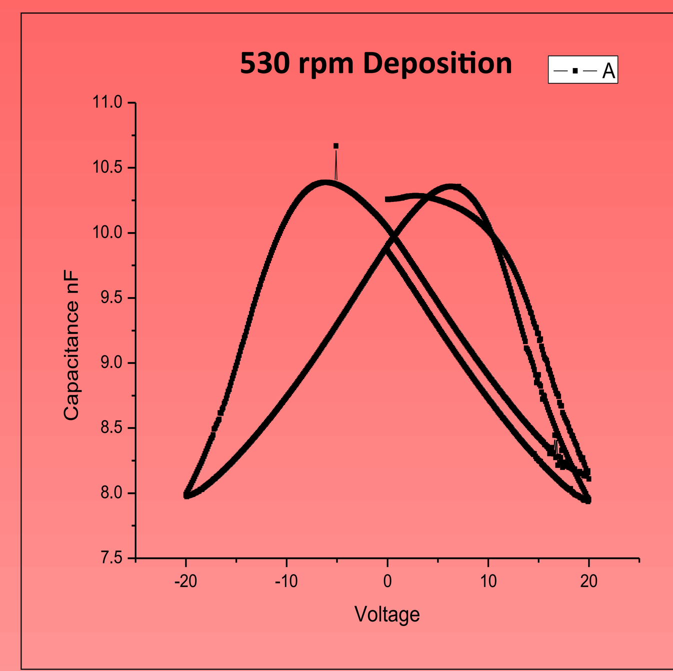


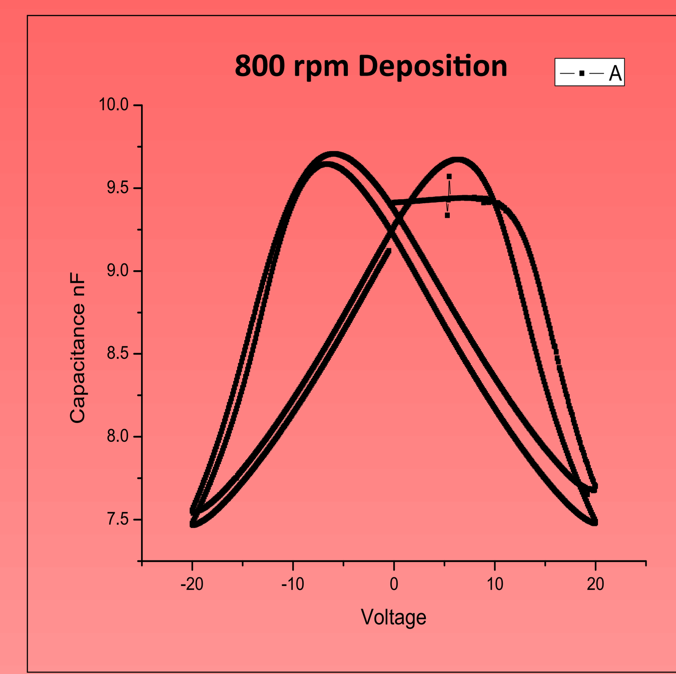
Aluminum
PVDF
Aluminum
Substrate

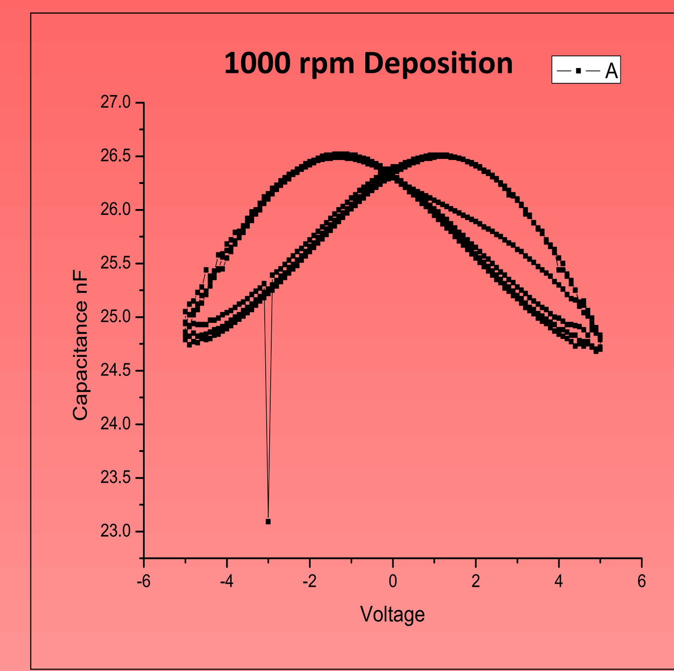
- After the polymer was spin coated on additional aluminum was then added to the top as well to create a capacitor as shown on the diagram to the right
- Such a method usually gave us four viable spots, as seen on the left, through which we could conduct various tests.
- The most common measurement used was to run a voltage sweep of the sample and see how the capacitance changed.
- An ideal ferroelectric material will exhibit a butterfly curve when exposed to a voltage sweep as shown later on.
- Often samples were annealed at high temperatures to improve structure
- Generally samples had varying amounts of holes or defects in them that would cause data to short or have a rough look to it. Our goal was to create samples with as few defects or holes as possible

Spin Speed

- We conducted tests to determine what speeds were most optimal for the process
- All samples shown were made by solution consisting of 5% by weight DMF solution of PVDF 65/35 copolymer
- All samples shown were spun at 40°C
- All samples had same final speed of 2000 rpm, but each had a different deposition speed. From left to right the samples had a deposition of 530, 800, and 1000 rpm respectively

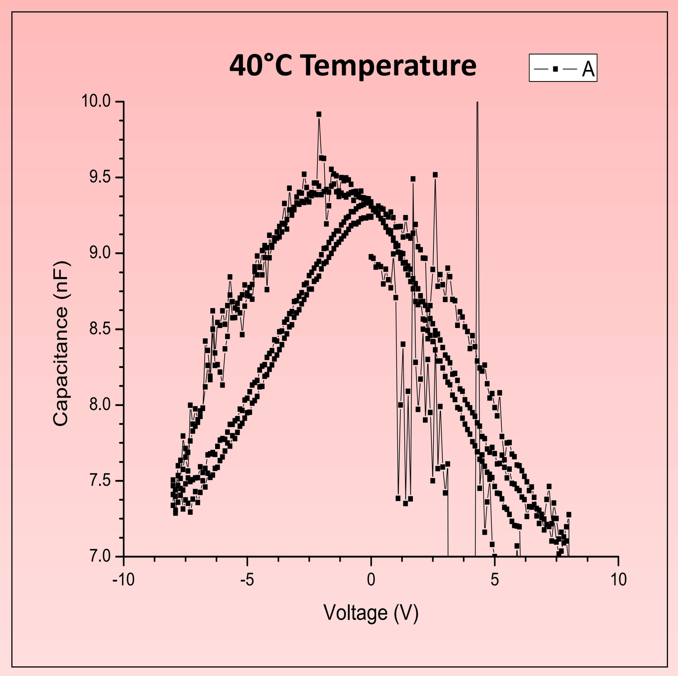


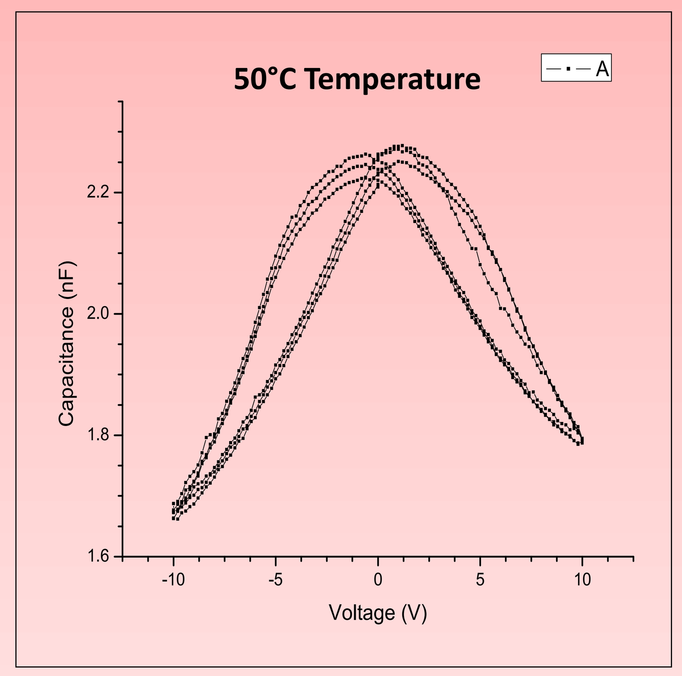


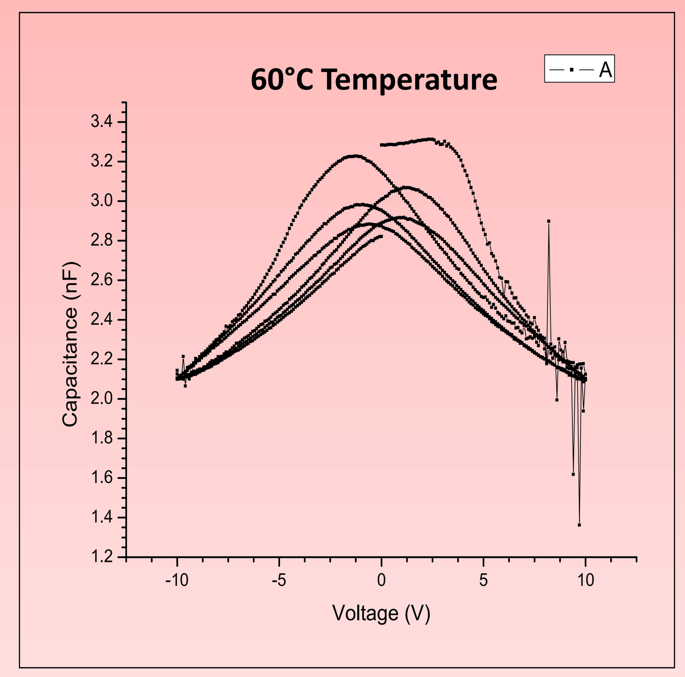


Temperature

- One of the key parameters that was alternated throughout the experiment was the atmospheric temperature. A box was built around the spin coater unit and outfitted with heaters in order to control the temperature.
- Samples were all made from a solution of 1% by weight DMF solution of PVDF 65/35 copolymer. Solutions were deposited at 800 rpm and final speed was 2000 rpm. 8 drops were deposited each time.
- The samples are respectively spun at 40°C, 50°C and 60°C







Thickness of films

- The thickness of the films was found to be reliant on a number of factors, most predominantly the concentration of solvent used. Thickness of film was related to solution concentration linearly.
- Deviations in thickness were also caused by other factors such as spin speeds and temperature. Higher temperatures generally increased the thickness slightly, likely due to the higher evaporation rates.
- A higher initial or final spin speed also created thinner films
- These additional effects were usually more or less around 5-10 nm thickness changes.
- It is worth noting that changes in the amount of drops seemed to have minimal or no effect on the overall thickness of the sample

Solvent concentration by weight	Approximate Thickness
1%	30 nm
2%	60 nm
3%	90 nm

Conclusions

We discovered that the slower speeds tended to produce more consistent data. However, we speculate that spinning at higher speeds is still theoretically viable, it just has a smaller margin for error. Generally higher depositions speeds produced more dispersed films than slower speeds. Thus a deposition speed of 800rpm was considered most optimal. Higher spin coating temperatures clearly seemed to improve overall structure and ferroelectricity of the material, especially with lower concentrated solutions. Generally it was found that thickness was dependent on the concentration, though other factors like spin speed or temperature did play apart.

Citations

[1] "70% PVDF - A Highly Weatherable and Sustainable Coating, by Linetec." *70% PVDF - A Highly Weatherable and Sustainable Coating, by Linetec*. Linetec, n.d. Web. 01 Aug. 2014. <http://www.linetec.com/Finishing_Facts/PVDF-promotes-sustainability.html>.

[2] Mathur, Neil. "DoITPoMS." - *TLP Library Ferroelectric Materials*. University of Cambridge, n.d. Web. 01 Aug. 2014. <http://www.doitpoms.ac.uk/tlplib/ferroelectrics/printall.php>.

Acknowledgements

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