THE PROCESSING AND POLARIZATION REVERSAL DYNAMICS OF THIN FILM POLY(VINYLIDENE) FLUORIDE

Noel Mayur Dawson

University of New Mexico

Follow this and additional works at: http://digitalrepository.unm.edu/nsms_etds

Part of the Nanoscience and Nanotechnology Commons, and the Polymer and Organic Materials Commons

Recommended Citation


This Dissertation is brought to you for free and open access by the Engineering ETDs at UNM Digital Repository. It has been accepted for inclusion in Nanoscience and Microsystems ETDs by an authorized administrator of UNM Digital Repository. For more information, please contact disc@unm.edu.
Noel Mayur Dawson
Candidate

Nanoscience and Microsystems Engineering
Department

This dissertation is approved, and it is acceptable in quality and form for publication:

Approved by the Dissertation Committee:

Kevin J. Malloy, Chairperson

Leah Appelhans

Yang Qin

Tito Busani
THE PROCESSING AND POLARIZATION REVERSAL DYNAMICS OF THIN FILM POLY(VINYLIDENE) FLUORIDE

by

NOEL MAYUR DAWSON

B.S., Applied Physics, University of California, Santa Cruz, 2010
M.S., Nanoscience and Microsystems, University of New Mexico, 2011

DISSERTATION
Submitted in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy
Nanoscience and Microsystems

The University of New Mexico
Albuquerque, New Mexico

December 2017
DEDICATION

To my Family
ACKNOWLEDGMENTS

First and foremost I would like to thank my advisor Dr. Kevin Malloy for his support and guidance throughout the years. I do not know how he managed to give me so much freedom in my research but also keep me on the right track to graduate, but I am grateful. You have taught me much about science and life, thank you.

I would like to thank all the staff at CTHM without you this place would crumble. You guys really keep this place running and all the great work that is done at CHTM could not be done without you.

I would like to thank Heather Armstrong who has supported me in so many ways in my career at UNM.

I would like to thank all the students at CHTM and NSMS who have made my time here amazing.

I am grateful to my committee members Dr. Tito Busani, Dr. Yang Qin, and Dr. Leah Appelhans, who reviewed my work and gave me useful feedback.

I would like to thank all my friends who have gotten me to this point. I could fill pages and pages with their names (but I will not). Know that you all are always in my heart and I am eternally grateful for you.

I would like to thank Shannon Landry for all of her support and love throughout the years. You have always been there for me, motivated me, supported me, and been my best friend. I love you and and very thankful you are in my life.

Finally, I would like to thank my parents for all their love and support throughout this crazy adventure and my brothers and sister who have given me all the love and teasing I needed to finish this degree.
THE PROCESSING AND POLARIZATION REVERSAL DYNAMICS OF THIN FILM POLY(VINYLIDENE) FLUORIDE

by

Noel Mayur Dawson

B.S., Applied Physics, University of California, Santa Cruz, 2010
M.S., Nanoscience and Microsystems, University of New Mexico, 2011
Ph.D., Nanoscience and Microsystems, University of New Mexico, 2017

ABSTRACT

Many ferroelectric devices benefit from the ability to deposit thin ferroelectric layers. Poly(vinylidene) fluoride (PVDF) is the prototypical ferroelectric polymer, but processing of thin film ferroelectric PVDF remains a challenge due to the formation of large voids in the film during traditional thin film processing. The research described in this dissertation starts by investigating the origin of these voids. The cause of these voids is found to be caused by vapor induced phase separation (VIPS). Guided by the thermodynamics of VIPS, a process is then designed to produce void-free ferroelectric PVDF thin films on polar and non-polar substrates. The films are shown to have a high remnant polarization (~6.5 C m⁻²). The later part of this dissertation is focused on understanding the temperature and structural phase dependent kinetics of polarization switching in PVDF films. A polarization switching model is developed with considerations of Avrami nucleation and growth, local electric fields, temperature and structural phase. The kinetics of polarization switching are shown to follow a universal behavior when correctly accounting for temperature and structural phase.
# TABLE OF CONTENTS

## CHAPTER 1 INTRODUCTION

1.1 POLY(VINYLIDENE FLUORIDE) ............................................. 1
1.2 PROCESSING OF FERROELECTRIC PVDF THIN FILMS ...................... 4
1.3 APPLICATIONS OF THIN FILM FERROELECTRIC PVDF .................... 7
1.4 OUTLINE OF DISSERTATION .................................................. 9

## CHAPTER 2 VAPOR INDUCED PHASE SEPARATION IN SPIN COATED PVDF  

2.1 OBSERVATION OF DEFECTS IN SPIN COATED PVDF FILMS ..................... 13
2.2 MONITORING OF PHASE SEPARATION IN PVDF/DMSO SOLUTIONS WITH LIGHT SCATTERING 16
2.3 CONCLUSIONS ........................................................................... 24

## CHAPTER 3 TEMPERATURE MODULATED SPIN COATING OF PVDF/DMSO SOLUTIONS

3.1 INTRODUCTION ......................................................................... 26
3.2 THERMODYNAMIC CONSIDERATIONS FOR VIPS .......................... 27
3.3 THERMALLY MODULATED SPIN COATING .................................... 29
3.4 CHARACTERIZATION OF FILM MORPHOLOGY AND PHASE COMPOSITION .............. 35
3.5 FERROELECTRIC CHARACTERIZATION ....................................... 41
3.6 CONCLUSION .............................................................................. 43

## CHAPTER 4 SWITCHING IN PVDF FILMS

4.1 INTRODUCTION TO POLARIZATION SWITCHING .......................... 46
4.2 KOLMOGOROV-AVRAMI-ISHBASHI MODEL .................................... 48
4.3 NUCLEATION LIMITED SWITCHING .......................................... 53
4.4 CONDUCTIVITY INDUCED POLARIZATION .................................. 58
4.5 LOCAL ELECTRIC FIELDS ............................................................... 66
4.6 SWITCHING IN TMSC FILMS ....................................................... 77
4.7 BUILDING A SWITCHING MODEL .............................................. 81
4.8 CONCLUSIONS ............................................................................ 93

## CHAPTER 5 EFFECT OF MICROSTRUCTURAL PHASE ON THE FERROELECTRIC AND 
DIELECTRIC PROPERTIES OF PVDF .................................................. 98

5.1 INTRODUCTION ......................................................................... 98
5.2 COMPOSITION AND MORPHOLOGY OF ANNEALED SAMPLS  .............. 99
5.3 DIELECTRIC PROPERTIES OF PVDF WITH COMPOSITION ................ 105
5.4 DEPENDENCE OF POLARIZATION REVERSAL DYNAMICS ON TEMPERATURE .......... 113
5.5 DEPENDENCE OF POLARIZATION REVERSAL DYNAMICS ON STRUCTURAL COMPOSITION .... 121
5.6 CONCLUSIONS ........................................................................... 128

## CHAPTER 6 SUMMARY AND FUTURE WORK

6.1 SUMMARY OF WORK .................................................................... 131
6.2 FUTURE WORK ........................................................................... 135
6.3 CONCLUSION .............................................................................. 137

## APPENDIX A: METHODS

................................................................. 139

## APPENDIX B: NUCLEATION THEORY

................................................................. 141
LIST OF FIGURES

Figure 1.1. A commercial guide describing traditional processing routes for PVDF. ...................... 2

Figure 1.2. a. FTIR spectra of melt crystallized PVDF b. FTIR spectra of solution cast PVDF. The melt crystallized PVDF clearly shows the presence of the α-phase while solution cast PVDF only shows the ferroelectric β and γ phases. ................................................................. 4

Figure 2.1. PVDF films spin coated in varying relative humidity conditions a. 0% b. 5% c. 10% d. 15% and e. 20% relative humidity. All films show large pore defects ................................................................. 16

Figure 2.2. Schematic of the modified spin coater used for SALS experiments ................................ 19

Figure 2.3. False color intensity maps showing the intensity of scattered light vs time and scattering vector for PVDF/DMSO solutions spun at a. 0% b. 5% c. 10% d. 15% e. 20% relative humidity. The scattered intensity starts at small $|q|$ and then grows suggesting spinodal phase separation process .............................................................................................................. 20

Figure 2.4. Normalized integrated intensity of the scattered light during spin coating, showing that the time elapsed before scattering occurs decreases with humidity .................................................. 21

Figure 3.1. A schematic representation of the ternary phase diagram of a polymer-solvent-nonsolvent system. The points within the binodal surface indicates the composition at which the polymer solution will phase separate. As temperature increases it takes an increased relative amount of non-solvent to be within the binodal. .................................................................................................................. 30

Figure 3.2. Schematic of the ternary phase diagram at a single temperature showing the relative composition pathway using arrows ................................................................. 32

Figure 3.3. Schematic of the TMSC process with the black arrows showing the compositional pathway. (S=solvent, NS=nonsolvent, P=polymer) ................................................................. 34

Figure 3.4. Optical images of films prepared using the TMSC process compared to films dried at room temperature. The films prepared using the TMSC process are transparent while the films dried at room temperature are opaque, suggesting the TMSC process has less pore defects than the samples dried at room temperature .................................................................................. 35

Figure 3.5. SEM micrographs of PVDF samples prepared using the TMSC process at a. 20 % b. 40 %, c. 60 % and d. 80% relative humidity showing the surfaces free of large pore defects. ...... 36

Figure 3.6. AFM micrographs (2 x 2 μm ) of PVDF films prepared using the TMSC process showing relatively low rms roughness and no large pores ................................................................. 37

Figure 3.7. FTIR spectra of (a-c) samples prepared using the TMSC process and (d-e) samples prepared by melt recrystallization .................................................................................. 39

Figure 3.7. Ferroelectric hysteresis measurements for samples prepared on a. Au, b. Al₂O₃ and c. SiO₂ ................................................................................................................................. 42

Figure 4.1. Plots of the polarization switching curves at 266K for different applied fields (250, 225, 200, and 175 MV m⁻¹ ). The inset shows characteristic curves for the KAI and NLS models on their predicted variation with voltage (and therefore electric field). Notice how the experimental data shows two regimes of distinct polarization growth behavior while the NLS model and KAI model only predict one ........................................................................................................................................... 59

Figure 4.2. A schematic showing the two dielectric layer capacitor model ........................................ 61
Figure 4.3. Electric Fields in each layer in the two dielectric layer capacitor model when there is a
non-zero conductivity. When the conductivity increases the time it takes for the electric fields in
different layers to equalize is shorter. ................................................................. 64

Figure 4.4. Schematic of ferroelectric spheres in an amorphous matrix used to describe the
microstructure of TMSC PVDF films. ........................................................................ 67

Figure 4.5. A simple schematic of the polarization and induced internal charge of a poled
ferroelectric. The blue arrows represent the polarization of a ferroelectric region and the red plus
and minus symbols represent the bound polarization charge caused by the polarization of the
ferroelectric regions ................................................................................................. 68

Figure 4.6. A ferroelectric where the internal polarization (blue arrows) produces the internal
bound charge (red plus and minus) that is compensated by free charge (green plus and minus).
.............................................................................................................................. 69

Figure 4.7. The current versus time curves for a) the entire switching process b) the part of the
switching process that is dominated by leakage current. ........................................... 71

Figure 4.8. Schematic of the instant when one ferroelectric region switches. The red and blue
arrows represent the polarization direction of the ferroelectric regions. The red plus and minus
symbols represent the bound polarization charge and the green plus and minus symbols
represent the free charge. Notice if the ferroelectric is fully compensated internally the charge at
the interface is double the polarization charge. ............................................................ 72

Figure 4.9. Polarization value at the end of the polarization reversal in the fast regime plotted
against the applied field. ............................................................................................ 76

Figure 4.10. Plots of the polarization switching curves at 266K for different applied fields (250,
225, 200, and 175 MV m\(^{-1}\)). The inset shows characteristic curves for the KAI and NLS models.
Notice how the experimental data shows two regimes of distinct polarization growth behavior
while the NLS model and KAI model only predict one. ................................................. 77

Figure 4.11. The effect of varying the model parameters on the resulting polarization curves .... 84

Figure 4.12. Plots showing the simulated polarization growth (line) and the experimental data
(points) for different applied fields as a function of activation field. ............................. 85

Figure 4.13. Plots showing the simulated polarization growth (line) and the experimental data
(points) for different applied fields (in MV/m) as a function of activation field when the applied field
is allowed to be a fitting parameter. ............................................................................. 86

Figure 4.14. Shows the model results when a field dependent conductivity is introduced.
Introducing a bulk conductivity reproduces the two regimes of switching but does not describe the
slow regime well. ........................................................................................................ 87

Figure 4.15. Avrami plots of the polarization growth versus time with the linear fits. The behavior
of the polarization in slow region is approximately linear in the Avrami plots. ................. 89

Figure 4.16. Plots of the simulated polarization growth for different conductivities of the screening
charge. Notice how a bulk conductivity of 10^{-9} S m\(^{-1}\) doesn’t screen the internal polarization in
the time of the experiment but a conductivity of 10^{-5} S m\(^{-1}\) screens the polarization fast enough
that the two regimes are not resolved. ........................................................................ 92
Figure 5.1. FTIR spectra of the As-Cast PVDF sample. Notice the absence of characteristic absorption features at 762 cm\(^{-1}\) and the strong absorption features at 1234 cm\(^{-1}\) and 1274 cm\(^{-1}\).

Figure 5.2. FTIR spectra of the PVDF sample annealed at 175 °C (AN-175C). Notice that the 1234 cm\(^{-1}\) has been enhanced and the shoulder peak at 1274 cm\(^{-1}\) reduced.

Figure 5.3. FTIR spectra of the sample annealed at 185 °C. Notice the increased absorption at 762 cm\(^{-1}\) and the decrease of absorption at 1234 cm\(^{-1}\) and 1274 cm\(^{-1}\).

Figure 5.4. AFM micrographs of as cast and annealed PVDF samples showing the differences in morphology between the as cast and annealed samples.

Figure 5.5. The real and imaginary part of the dielectric constant as a function of temperature for 10 different frequencies for the As-Cast sample before and after poling, showing that there is no strong effect of poling on the dielectric constants.

Figure 5.6. The real and imaginary part of the dielectric constant as a function of temperature for 10 different frequencies for the An-175C sample before and after poling, showing that there is no strong effect of poling on the dielectric constants.

Figure 5.7. The real and imaginary part of the dielectric constant as a function of temperature for 10 different frequencies for the An-185C sample before and after poling, showing that there is no strong effect of poling on the dielectric constants.

Figure 5.8. Loss tangent versus frequency for all samples at various temperatures.

Figure 5.9. Arrhenius plots of the As-Cast and annealed samples showing that relaxation behavior of all three samples is similar.

Figure 5.10. Polarization growth versus time behavior at 300 K for all three samples.

Figure 5.11. Polarization growth behavior at 266 K for all three samples.

Figure 5.12. Polarization growth behavior at 233 K for all three samples.

Figure 5.13. a) Applied electric field versus Polarization state at the end of the fast regime b) \((E_{\text{applied}} + \Delta ET2 - T1)\) versus the polarization state at the end of the fast regime showing the universal temperature behavior of polarization at the end of the fast regime for the As-Cast sample.

Figure 5.14. \((E_{\text{applied}} + \Delta ET2 - T1)\) versus the polarization state at the end of the fast regime showing the universal temperature behavior of polarization at the end of the fast regime for the As-Cast, AN-175C and AN-185C samples.

Figure 5.14. a) \((E_{\text{applied}} + \Delta E_{\text{min}}T2 - T1)\) versus the polarization state before being adjusted for different minimum switching fields b) \((E_{\text{applied}} + \Delta E_{\text{min}}T2 - T1 - \Delta E_{\text{min}}S2 - S1)\) versus the polarization state. Universal behavior is demonstrated for polarization reversal when the appropriate adjustments are made to the applied field.

Figure 5.15. Polarization growth curves for similar driving fields for all samples. The applied field and the temperature at which the data was collected for the plots are:
Plot a. As-Cast \(T=233\) K \(E_{\text{app}} = 250\) MV m\(^{-1}\); An-175C \(T=266\) K \(E_{\text{app}} = 200\) MV m\(^{-1}\); An-185C
Figure 5.16. Avrami plots of the As-Cast, AN-175C, and AN-185C samples at 233 K. Notice the linearity of the growth from $2 \times 10^{-4}$ s to $2 \times 10^{-3}$ s suggesting that the polarization reversal follows an Avrami type behavior.

Figure 5.17. Avrami plots of the As-Cast, AN-175C, and AN-185C samples at 266 K. Notice the linearity of the growth from $2 \times 10^{-4}$ s to $2 \times 10^{-3}$ s suggesting that the polarization reversal follows an Avrami type behavior.

Figure 5.18. Avrami plots of the As-Cast, AN-175C, and AN-185C samples at 300 K. Notice the linearity of the growth from $2 \times 10^{-4}$ s to $2 \times 10^{-3}$ s suggesting that the polarization reversal follows an Avrami type behavior.

Figure 5.19. Avrami constants plotted as a function of driving field defined earlier in this section showing that the polarization reversal behavior in the slow regime is similar for all samples when the temperature and structural phase variation is properly accounted for.
LIST OF TABLES

Table 3.1 The α/δ fraction of the crystalline phase content in the TMSC films showing that the films primarily consist of the ferroelectric β/γ phases. .................................................................41

Table 4.1. Values for the electric field in layer 1 and 2 with respect to changing a. thickness b. dielectric constants of the two dielectric layers in a two layer capacitor structure. .........................62

Table 4.2. The fit values for the Avrami constants.................................................................90

Table 5.1. Location of characteristic absorptions features in PVDF and the corresponding structural phases..............................................................................................................100

Table 5.2. The values of the temperature, applied field and driving field for all three samples at a polarization state of ~.03 C m⁻². The table shows that the driving field is approximately equal for a similar polarization state while the temperature and applied field vary. ........................................123
Chapter 1 Introduction

Abstract

The prototypical ferroelectric polymer poly(vinylidene fluoride) is discussed with respect to micro-structure. The state-of-art processing techniques for depositing thin film ferroelectric PVDF are reviewed with a focus on current limitations of processing thin films. Applications of thin film ferroelectric PVDF are discussed.

1.1 Poly(vinylidene fluoride)

Poly(vinylidene fluoride) (PVDF) is a linear fluoro-polymer with a repeat unit of \(-\text{(CH}_2\text{-CF}_2\text{)}\). The large electronegativity of the fluorine atoms causes large dipole moments to form between carbon backbone and fluorine atoms. Due to these large permanent dipoles, it was theorized that some of the crystal phases of PVDF should be ferroelectric. In 1969 Kawai et. al. reported the piezoelectric nature of PVDF. \(^1\) In 1971 Bergman et. al. reported the discovery of pyroelectricity and second harmonic generation in PVDF thin films. \(^2\) Due to the absence of a Curie temperature and the possibility of other explanations for the piezoelectric and pyroelectric behavior in PVDF, the ferroelectric nature of PVDF was contested. Then in the mid-1980s several groups showed that introducing defects into the polymer chain by including the co-polymer trifluoroethylene (TrFE) a clear ferroelectric to paraelectric transition exists and PVDF is indeed ferroelectric. \(^3,4\)
PVDF exists in at least 4 crystalline phases summarized in Fig. 1.1 (taken from Solvay Inc.). The chain conformation and the crystal structure determine if the resulting films have polar or non-polar unit cells which in turn determine if the films are ferroelectric or non-ferroelectric. \(^5,6\) Generally when PVDF is cooled from a temperature above its melting point, it crystallizes into the \(\alpha\)-phase with an alternating TG-TG\(^+\) conformation; this structure is non-polar due to the net zero polarization of the unit cell. \(^5,6\) In the \(\alpha\) phase, application of a large electric field (~250 MV m\(^{-1}\)) parallel to one of the dipole moments in the unit cell causes the chain with dipole moments anti-parallel to the electric field to reorient itself to become parallel to the applied electric field, converting the \(\alpha\)-phase to the \(\delta\)-phase. This electro-forming process, as shown in the work of Li et. al., converts the \(\alpha\)-phase to the ferroelectric \(\delta\)-phase. \(^7\) The ferroelectric...
β-phase is usually formed by mechanically straining the α-phase at elevated temperatures.\textsuperscript{5,6} Introducing defects into the PVDF chain by copolymerizing with trifluoroethylene or tetrafluoroethylene makes the β-phase thermodynamically favorable and causes the β-phase to form when cooled from the melt.\textsuperscript{3,4} The β-phase is also formed by applying an electric field greater than 500 MV m\textsuperscript{-1} across a PVDF film in the α/δ phase as shown in Davis \textit{et. al.}\textsuperscript{8} The ferroelectric γ-phase is usually formed when PVDF films are cast from solutions with dimethylformamide (DMF) or dimethylsulfoxide (DMSO).\textsuperscript{5}

Identification of the four phases of PVDF is accomplished through infrared absorption and x-ray diffraction but we use infrared absorption in this dissertation. Infrared absorption is sensitive to the local chain conformation and can help us identify the phase of PVDF films.\textsuperscript{9,10} Examples of infrared absorption spectra in PVDF films are shown in Fig. 1.2. The α-phase and δ-phase have the same chain conformation and similar crystal structure; therefore, they have the same infrared absorption spectra and x-ray diffraction pattern. The α/δ-phase has unique infrared absorptions at 762 cm\textsuperscript{-1}, 976 cm\textsuperscript{-1}, and 1210 cm\textsuperscript{-1}.\textsuperscript{9,10} The β-phase has a unique absorption at 1274 cm\textsuperscript{-1} and shares an absorption with the γ-phase at 840 cm\textsuperscript{-1}.\textsuperscript{9,10} The γ-phase has a unique absorption at 1234 cm\textsuperscript{-1}.\textsuperscript{9,10}
1.2 Processing of Ferroelectric PVDF thin films

Methods of depositing high quality thin (≤ 1 µm) ferroelectric poly(vinylidene fluoride) (PVDF) films compatible with current electronic and photonic device technologies are of great interest for many applications but have been difficult to achieve. Several authors have found that films of the homopolymer deposited at room temperature suffer from large pinholes or pores and have root mean squared (rms) roughness values that are of the order of the film thickness, both of which limit electrical or photonic applications. Current methods to deposit thin films of ferroelectric PVDF are discussed below.
Thermal annealing of spin-cast PVDF-trifluoroethylene (TrFE) co-polymer films at ~150 °C is the most common approach to incorporating ferroelectric polymer films in devices, as the elevated temperature improves the morphology and the TrFE defects stabilize the ferroelectric β-phase. However, drawbacks of using the copolymer include the more complex, higher cost polymer synthesis, the increased dielectric leakage current of spin coated copolymer and a lower limiting operating temperature compared to the homopolymer.

Li. et al. and Ramasundaram et al. showed that spin coating PVDF homopolymer solutions at temperatures ≥ 100 °C improves the structural quality of PVDF, however these temperatures lead to the formation of the non-ferroelectric α-phase. Li et al. showed that the improved structural quality obtained allowed fields of ~250 MV m⁻¹ to be applied across the α-phase films thus converting the film to the ferroelectric δ-phase. This is a significant step towards developing a method for depositing ferroelectric thin film PVDF, although it requires an additional forming step and the films DC dielectric strength is below 250 MV m⁻¹, however Li et al were able to use AC pulses at 100 Hz to pole the films at this electric field.

Cardoso et al. were able to make thin PVDF films that have high β-phase content and have a high optical transmittance by thermally annealing spin cast films at 70 °C after spin coating. At this temperature the morphology is improved and the films remain in the β-phase. SEM images show improved morphology of samples annealed at 70 °C, however pin-hole like defects are still
present in the film. These films were corona poled and had a maximum piezoelectric coefficient of $-21 \text{ pC N}^{-1}$. Although the piezoelectric qualities of these films are excellent, the dielectric strength or ferroelectric switching of these films was not reported. Characterization of ferroelectric switching and the dielectric strength is important for energy storage and direct ferroelectric applications such as ferroelectric memory or nonlinear capacitors.

Kang et al. demonstrated that annealing of α-phase films above the melting point of PVDF and subsequent cooling of the film while applying pressure through a polar poly(dimethylsiloxane) (PDMS) mold converted the films to the ferroelectric γ phase. Later they showed that melt recrystallization of PVDF films that are sandwiched between two surfaces can produce γ-phase PVDF if both surfaces are polar. They suggested that the polar nature of the surface restricts the formation of the non-polar α-phase (in hindsight, analysis of the two papers suggest that formation of the γ-phase in the first paper is due to the melting and crystallization of PVDF between polar surfaces since pressure did not affect phase formation below the melting temperature). In other work, Kang et al. showed that rapid thermal annealing of PVDF thin films produced ferroelectric films on Au surfaces while films prepared with this method on SiO$_2$ and Al$_2$O$_3$ surfaces formed the α-phase. Since this method only worked for films on the order of 100 nm, this suggests that the Au surface nucleated the formation of the β-phase and that the rapid thermal annealing improved the morphology of the films.
Benz et al. and He et al. showed that by adding hydrated salts to PVDF solution the β-phase was stabilized at temperatures well above 100 °C, allowing for a relatively high temperature annealing step (145 °C) and once again improving the morphology of PVDF thin films while preserving the β-phase. 9,12 Although, the exact mechanism for the stabilization of the β-phase by the hydrated salts is unknown, it is thought that there is hydrogen bonding between the hydrated salts and the PVDF chains which stabilizes the β-phase.

Lastly, Zhu et al. showed that homopolymer β-phase PVDF films could be deposited using Langmuir-Blodgett techniques. 20 These films are highly crystalline and have been shown to be ferroelectric, with a remnant polarization of 6.6 C m⁻². However, Langmuir-Blodgett techniques deposit one monolayer at a time making them time intensive for applications that need several hundred monolayers. The research presented in this dissertation is focused on the deposition of thin film PVDF using the manufacturable spin coating method.

1.3 Applications of Thin Film Ferroelectric PVDF

The micro-structure of PVDF leads to many advantages for device applications. 21 PVDF, similar to the more common fluoropolymer PTFE (poly(tetrafluoroethylene)), is chemically inert, a large advantage over other ferroelectric materials. The relatively linear flexible backbone and the compact packing of the PVDF chains compared to other ferroelectric polymers lead to a high dipole density suggesting a high remnant polarization and a manageable coercive field. 21 The flexibility of PVDF allows for arbitrary shapes and its mechanical toughness allows it to be used in conditions where it is exposed to
sudden forces such as in pressure sensors. The acoustic impedance of PVDF, unlike many inorganic materials, is close to that of water (human tissue) which makes it useful for medical imaging and hydrophone applications.\(^{22}\) The specific benefits to some of these applications by being able to deposit thin films of ferroelectric materials is described below.

Two of the more general benefits of being able to deposit thin film ferroelectric PVDF are as follows. Thin film deposited PVDF could be easily integrated into standard MEMS fabrication processes. Without this ability free standing sheets of PVDF would have to be adhered to a substrate or device. A standard method for deposition of thin ferroelectric PVDF films would significantly reduce the cost of incorporating PVDF into a device. For instance, a 8 x 11 inch sheet of metallized PVDF from Measurement Specialties is quoted at $169.20 (on digikey.com), a standard thin film process could reduce the cost. Ferroelectric PVDF thin films also have more specific advantages for particular applications.

For flexible memory applications it is important to be able to integrate PVDF thin films into a ferroelectric RAM structure.\(^{23}\) This is most easily done if there is a direct way to deposit a uniform thin film onto a processed substrate. Furthermore the film thickness needs to be reduced to sub 100 nm to allow for \(~5\) volt operation.\(^{15}\) Although this work does not explore films of this thickness it does allow the fabrication of micrometer films (average thickness of the films in this work is \(1.2\ \mu m\) measured by alpha-step).
For acoustic medical imaging purposes it is important to increase the resonant frequency of the acoustic transducer to obtain higher resolution images. A 9.4 μm PVDF transducer resonates in the ½ wave mode at 104 MHz. By decreasing the thickness of the transducer to ~1 μm, the frequency of the transducer could be ~1 GHz possibly allowing for the differentiation of cancer cells and healthy cells on the skin.

For PVDF pyroelectric detectors it is important to improve speed and sensitivity. Kuroda et al. showed that by decreasing the thickness of the film they were able to improve the sensitivity of co-polymer sensors. We estimate that by being able to deposit thin films in a process that can be integrated into standard MEMs processes we can improve the sensitivity of PVDF pyroelectric detectors and incorporate the readout electronics using standard processes. It would be plausible that it would become feasible to make high density focal plane arrays of PVDF pyroelectric detectors leading to cost effective pyroelectric cameras.

1.4 Outline of Dissertation

The next chapter will focus on understanding the morphology of spin coated PVDF films. In particular we will research the variation in morphology with relative humidity. We will study the morphology formation in situ using laser scattering and observe the final morphology of the films using scanning electron microscopy. We will then use the data to show that the morphology is caused by vapor induced phase separation.
The third chapter will build upon our understanding of the film structure evolution from chapter two and investigate a new method to spin coat PVDF films while minimizing the effect of vapor induced phase separation. We will use this method to deposit ~1 μm thick ferroelectric films of PVDF on Au, Si (with a native oxide), and Al (with a native oxide) substrates.

The fourth chapter will develop a polarization switching model derived from nucleation and growth and from local field effects. That will be used in the fifth chapter to understand polarization reversal in PVDF films of different structural phases.

The fifth chapter will use thermal annealing to produce films that have different structural phases. Specifically, thermal annealing will be used to control the majority structural phase of the polymer in the films. The temperature dependent ferroelectric and dielectric properties are analyzed to find the effect of chain conformation on polarization switching.
References


13. Furukawa, Takeo, Takashi Nakajima, and Yoshiyuki Takahashi. "Factors governing ferroelectric switching characteristics of thin VDF/TrFE copolymer..."


Chapter 2 Vapor Induced Phase Separation in Spin Coated PVDF

Abstract

Morphological defects in spin coated PVDF are studied. Large porous defects are found to be correlated with the relative humidity of the casting environment. In-situ light scattering experiments are carried out to determine the evolution of these porous defects in different relative humidity environments. Light scattering data along with SEM data strongly suggest that vapor induced phase separation is a major cause for large porous defects in spin coated PVDF films.

2.1 Observation of Defects in Spin Coated PVDF Films

PVDF spin coated films prepared in humid environments have voids or pores throughout the film as shown in Fig 2.1. These films are of questionable electrical quality and no reports of their use in ferroelectric or electronic devices have been found.\textsuperscript{1,2} A better understanding of the process (or processes) that cause these defects to form is needed to be able to design a technique to deposit pore-free PVDF thin films by spin coating. A survey of the literature shows that only a few studies have studied the cause of poor morphology in spin coated PVDF films.\textsuperscript{1,2}

Benz \textit{et al.} found that relative humidity effects the morphology of PVDF films cast from DMF/acetone solutions greatly but did not propose a mechanism for this effect.\textsuperscript{3} In a separate paper they suggested that the relative humidity controlled the evaporation rate of water from the precursor solution during spin coating and this is what caused the poor morphology.\textsuperscript{1} This hypothesis was examined by monitoring the infrared (IR) absorption bands of water during spin
coating. The infrared absorption showed that the amount of water in the precursor solution increased during the initial stages of spin coating. After some time the IR bands showed that the water content decreased at a rate dependent on the relative humidity. Benz et al. suggested that the observation of the initial water uptake was due to condensation of water on the film due to evaporative cooling of the film caused by solvent evaporation.

The studies of Cardoso et al., Li et al. and Ramasundaram et al. described in Chapter 1 all demonstrated that PVDF films with improved morphologies could be produced by increasing the temperature at which the solvent was removed from PVDF solutions. These findings support the common hypothesis that the evaporation rate of the solvent controls the pore formation in spin coated PVDF films. However, there are clear experimental observations that fail to support the hypothesis that the evaporation rate of the solvent primarily controls the pore formation in spin coated PVDF films.

1. The uptake of water during the initial stages of spin coated as shown by Benz et al. suggests that the introduction of water may play a role in the formation of pores during spin coating of PVDF films.

2. Increasing the spin speed during spin coating or using low boiling point solvents increases the removal rate of solvent from the solution during spin coating. Neither of these methods have resulted in improvement in the morphology of spin cast PVDF films, suggesting that the evaporation
rate of the solvent does not control pore formation during spin coating of PVDF films. 1,2

In a series of papers Matsuyama et al. suggested that vapor induced phase separation (VIPS) induces a porous structure in cast PVDF solution when hygroscopic solvents are used to form the solution. 6,7 VIPS is a process in which a non-solvent is absorbed by the polymer solution from the vapor phase and causes the solution to phase separate into regions that are high in polymer concentration (polymer-rich) and regions that have low or no polymer concentration (polymer-lean). When the solvent and non-solvent in the polymer-lean regions evaporate, voids or pores are left behind creating a web-like morphology. 8 The morphology seen in Fig 2.1 is consistent with a phase separation process.

VIPS provides a plausible explanation of the observation of initial water uptake during spin coating as the extremely hygroscopic solvents used to solvate PVDF could absorb water from the vapor phase. VIPS also provides an explanation for the absence of impact on the morphology with choice of solvent since all current solvents for PVDF are very hygroscopic. Also, if VIPS occurs at timescales shorter than the timescale to remove the solvent from PVDF solutions during spin coating, the spin speed would have a minimal effect on the morphology spin coated PVDF films. Lastly, since VIPS is a thermodynamic process, as will be discussed in the next chapter in detail, it is likely that the temperature at which the film is cast or annealed would have an effect on the morphology of the spin
coated film. These observation suggests that a model based on vapor induced phase separation may be more appropriate than a purely evaporative model to explain void formation in spin coated PVDF films.

![PVDF films spin coated in varying relative humidity conditions](image)

Figure 2.1. PVDF films spin coated in varying relative humidity conditions a. 0% b. 5% c. 10% d. 15% and e. 20% relative humidity. All films show large pore defects.

### 2.2 Monitoring of Phase Separation in PVDF/DMSO solutions with Light Scattering

As seen in the SEM micrographs in Fig 2.1, films deposited in non-zero relative humidity conditions have pores that are relatively large compared to optical wavelengths. Small angle light scattering (SALS) is a technique used to study the scattering of collimated light from structures that are larger than the wavelength of the incident light and offers a way to study the formation of pores in spin coated PVDF films non-destructively and *in-situ*. 
Optical scattering occurs when an electromagnetic wave encounters changes in the refractive index of a material (scattering center). If a material has an inhomogeneous refractive index and the inhomogeneity can be written as a scalar function, \( \varphi(r) \), that is mathematically integrable then the Fourier transform, \( \Psi(q) \), of this function is

\[
\Psi(q) = \int \varphi(r) \ast \exp(-iqr) \, dr,
\]

where \( q \) is the scattering vector which equals (in the case of elastic scattering)

\[
|q| = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right),
\]

where \( \theta \) is the scattering angle and \( \lambda \) is the wavelength of the incident light.

Assuming that the scattered electromagnetic field is small compared to the incident electromagnetic field (Born approximation) the scattering vector \( q \sim \Psi(q) \). (The Born approximation allows for the use of the incident electromagnetic field to be used as the field that each region is interacting with as opposed to both the incident electromagnetic field and the electromagnetic field produced by other scattering regions.)

Variations in the index of refraction in phase separated samples originate in the compositional variation of the sample. Matsuyama showed that two possible mechanisms, nucleation and growth (NG) or spinodal decomposition (SD), can lead to compositional variation in vapor induced phase separated PVDF films where the solvent was dimethylformamide and the non-solvent was water. The form of the structure factor resulting from NG is very different than the form of the structure factor expected from SD.
In NG small nuclei of the minority phase (non-solvent/solvent mixture) will nucleate in a matrix of the majority phase (polymer/solvent). These nuclei are smaller than optical wavelengths and are formed randomly throughout the material. The inhomogeneity of the index of refraction can be modeled as randomly distributed delta functions in space. This type of distribution leads to diffuse scattering.

In SD the film will form regions with a high concentration of polymer and solvent and regions with a high concentration of non-solvent and solvent. The concentration of the components has to vary continuously in the film causing large structures with varying index of refractions to form.

Cahn showed that initially in a system undergoing SD the inhomogeneity of the composition can be described by a series of Fourier components whose amplitudes are determined by an amplification factor. The amplification factor is wavenumber dependent. There is a maximum wavenumber (minimum wavelength) that limits the number of Fourier components needed to define the compositional variation. This maximum wavenumber, called $\beta_c$, can be calculated from the 2nd derivative of the free energy with respect to the composition. The amplification factor has a sharp maximum that occurs at the wavenumber $\beta_c/\sqrt{2}$ and falls off at wavenumbers lower than $\beta_c/\sqrt{2}$. This defines a limited range of sine waves that describe the variation of the index of refraction in the phase separated sample. The Fourier transform of a sine wave is a delta function centered at the wavenumber. Because there is no expected preferred orientation in phase separated PVDF samples the scattering is expected to
occupy a band in q space whose width and intensity is determined by the amplification factor.

Figure 2.2. Schematic of the modified spin coater used for SALS experiments.

To study humidity dependent defect formation in spin coated PVDF solutions a 10% solution by weight of PVDF in DMSO was prepared. The solution was heated to 100 °C and mixed overnight. The solutions was then cooled to 30 °C. The solution was then deposited onto a gold coated silicon substrate spun at 4000 RPM for ten minutes in a controlled humidity environment. To obtain SALS data during spin coating of PVDF/DMSO solutions under varying relative humidity conditions, a modified spin coater schematically depicted in Fig 2.2 was
utilized. Using a laser with the wavelength of 632.8 nm and knowing the geometry of the setup the position of the scattered light on the screen is converted to the magnitude of the scattering vector \( q \). Matlab was used to extract intensity, scattering position and time from the scattering data and plot it in 2-dimensional false color intensity maps shown in Fig. 2.3. It is also useful to analyze the normalized integrated intensity of the scattered light during spin coating for various relative humidity conditions. To accomplish this the reflected specular beam was digitally blocked and the intensity of light gathered from the detector was integrated using Matlab. The integrated intensity of the scattered light as a function of spin time is shown in Fig. 2.4.

Figure 2.3. False color intensity maps showing the intensity of scattered light vs time and scattering vector for PVDF/DMSO solutions spun at a. 0% b. 5% c. 10% d. 15% e. 20% relative
humidity. The scattered intensity starts at small $|q|$ and then grows suggesting spinodal phase separation process.

Figure 2.4. Normalized integrated intensity of the scattered light during spin coating, showing that the time elapsed before scattering occurs decreases with humidity.

Analyzing these data helps understand the process that forms these large pores in spin coated PVDF films. Three different periods can be identified by using the data in Figs. 2.3 and 2.4.
**Period 1**

At all relative humidity conditions there is an initial phase where there is no scattering outside of the reflected specular beam. This suggests that during this time the film is optically homogenous and the surface is smooth.

**Period 2**

The second period starts at the time which non-specular scattering begins and ends when the integrated scattered intensity begins to decrease.

The data show that the time at which the second period begins decreases as humidity increases and seems to be approaching a constant value. This observation is consistent with a vapor induced phase separation process, since water is absorbed into the film through interactions with DMSO. The rate of at which the concentration of water in the film increases will be determined by the number of surface sites at which the gas phase water can interact and the number of water molecules available to interact. In the experiment the number of DMSO molecules at the surface is kept constant by keeping the initial solution concentration constant. Initially the absorption process is limited by the number of water molecules at the surface. As the relative humidity is increased the number of water molecules available at the surface increases and the rate at which water is being introduced into the solution increases. After a critical relative humidity the absorption will be limited by the number of DMSO site at the
surface. Because the number of DMSO sites at the surface is kept constant the rate of water absorption into the film reaches a constant value.

The false color intensity maps show that during the second period scattering starts at small \(|q|\) values and then increases to larger \(|q|\) values. This indicates the scattering structures start out large and then decrease in size. This observation is consistent with a SD process and not consistent with a NG process.\(^6\)\(^8\) As mentioned earlier a NG would result in diffuse scattering while a SD process forms a scattering band. The SEM micrographs in Fig. 2.1 also suggest a SD process according to Annamalai et al.\(^8\) The false color intensity maps show a decrease in the intensity of scattered light as \(|q|\) increases this is consistent with Cahn's findings that the amplification factor falls off at wavenumbers lower than \(\beta_c \sqrt{2}\). The sharp maximum at \(\beta_c / \sqrt{2}\) is not seen in the data, possibly because it is too small to resolve in our setup.

**Period 3**

Period 3 begins when the integrated intensity of the scattered beam start to decrease. A plausible explanation for the decrease in integrated scattered intensity is the onset of diffuse scattering. As the polymer lean regions start to evaporate the surface becomes rough (variations in the height of the sample increase). This roughness leads to diffuse scatter. Another possible explanation for the decrease in integrated scattered intensity is that all types of scattering decreased. An increase in the reflected specular beams would be expected if this was the case. Figure 2.3. does not show an increase in the reflected specular
beam and does not support this explanation. The data in Fig. 2.5 also supports the hypothesis that the integrated scattering intensity decreases at late times due to surface roughening. The evaporation rate of the polymer-lean regions would be faster in low humidity environments and slower in higher humidity conditions. The data in Fig. 2.5 show that in high humidity conditions we see a smaller decrease in integrated scattering intensity than we do when the relative humidity is low.

2.3 Conclusions

Optical scattering during spin coating of PVDF/DMSO solutions in controlled humidity environments along with SEM micrographs of the resulting film morphology are consistent with a VIPS process occurring during film formation. The in-situ SALS experiments reveal the dynamics of morphology evolution during the spin coating of PVDF solutions (when hygroscopic solvents are used) in humid environments. A VIPS process explains the porous morphology, dependence on humidity and improvement of morphology at elevated temperatures better than a previously purely evaporative model. SALS enables in-situ, real-time identification of the film formation process, suggesting that monitoring of optical scattering is a basis for process control during spin coating and hence, a basis for tailoring film morphology for specific applications. This is the subject of the next chapter.
References


Chapter 3 Temperature Modulated Spin Coating of PVDF/DMSO Solutions

Abstract

A method of depositing high quality thin ferroelectric PVDF is developed. The method is guided by the theoretical understanding of vapor induced phase separation using Flory-Huggins theory. The method is used to deposit high quality ferroelectric thin PVDF films in relative humidity environments ranging from 20%-80% on Au, Al$_2$O$_3$, and SiO$_2$ surfaces. Film quality is determined by scanning electron and atomic force microscopy. The crystalline phase is determined by Fourier transform infrared spectroscopy. The ferroelectric nature of the films is confirmed by polarization hysteresis measurements.

3.1 Introduction

Methods of depositing high quality thin (≤1 μm) ferroelectric poly(vinylidene) fluoride (PVDF) films compatible with current electronic and photonic device technologies are of interest for many applications but have been difficult to achieve. ¹ As discussed in Chapter 1, previous methods of depositing high quality ferroelectric PVDF films on polar and non-polar substrates have had limited success. ²³⁴⁵ Static annealing strategies improve the morphology significantly but the films still contain pin-hole-like defects as seen in the SEM images of Cardoso et al. ⁵ Methods that use the surface interactions to stabilize the ferroelectric phase are limited to specific substrates. ² A more in depth discussion on the current state of processing thin film ferroelectric PVDF films is found in Chapter 1.
The formation of pores during spin coating is a major obstacle that must be overcome to achieve high quality ferroelectric PVDF thin films. As shown in Chapter 2, spin coating experiments support the hypothesis that pore formation is caused by vapor induced phase separation (VIPS). The thermodynamics of VIPS can be understood using Flory-Huggins polymer solution theory. The thermodynamics then guides the development of a process for depositing high quality ferroelectric PVDF films.

3.2 Thermodynamic Considerations for VIPS

A phase separation process is one in which an initially homogeneous solution separates into at least two chemically different solutions due to a thermodynamic instability. In a polymer solution consisting of a polymer, solvent, and non-solvent the solution can phase separate into a polymer-rich phase and a polymer-lean phase. Flory-Huggins polymer solution thermodynamics extended to three components by Tompa takes the Gibbs free energy of a 3 component polymer solution as

\[
\frac{\Delta G}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1 \phi_2 \chi_{12} + n_1 \phi_3 \chi_{13} + n_2 \phi_3 \chi_{23}, \quad \text{(Eq. 3.1)}
\]

where \( R \) is the gas constant and \( T \) is the temperature. \( n_1, n_2, n_3 \), are the mole fractions of the polymer, solvent, and non-solvent, and \( \phi_1, \phi_2, \phi_3 \), are the volume fractions of the polymer, solvent, and non-solvent, respectively. \( \chi_{12}, \chi_{13}, \chi_{23} \) are the Flory-Huggins interaction parameters between the polymer-solvent, polymer-nonsolvent, and the solvent-nonsolvent. The interaction
parameter is a function of the temperature and most often is proportional to $1/T$.

The first three terms of Eq. 3.1 are due to the combinatorial entropy of mixing and are always negative. The last three terms come from contact interactions between the polymer, solvent, and non-solvent and can be positive or negative.

At equilibrium the chemical potential difference ($\Delta \mu$) between each component in the polymer-lean phase and the polymer rich-phase in the mixture is equal as shown in Eq. 3.2, where $i$ denotes each component and the superscript prime and double prime denote the polymer-rich and polymer-lean phases. $^{10}$

$$\Delta \mu'_i = \Delta \mu''_i, \quad i = 1,2,3.$$ \hspace{1cm} (Eq. 3.2)

The binodal curve is defined as the series of points at which the polymer-lean and polymer-rich phases are in equilibrium. The spinodal curve is the locus of points where the second derivative of the Gibbs free energy is zero. At compositions between the bimodal and the spinodal, a phase separated state is lower chemical potential than the homogeneously mixed state but there is an energy barrier present for the system to go from a homogeneously mixed state to a phase separated state. $^{10,11}$ Due to this energy barrier, phase separation occurs through a nucleation and growth process. The thermodynamics of nucleation and growth are described in detail in Appendix B. Within the spinodal curve there is no energy barrier for the system to go from a homogeneously mixed state to a phase separated state. Within the spinodal curve, any infinitesimal fluctuation in
composition will lead to phase separation via spinodal decomposition. Tompa showed that in a solution of polymer, solvent, and non-solvent the spinodal can be found using Eq. 3.3.  

\[ G_{22}G_{33} = (G_{23})^2, \]  

(Eq. 3.3)

where

\[ G_{ij} = \frac{\partial^2 \Delta G}{\partial \varphi_i \partial \varphi_j} \]

As discussed in Chapter 2, the in-situ small angle light scattering data suggest that solutions of PVDF/DMSO undergo phase separation via spinodal decomposition. As will be shown in the next section, it is important for the system to phase separate via spinodal decomposition because there is no energy barrier to overcome for the solution to go from a homogeneously mixed state to a phase separated state and vice versa. This means that going between both states is not controlled by nucleation statistics, can happen at a much faster time scale and is driven by small differences between the chemical potentials of homogeneously mixed state and the phase separated state.

### 3.3 Thermally Modulated Spin Coating

If the Flory-Huggins interaction parameter is known, ternary phase diagrams can be produced using Eq. 3.1. If the interaction parameter has a typical $1/T$ dependence the phase diagram look like Fig. 3.1 (reproduced with permission from ref. 12).
Figure 3.1. A schematic representation of the ternary phase diagram of a polymer-solvent-nonsolvent system. The points within the binodal surface indicates the composition at which the polymer solution will phase separate. As temperature increases it takes an increased relative amount of non-solvent to be within the binodal.

Figure 3.1 only shows the binodal surface but a spinodal surface generally exists within the binodal surface. The binodal surface exists at the boundary between compositions at which the homogeneously mixed state goes from being thermodynamically favorable to compositions at which the phase separated state becomes more favorable. As depicted in Fig. 3.1, a temperature increase shifts the binodal to compositions with increased relative non-solvent content. Using these phase schematics the morphology of spin coated PVDF films dried at room can be understood.

At room temperature the ternary phase diagram schematically looks like Fig. 3.2. The relative composition path way of the solution during spin coating follows
the black arrows. Initially the solution is in a mixed state. During spin coating the
absolute water (non-solvent) content in the solution increases initially (due to the
hygroscopic nature of the solvent) but then decreases due to evaporation. The
absolute solvent content decreases due to evaporation and the absolute polymer
content stays the same (but the relative polymer content goes to 100% due to
evaporation of the solvent and non-solvent). After enough nonsolvent has been
taken up by the solution vapor induced phase separation occurs via spinodal
decomposition as shown in Chapter 2. After spinodal decomposition the solvent
and non-solvent continue to evaporate eventually causing the solution to become
a gel and then to become a porous polymer film. The term gel in this context is
used to describe a state of the solution when the viscosity has increased (due to
solvent evaporation) to a point that the solution is kinetically hindered from further
phase separation.
Figure 3.2. Schematic of the ternary phase diagram at a single temperature showing the relative composition pathway using arrows.

Since an increasing temperature shifts the boundary between a singly phase and two phase system, solutions deposited/dried at elevated temperatures will suffer less from defects caused by phase separations. As evidenced in the examples illustrated in Chapter 1, increased deposition/drying temperature does indeed improve morphology of spin coated PVDF films. However, as shown by Li et al. and Cardoso et al. the temperature needed to deposit films free from porous defects also induces the formation of the α-phase.

Using knowledge of the general thermodynamics of PVDF/Solvent/Nonsolvent system, a temperature modulated spin coating (TMSG) process is designed to mitigate defects resulting from phase separation while allowing PVDF to
crystallize into a ferroelectric phase. Figure 3.3 schematically shows the TMSC process which is described as follows:

1. A solution of PVDF and DMSO is deposited onto the substrate and spin coating starts

2. The solution phase separates which is monitored by the laser scattering described in Chapter 2. Spinning is stopped.

3. The solution is heated to a temperature which shifts the phase boundary and reestablishes the thermodynamic stability of the single phase in the film. If phase separation happens via spinodal decomposition then the solution the can remix quickly because there is no energy barrier for the system to go from a separated phase state to a homogeneous phase state. This is important because if there is an energy barrier for the system to go from a separated state to a homogeneous state, the time needed to reach such a homogeneous state would be much longer than if there is no energy barrier. This means that the system is at an elevated temperature for an extended period of time which could cause the solution to enter a gel phase before the solution reaches a completely homogeneous state.

4. Once the solution remixes the spinning is restarted to continue the removing solvent. If the viscosity of the solution is high enough vapor induced phase separation will not reoccur and the sample is left to
continue to dry and crystallize at room temperature. If the viscosity is not high enough phase separation will reoccur and step 3 is repeated.

Fig. 3.4 shows an optical image of samples prepared using the TMSC process and samples dried at room temperature. The films prepared using the TMSC process are transparent enough to show a reflection of the CHTM logo from the underlying substrates. The films dried at room temperature are optically opaque. This observations suggest that the quality of the TMSC films is high. In the next section the morphology and phase composition of TMSC PVDF films prepared
on Au, Al₂O₃, and SiO₂ in relative humidity environments ranging from 20% to 80% relative humidity are analyzed using SEM, AFM and FTIR.

Figure 3.4. Optical images of films prepared using the TMSC process compared to films dried at room temperature. The films prepared using the TMSC process are transparent while the films dried at room temperature are opaque, suggesting the TMSC process has less pore defects than the samples dried at room temperature.

3.4 Characterization of Film Morphology and Phase Composition

PVDF films prepared using the TMSC process on AU substrates at 20 %, 40 %, 60 %, and 80 % relative humidity were coated with a thin layer (~10 nm) of gold and imaged using SEM. Fig. 3.5 shows the SEM micrographs of the TMSC samples. The micrographs show no large pores or voids compared to the samples prepared at room temperature shown in Fig. 2.1 (Chapter 2) and the small morphological defects seen in films do not hinder electrical performance as shown later.
Samples of PVDF using the TMSC method were prepared on Au, Al₂O₃, and SiO₂ in relative humidity environments ranging from 20 % to 80 % relative humidity. AFM was used to measure the surface roughness to evaluate the quality of the films. Fig. 3.6 shows the AFM micrographs (2 x 2 μm ) of the films. The films have a low root mean squared (rms) roughness, below 17 nm, regardless of the relative humidity or the substrate. This AFM and the SEM micrographs support the hypothesis that the TMSC process produces PVDF films that have a very small number of pore defects compared to films dried at room temperature.
The AFM micrographs in Fig. 3.6 show that the films have small variations in height (~100 nm) that exist in the films. These variations are speculated to arise from imperfect remixing after phase separation and as will be seen in the next section do not prevent the films from withstanding electric fields of up to 500 MV m\(^{-1}\). Figure 3.6 reveals small needle-like (column 3 row 3) or globular features (column 1 row 3) exist at the surface of the PVDF films. These features are consistent with observations of ferroelectric crystallites in the literature.\(^3\)\(^{,13}\) The
variation in these features is not investigated in this thesis and is surmised to exist due to interfacial effects.

FTIR spectroscopy was used to analyze the phase composition of films prepared using the TMSC method. The data for samples prepared on Au and Al2O3 surfaces were collected in reflection mode. Due to the absorbance of bulk Si the spectroscopy data for the sample prepared on a SiO2 surface were collected using attenuated total reflectance (ATR). Separate PVDF films on Au and SiO2 surfaces were annealed above the melting point of PVDF and cooled to room temperature (melt recrystallized) to produce films with a predominant α-phase composition for comparison. 14
Figure 3.7 shows that films prepared using the TMSC process all show the characteristic γ-phase absorption at 1234 cm$^{-1}$, the γ/β-phase absorption at 840 cm$^{-1}$ and the β-phase absorption shoulder at 1274 cm$^{-1}$. Films prepared using the TMSC process show trace absorption at 762 cm$^{-1}$, 976 cm$^{-1}$ and 1210 cm$^{-1}$. 

Figure 3.7. FTIR spectra of (a-c) samples prepared using the TMSC process and (d-e) samples prepared by melt recrystallization.
which is characteristic of the \( \alpha/\delta \)-phase. Films that were melt recrystallized show a large amount of absorption at the characteristic \( \alpha/\delta \)-phase wavenumbers. \(^{15,16}\)

Due to the similarities of the chain conformation in the \( \beta \) and \( \gamma \)-phases, distinguishing the quantitative contributions to the infrared absorption spectrum from each of these phases is difficult. \(^{15,16}\) Osaki \textit{et al.} showed that \( \gamma \) phase PVDF contains rotational defects that lead to extended all-trans sections in the polymer chain. \(^{17}\) The all-trans \( \beta \)-like sections in the \( \gamma \) phase polymer chain results in \( \beta \) and \( \gamma \) phases having similar infrared absorption spectra. However, the strong trans-trans-trans-gauche absorption at 1234 cm\(^{-1}\) suggest the \( \gamma \) phase.

Because the \( \alpha/\delta \)-phases have absorptions in the infrared that are distinguishable from the \( \beta/\gamma \) absorptions, we can quantify the fraction of \( \alpha/\delta \) in the crystalline phase of the films. Using the procedure reported in Benz \textit{et al.} and Martins \textit{et al.}, we characterize the amount of the \( \alpha/\delta \)-phase \((X^{\alpha,\delta})\) by using the peak height at 762 cm\(^{-1}\) \((A_{762})\), the thickness measured by alpha step and the absorption coefficient \((K^{\alpha,\delta}_{762})\) reported in the literature. \(^{6,14}\) Using Eq 3.1 we can determine the \( \alpha/\delta \) fraction of the crystalline phase content in the films.

\[
A_{762}=K^{\alpha,\delta}_{762} \cdot X^{\alpha,\delta} \cdot \text{thickness.} \tag{Eq. 3.4}
\]

For the samples prepared on metal-coated substrates, the infrared absorption spectrum is collected in reflection mode and the infrared beam interacts with double the thickness. The amount of PVDF that interacts with the infrared beam in ATR setup is difficult to know and therefore this analysis is only done for data
collected in reflection mode. Table 3.1 shows the \( \alpha,\delta \) fraction of the crystalline phase in all films deposited on metal surfaces are below 5%.

<table>
<thead>
<tr>
<th></th>
<th>20% r.h.</th>
<th>40% r.h.</th>
<th>60% r.h.</th>
<th>80% r.h.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>0.88%</td>
<td>2.02%</td>
<td>1.07%</td>
<td>0.96%</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>3.49%</td>
<td>3.75%</td>
<td>2.14%</td>
<td>2.55%</td>
</tr>
</tbody>
</table>

Table 3.1 The \( \alpha/\delta \) fraction of the crystalline phase content in the TMSC films showing that the films primarily consist of the ferroelectric \( \beta/\gamma \) phases.

The films do not show a noticeable trend in the phase composition with increasing relative humidity in the absorption spectra. This is in contrast to previous reports that the \( \beta \) phase is enhanced when PVDF is cast in humid environments. \(^6\) During TMSC, the surface area that interacts with water molecules during crystallization is constrained. However, if the film is allowed to phase separate due to VIPS, the surface area of the polymer that is able to interact with water molecules during crystallization is larger. The increased surface interaction of polar water molecules encourage nucleation of the \( \beta \) phase in phase-separated films but have less effect on crystallization in TMSC films.

### 3.5 Ferroelectric Characterization

Metal-ferroelectric-metal/semiconductor structures (MFM or MFS) were fabricated to characterize the ferroelectric properties of the TMSC films. MFM samples were poled at 500 MV m\(^{-1}\), while MFS samples were poled at 350 MV m\(^{-1}\). TMSC films were poled using the direct contact method, where a voltage was applied directly across the film (using deposited metal contacts). This is in contrast to corona poling where an electric field is indirectly placed across a film by accelerating charged species onto the surface of the film. The ability of the
TMSC PVDF films to withstand these large electric fields directly without breaking down gives support to the high quality of the films.

The ferroelectric hysteresis loops in Fig 3.7 clearly show ferroelectric behavior in all samples with a maximum remnant polarization of $6.5 \mu$C cm$^{-2}$, which is among the highest reported values in thin film PVDF and is comparable to the remnant polarization in copolymer films. The coercive field varies for samples prepared on substrates with a native oxide layers but is nearly constant at 118 MV m$^{-1}$ for samples prepared on Au (except for the sample prepared at 80% relative humidity), suggesting that the interface plays a role in setting the coercive field for thin film PVDF devices.

Figure 3.7 Ferroelectric hysteresis measurements for samples prepared on a. Au, b. Al$_2$O$_3$ and c. SiO$_2$. 
3.6 Conclusion

In conclusion a general and robust process has been developed for depositing high quality, thin (~1 μm), ferroelectric PVDF films from PVDF/DMSO solution. By modulating the temperature and therefore the free energy of the solution during spin coating, TMSC minimizes defects formed by vapor induced phase separation. The large remnant polarization is indicative of highly crystalline films suitable for device applications. FTIR absorption spectra showed the films are primarily in the γ phase. Thermally modulated spin coating is a valuable process for the deposition of PVDF films and potentially useful for integration of PVDF into microelectronic, micro-electromechanical and optoelectronic devices.
References


12. Jung, Jun Tae, et al. "Understanding the non-solvent induced phase separation (NIPS) effect during the fabrication of microporous PVDF
membranes via thermally induced phase separation (TIPS).” *Journal of Membrane Science* 514 (2016): 250-263.


Chapter 4 Switching in PVDF films

Abstract

Current understanding of ferroelectric switching in PVDF is briefly reviewed. Ferroelectric switching is discussed in terms of nucleation and growth, and local electric fields. A switching model is developed. Experimental switching data is used to validate the model.

4.1 Introduction to Polarization Switching

Understanding of polarization switching in ferroelectric materials is important for applications that take advantage of switching in ferroelectrics such as ferroelectric memory and MIS field-effect structures exhibiting negative capacitance.\(^1,2\) In ferroelectrics the polarization plays the role of an order parameter and transforms from one orientation (or phase) to another upon the application of an external driving field.\(^3\) The physics of this phase transition are similar to the physics of many phase transitions such as the formation of ice from liquid water.

There are two general types of phase transformations that occur in materials, homogenous and heterogeneous. Homogenous transformations occur simultaneously throughout the material and occur when there is no thermodynamic barrier for the transition to overcome. Heterogeneous transformations occur through a nucleation and growth process, where fluctuations in the Gibbs energy cause small volumes of the transformed phase to form (nuclei), which can grow depending on criteria developed later.\(^4\) In ferroelectrics polarization switching can occur though either homogenous or
heterogeneous processes. The electric fields needed for a homogenous transformation are much higher than typically applied experimentally (and in this study). Therefore, a heterogeneous nucleation and growth model of the experimentally observed polarization switching in the PVDF films described in Chapter 3 will be developed in this chapter.

Studies of the polarization switching process of thin film homopolymer PVDF is limited due to the difficulties in processing the homopolymer discussed in Chapters 1 and 2. Prior studies of the copolymer (PVDF-TrFe) are more common and will be used to guide the development of a polarization switching model in TMSC PVDF films. Ferroelectric polarization switching is commonly modeled using either the Kolmogorov-Avrami-Ishibasi (KAI) model or the Nucleation Limited Switching (NLS) model. These models will be discussed in sections 4.2 and 4.3.

As will be discussed in detail in section 4.2 the KAI model describes polarization switching that primarily occurs through ferroelectric domain growth (domain wall motion). This model is suitable for systems in which the movement of the domain wall is not strongly pinned at boundaries. Hu et al. showed that for a highly crystalline sample of the copolymer the KAI model sufficiently described the polarization switching. As will be shown later the ferroelectric polarization growth in TMSC films primarily occurs through nucleation and not domain wall motion. Therefore, switching in TMSC PVDF films is not described by the KAI model, but since the basis of nucleation in the NLS model lies in Avrami nucleation the KAI models is reviewed.
The NLS model discussed in section 4.3 describes polarization switching that primarily occurs through ferroelectric domain nucleation.\textsuperscript{12,13} This model is suitable for systems in which the movement of the domain wall is strongly pinned at the domain boundary. Mao \textit{et al.} showed that the polarization switching of the copolymer can also be described using the NLS model.\textsuperscript{10,15} Although the TMSC films are highly crystalline as evidenced by the high remnant polarization in Chapter 3 the small amount of amorphous content in the film pins the domain wall. Therefore, the NLS model is an appropriate starting point to describe the polarization switching in TMSC films.

4.2 Kolmogorov-Avrami-Ishibashi model

Often solid state transformations in solids are characterized by the time evolution of the order parameter \textit{i.e.} the time dependence of the polarization in the case of ferroelectrics. Typically, the time dependence of the order parameter functionally follows an ‘S-curve’ behavior. Such behavior is not easily modeled in terms of the fundamental nucleation and growth mechanisms because the rates of addition to and subtraction from the growth nuclei are not known (outlined in Appendix B). Kolmogorov and Avrami are credited with developing a model that reproduces the experimentally observed ‘S-curve’ of a nucleation and growth process.\textsuperscript{6,7,8}

Most of this section is a summary of the findings of Avrami in ref. 7. Avrami’s model assumes that in a system there are \(N\) germ nuclei and the number of germ nuclei is time dependent \(N=N(t)\). Germ nuclei are defined as nuclei that are already present in the system and can start the growth of the new phase. The
model supposes that germ nuclei can either start to grow or get consumed by a growing region. The probability of the germ nuclei turning into growth nuclei $N^*$ is given by $pN$ where $N$ is the number of germ nuclei and $p(T)$ is the probability of formation of growth nuclei per germ nuclei per unit time and is of the form

$$p(T) = K \exp \left( - \frac{Q + A(T)}{kT} \right).$$  \hspace{1cm} (Eq. 4.1)

Here $Q$ is a constant activation energy and $A(T)$ is the energy per molecule required to form a growth nucleus at temperature $T$. This probability is similar to the rate of forming a cluster of critical size described in Appendix B. The number of germ nuclei consumed by the growing phase is designated as $N'$ which is a function of time. The change in the number of germ nuclei is

$$dN = -dN^* - dN',$$

where

$$dN^* = pN \, dt,$$

and

$$dN' = \frac{N}{1-V} \, dV.$$

$dV$ is the increase of the volume of the new phase per unit volume of space in time $dt$. The term $N/(1-V)$ takes into consideration that the density of germ nuclei that exist is not constant but is dependent on the time dependent number of germ nuclei divided by the amount of untransformed material.
If $p$ is very large or if the growth of the transformed phase is limited most germ nuclei are transformed into growth nuclei before being consumed by a growing phase. These criteria describes a situation where nucleation (as opposed to growth) is the dominant factor contributing to the formation of the new phase (polarization reversal) and will be used later to describe switching in TMSC films. With this criteria the change in the number of germ nuclei is then represented by Eq. 4.2.

\[
\frac{dN}{dt} = -\frac{dN^*}{dt} = -pN. \tag{Eq. 4.2}
\]

Assuming $p$ is constant, that is the driving force for the transformation is kept constant. The number of germ nuclei at time $t$ is

\[N = N_0 \exp(-pt).\]

Here $N_0$ is the number of germ nuclei at $t=0$. The number of growth nuclei at a given time is given by

\[N^* = \int_0^t pN dt = N_0(1 - \exp(-pt)). \tag{Eq. 4.3}\]

If the consumption of germ nuclei is a significant term the formation of the new phase is dominated by the growth of the new phase. The change in germ nuclei for this condition is

\[dN = -pN dt - \frac{N}{1-V} dV.\]

Following Avrami, $pdt$ is replaced with a new variable $\tau$, referred to as the characteristic time. The derivative is taken with respect to this variable giving
\[
\frac{dN(\tau)}{d\tau} = -N(\tau) - \frac{N(\tau)}{1-V(\tau)} \frac{dV}{d\tau}.
\]

The solution to this differential equation is

\[N(\tau) = N_0 e^{-\tau}[1 - V(\tau)].\]

This is the number of germ nuclei formed in the time interval \(dt\) corrected for the expansion of the new phase in the time interval \(dt\). The number of growth nuclei becomes

\[N^*(\tau) = N_0 \int_0^{\tau} e^{-z}[1 - V(z)] \text{d}z.\]

This formulation is only valid until an exhaustion time \(\tau_{ex}\) as at this time the number of growth nuclei \(N^*\) become constant and the germ nuclei are exhausted. The derivation of this result is not valid (since the number of germ nuclei \(N(\tau)\) is 0). However the volume of the transformed region \(V\) can be found. Avrami starts with the volume of a region that can grow unrestrictedly and then corrects for impinging regions by calculating and subtracting the overlap of several unrestricted regions. The derivation is not discussed here but the result is that in a situation where growth dominates the phase transformation, the transformed volume can be shown to be of the form of Eq. 4.4. In general Eq. 4.4 will produce an ‘S-curve’ that functionally matches experimental observation of nucleation and growth phenomenon. It has been shown that under very specific conditions and assumptions, the constants \(B\) and \(k\) can be related to the probability and dimensionality of the growth of the new phase. \(^7,8\)

\[V = 1 - e^{-Bt^k}.\] (Eq. 4.4)
Ishibashi then applied these ideas to the phase transformation in ferroelectrics solving for the polarization (a volume-like term), deriving the following for the polarization as a function of time

\[ P(t) = 2P_s(1 - e^{-\left(\frac{t}{t_0}\right)^n}), \]

where \( P_s \) is the spontaneous polarization, \( t_0 \) is the ratio of nuclei radius to domain wall speed. The derivation of Ishibashi only included the Avrami model where domain growth was the dominant factor contributing to phase change and thus the KAI model is well-suited to describing polarization reversal in ferroelectrics when the reversal is dominated by domain wall motion. Examination of this relation shows that for a specific value of \( n \), the shape (logarithmic steepness) of the polarization ‘S-curve’ does not change in \( P \) vs \( \log(t) \) plot but only shifts in position with \( t_0 \).

KAI theory has been successful in describing the switching in many ferroelectrics especially in single crystals and thin films. \(^9,^{10,11}\) For example experimental evidence in barium titanate polarization switching show that thin needle-like reversed domains form and then grow laterally until the entire crystal is switched, a process that is modeled well by the KAI assumptions. \(^{11}\) However there are also many cases in which KAI theory does not describe the switching data such as for lead zirconate titanate thin films in which the logarithmic steepness of the polarization switching varies significantly. \(^{12,13}\)
4.3 Nucleation Limited Switching

The KAI model in its current form is limited to systems in which domain wall growth is a significant part of the polarization switching process. In samples that have a significant amorphous fraction the ferroelectric domain wall of one region cannot traverse the amorphous region to continue growth of the polarization in another ferroelectric region. In other words polarization growth by domain wall motion is limited to individual ferroelectric regions. In this scenario the time dependence of the polarization switching will be determined by the nucleation of individual ferroelectric regions.

Crystallinity of films of the homopolymer are in the range of 50 %-70 %, which is high for spin coating ferroelectric thin film PVDF, which is high for spin coated PVDF. The crystallinity of the TMSC samples is believed to be in this range because the remnant polarization of the TMSC films shown in Chapter 3 is comparable to samples that have 50 % to 70 % crystallinity. As such there is reason to believe that domain walls cannot travel between ferroelectric regions, and in TMSC films the time dependence of the polarization growth will be determined by the nucleation of polarization reversal in individual ferroelectric regions.

The original Avrami derivation does take into account a situation where the phase transformation is dominated by nucleation, and the formation of growth nuclei is expressed by Eq. 4.3 (repeated below for convenience).

\[ N^* = \int_0^t pN dt = N_0 (1 - exp(-pt)). \]
Du and Chen initially published results developing the concept of nucleation limited switching. However due to a more instructive formulation, the following discussion will be based on the paper by Tagantsev et al.

Tagantsev et al. developed a model of ferroelectric switching that is based on a nucleation dominant phase transition called the NLS model and begins with these assumptions.

1. The film is presented as an ensemble of elementary regions.
2. The switching of an elementary region occurs once a domain of reversed polarization is nucleated in the region.
3. Time needed for switching of an elementary region is equal to the waiting time for the first nucleation, i.e., the time needed for filling the region with the expanding domain is assumed negligible compared to the waiting time.
4. The function describing the distribution of waiting times for the ensemble of the elementary regions is smooth and exponentially broad.

Tagantsev et al. states that if all the switching times of an elementary region are the same then we get the result for 1-dimensional Avrami nucleation and growth. This statement is incorrect since the characteristic time in the KAI model is strictly not equivalent to the nucleation time. (see derivation above).
proper nucleation time in the NLS model is the inverse of the probability of
nucleation in the original Avrami formulation. Including considerations of regions
with different nucleation times in the film the polarization as a function of time,
according to Tagantsev is

\[ P(t) = 2P_s \int_{-\infty}^{\infty} (1 - e^{-\left(\frac{t}{tn_0}\right)^n}) F(\log(t_0)) d(\log(t_0)), \quad \text{(Eq. 4.5)} \]

where the \( F(\log(t_0)) \) is a function that describes the distribution of the \( \log(t_{n0}) \),
where \( t_{n0} \) is the characteristic switching time and \( n \) is the dimensionality of the
problem according to Tagantsev et al. (despite the fact that growth is not being
considered in the problem). \(^{12}\) The integral of \( F(\log(t_{n0})) \) with respect to \( \log(t_{n0}) \)
from negative infinity to infinity has to meet the normalizing condition of being
equal to 1.

Tagantsev argues that the likely physical reason for a distribution of nucleation
times in polycrystalline materials is that different defects throughout the film
reduce the nucleation energy of each region by different amounts. To fit
experimental data, Tagantsev et al. had to vary the distribution of the
characteristic switching times for different applied electric fields. \(^{12}\) This is
inconsistent with his argument for permanent physical defects causing the
nucleation energy to differ in each region, because it is unlikely that the defect
would have a response that varied several orders of magnitude with a small
change in the applied electric field. Schutrumpf et al. suggested that it is actually
variations in the local electric field due to these defects the causes the variation
in the characteristic switching time. \(^{14}\)
A noticeable difference in the NLS and KAI models is that the logarithmic slope of $P(t)$ is not invariant in the NLS model and changes dramatically with changes in the distribution of characteristic switching times. In the literature switching in the thin films of the PVDF-TrFE copolymer has been shown to be equally well described by both the NLS (Mao et al.) and the KAI (Hu et al.) models (the studies of Mao and Hu do not provide enough details on material characterization to understand possible differences between their sample sets). A narrow distribution of switching times in the copolymer could explain this discrepancy and Mao showed that at electric fields above $\sim 80$ MV m$^{-1}$ the switching times vary by a factor of $\sim 2$, narrow compared to the 5 orders of magnitude variation in Tagantsev's work.  

An additional difference in the NLS and KAI model is that, in the NLS model as it is developed by Taganstev there should be a maximum polarization that is dependent on the applied field. According to Taganstev the distribution in nucleation times is due to the distribution in nucleation activation energy. In the NLS model if the applied electric field is such that it is large enough to activate nucleation in some but not all of the ferroelectric regions, the maximum polarization will be reduced in comparison to an applied electric field large enough to activate nucleation in all the ferroelectric regions. If the applied electric field is larger than the minimum electric field needed to nucleate all regions, further increase in the applied electric field above the minimum changes the slope of polarization growth as discussed above without changing in the maximum polarization achieved in the film. In the KAI model the maximum
polarization is constant as long as the applied field remains above a critical switching field and enough time is allowed for the polarization to switch.

Distinguishing between switching mechanisms in PVDF and the copolymer is rather difficult. One way is to look at the ferroelectric domains microscopically and see how they switch. Using piezo-force microscopy, Sharma et al. showed that domains in the copolymer grow with a restricted geometry supporting the NLS model, while Hu et al. showed that domains can grow in an unrestricted fashion supporting the KAI model. This is a clear indication that both KAI and NLS like models can be used to describe switching in PVDF and the copolymer depending on the physical characteristics of the deposited film. For instance if the copolymer or homopolymer is highly crystalline (>90 %) the number of ferroelectric regions that share an interface is high and a domain wall could travel from region to region. If the the polymer film is moderately crystalline (~50 %), as in the case of TMSC films, then the domain wall cannot travel across the amorphous boundaries from a ferroelectric region to another ferroelectric region. Accordingly a NLS model will be used to start to develop a polarization switching model in TMSC PVDF films in the next section.

The ideas in Tagantsev’s formulation are useful to understanding the switching in TMSC PVDF films, however there are certain differences that will be discussed later that should be kept in mind.
1. Taganstev uses a spatial distribution of nucleation times and but to describe switching in TMSC films, a distribution of nucleation times in time is used instead.

2. For an unknown reason Tagantsev uses Ishibashi’s model (Eq. 4.3) as the starting point for his model. This is a fundamental flaw in Tagantsev’s model because the Ishibashi model is derived using the criteria that domain growth is the dominant factor in polarization reversal. To describe switching in TMSC films, Eq. 4.2 will be used as the starting point for the model.

4.4 Conductivity Induced Polarization

In this section it will be shown that the complete behavior of polarization reversal versus time in TMSC PVDF films is not well-described by either the KAI or NLS model. To overcome this shortcoming, the concept of variations in the local electric field during polarization reversal, developed by Seggern and Fedosov in PVDF, is introduced using a two layer dielectric capacitor model. Experimental data for polarization of TMSC films are modeled using this concept.

Polarization switching data was gathered on TMSC films using the double wave method. A square voltage pulse with varying magnitude is applied across the sample and the current is measured. This current includes charge flow terms owing to the ferroelectric, dielectric and conductive properties of the film. A second square pulse with the same voltage as the previous pulse and of the same polarity is applied and the current measured. Assuming the ferroelectric domains remain polarized, the current flowing due to this pulse just contains
contributions from the dielectric and conduction mechanisms. The current of the second pulse is subtracted from the current of the first pulse thus leaving just the current due to the ferroelectric polarization. This current is then integrated to find the polarization as a function of time.

Figure 4.1. Plots of the polarization switching curves at 266K for different applied fields (250, 225, 200, and 175 MV m$^{-1}$). The inset shows characteristic curves for the KAI and NLS models on their predicted variation with voltage (and therefore electric field). Notice how the experimental data shows two regimes of distinct polarization growth behavior while the NLS model and KAI model only predict one.

Figure 4.1 shows the polarization as a function of elapsed time after a step potential is applied across the sample. The step potential is chosen such that the average electric field across the capacitor is 250, 225, 200, and 175 MV m$^{-1}$. The data is not well-represented by either the KAI model or NLS model also shown in Fig. 4.1. The data clearly show two regimes of polarization growth: a fast regime between $3 \times 10^{-5}$ and $1 \times 10^{-4}$ seconds where the polarization exponentially reaches some value that is field dependent, and a slow regime where the
polarization grows over several decades of time to a final polarization value. Both the standard KAI and NLS models cannot account for these two regions since in both models the reversed polarization grows continuously until reaching a saturation value.

To account for the two switching regimes in the data the conductivity induced polarization model put forth by Seggern and Fedosov is considered. Seggern and Fedosov propose that the electric field experienced by the ferroelectric regions in PVDF is not the average field applied across the PVDF film. The difference in the dielectric properties of ferroelectric and non-ferroelectric regions present in PVDF films causes the electric field to vary spatial and as a function of the polarization. They model a PVDF capacitor as a two layer dielectric sandwiched between two conducting electrodes. The physical model is shown in Fig. 4.2 with the non-ferroelectric layer being layer 1 and the ferroelectric layer being layer 2
In general, the respective electric fields can be found using the boundary conditions \( \nabla \cdot D = \text{free charge} \) and the total voltage drop over the capacitor \( V_{\text{total}} = E_1 d_1 + E_2 d_2 \). To familiarize the reader with the properties of two layer dielectrics a few case studies are presented.

**Case 1: Ideal linear dielectrics**

In the ideal case the conductivity of the dielectric layers is 0. We choose the thickness of .5 μm for each layer and the dielectric constants to be \( \epsilon_1 = 10 \) and \( \epsilon_2 = 15 \) for the purpose of the case study. We apply a voltage of 200 V across the capacitor. Because the conductivity is 0 the free charge at the interface is also 0. The electric field in each region can be solved for analytically.

\[
D_1 = D_2, 
\]
which becomes

$$\varepsilon_0 \varepsilon_1 E_1 = \varepsilon_0 \varepsilon_2 E_2.$$ 

And we have the relation

$$V_{app} = d_1 E_1 + d_2 E_2.$$ 

The average electric field over the capacitor is 200 MV m\(^{-1}\) the electric field in region 1 is 240 MV m\(^{-1}\) and in region 2 is 160 MV m\(^{-1}\). Table 4.1a shows how the electric fields change for different values of the relative thickness and Table 4.1b shows how the electric fields change for different values of the dielectric constant.

<table>
<thead>
<tr>
<th>a.</th>
<th>$V_{app}=200 \text{ V}; \varepsilon_1=10; \varepsilon_2=15$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d_1 (\mu m)$</td>
</tr>
<tr>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>0.9</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b.</th>
<th>$V_{app}=200 \text{ V}; d_1=d_2=.5 \mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon_1$</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>18</td>
</tr>
</tbody>
</table>

Table 4.1. Values for the electric field in layer 1 and 2 with respect to changing a. thickness b. dielectric constants of the two dielectric layers in a two layer capacitor structure.

Of course the solution becomes more interesting for non-ideal cases.

**Case 2: Linear Dielectrics that have mobile free charge**
In the case of dielectrics that have mobile free charge, the difference in electric fields will cause a free charge density \( \rho_{\text{free}} \) to accumulate at the interface (the interface is assumed to be infinitesimally thin in the solution)

\[
\nabla \cdot D = \rho_{\text{free}},
\]

\[
\epsilon_0 \epsilon_1 E_1 - \epsilon_0 \epsilon_2 E_2 = \rho_{\text{free}},
\]

where the free charge density is related to the difference in electric fields

\[
\rho_{\text{free}} = (E_2 - E_1) \sigma \times \text{time},
\]

where \( \sigma \) describes the conductivity of the material near the interface. Since the difference in the electric field is time dependent, the solution involves discretizing the equation for small time intervals \( dt \) where the difference in the electric fields can be assumed to be constant. The results for different \( \sigma \)'s are
shown in Fig 4.

Figure 4.3. Electric Fields in each layer in the two dielectric layer capacitor model when there is a non-zero conductivity. When the conductivity increases the time it takes for the electric fields in different layers to equalize is shorter.

**Case 3: Linear Dielectric + Ferroelectric with mobile charge carriers**

In a ferroelectric there is a contribution to the polarization from the alignment of permanent dipoles with the electric field. This polarization introduces another term in the $D$ field of the ferroelectric layer resulting in

$$\varepsilon_0\varepsilon_1 E_1 - (\varepsilon_0\varepsilon_2 E_2 + P_{ferro}) = \rho_{free}.$$  

$P_{ferro}$ is both a function of the electric field experienced by the ferroelectric layer and time, and the electric fields in both layers are a function of the polarization. Qualitatively, for the case of a two phase dielectric and ferroelectric combination
with zero conductivity, as the polarization increases in the ferroelectric regions, the electric field will drop in the ferroelectric layer until it drops below the minimum field needed to switch the polarization. At this point the polarization stops increasing. If the conductivity in the material is non-zero then the as the polarization increases the electric field in the ferroelectric layer decreases, but as free charge accumulates at the interface of the ferroelectric and non-ferroelectric dielectric layer the field in the ferroelectric layer will increase eventually reaching the average field value.

Von Seggern and Fedosov modeled $P_{\text{ferro}}$ as a linear function of the applied electric field and $dP_{\text{ferro}}/dt$ as a linear function of a characteristic switching time. These approximations are useful for understanding the characteristic behavior of a two phase model but turn out not to be a useful model of the fundamental switching process.

Instead of directly using the boundary conditions of the electric and $D$ fields to solve the set of differential equations they set the series current equal in both the layers and solved the resulting differential equations numerically to show that the polarization was indeed dependent on the conductivity of the sample. Seggern and Fedosov experimentally showed that current through a shunt resistor in series with a PVDF sample qualitatively matched their model. They did not study the temperature, applied field, or crystalline phase dependence on the switching as is the subject of Chapter 5. Seggern and Fedosov showed that electric fields inside a ferroelectric can be very different from the applied field.
Therefore it is important to understand the origin of the variation in the local electric field in TMSC films.

In the next section an expression for the local fields inside a TMSC PVDF film is developed.

4.5 Local Electric Fields

The local electric field at a domain wall boundary or at a nucleation site is the field that drives polarization reversal. In a homogenous dielectric the local electric field is very different from that of the average electric field applied to the material as clearly shown in the derivation of the Clausius-Mossotti relation. Seggern and Fedosov showed that in ferroelectrics the local field experienced by ferroelectric regions in the material is dependent on the location of the region and the polarization of the material. Kliem and Kuehn show that by using a mean field approach, the average local field at an individual dipole in a ferroelectric can be written as 17,18

\[ \langle E_{\text{local}} \rangle = E + \alpha P, \]  

(Eq. 4.6)

where \( \alpha \) is a parameter that describes the interaction strength of the dipoles and \( P \) is the macroscopic polarization of the sample, and \( E \) is the applied electric field. A mean field approach is needed to replace the state of every dipole in the material by the average state of the dipoles in the film (the macroscopic polarization).

The local electric fields experienced at domain walls and between ferroelectric regions is very different. In a single ferroelectric domain region, where
polarization reversal is dominated by domain wall motion, the closest dipoles to the domain wall interface will have the largest effect on the local field at that interface. In other words the local electric field that drives polarization reversal will be dominated by the polarization of the nearest neighbor molecular dipoles at the domain wall interface. In the case of PVDF it will be the nearest -CF$_2$- molecules. In nucleation limited switching the polarization is reversed through nucleation and not domain wall motion. The local electric field that drives the polarization reversal is the local electric field experienced by nucleation centers. This local electric field is dominated by the polarization of the nearest neighbor ferroelectric regions not individual -CF$_2$- molecules. The next few paragraphs describe a unique method to derive the local field in PVDF.

A simple model for a two-component material such as PVDF is spherical ferroelectric regions embedded in an amorphous matrix as shown schematically in Fig. 4.4.

Figure 4.4. Schematic of ferroelectric spheres in an amorphous matrix used to describe the microstructure of TMSC PVDF films.
The local electric field experienced by a ferroelectric region (the yellow region), will be determined by the polarization state of all the other ferroelectric regions. Using a mean field approach we can write the local electric field as before in Eq. 4.6, but the polarization field opposes the average applied field.

Before a model for switching is developed it should be noted that if the ferroelectric regions are sparsely dispersed in an non-ferroelectric matrix they will not influence each other since dipole interactions fall off quickly with distance. In this case the local electric field, $E_{\text{local}}$ will approach the the local field for a homogenous dielectric.

A PVDF ferroelectric film that has been poled exists in a known polarization state. For the simplicity of the model we assume that all the dipole moments are pointing parallel to the poling field as shown in Fig 4.5 by the blue arrows.

![Figure 4.5. A simple schematic of the polarization and induced internal charge of a poled ferroelectric. The blue arrows represent the polarization of a ferroelectric region and the red plus and minus symbols represent the bound polarization charge caused by the polarization of the ferroelectric regions.](image)

The polarization difference between the ferroelectric and non-ferroelectric regions causes bound polarization charge to appear in the film at the interface
between these two regions. This polarization charge is represented by the red plus and minus symbols in Fig. 4.5. Since the polarization difference between the two regions is the result of ferroelectricity, this polarization charge will remain after the external electric field is removed.

The polarization charge creates the so called depolarization field, the electric field that is produced as a result of a switched ferroelectric region and is in the opposite direction of the applied electric field. In a ferroelectric this polarization charge can either remain internally uncompensated or some free charge can move to the interface to compensate the bound polarization charge. One mechanism for the screening of this polarization charge by free charge would be the introduction of free charge into a film with a non-zero conductivity. A situation where the bound polarization charge is screened by free charge is shown in Fig 4.6, the green plus and minus symbols represent free charge and the red plus and minus symbols represent the bound polarization charge.

Figure 4.6. A ferroelectric where the internal polarization (blue arrows) produces the internal bound charge (red plus and minus) that is compensated by free charge (green plus and minus).
The situation in Fig. 4.6 may or may not exist after poling. A relatively large leakage current would strongly suggest that the situation in Fig. 4.6 exist since the conduction of free charge through the material provides a mechanism for the polarization charge to be screened internally. However, the situation remains unclear because the leakage current cannot be measured experimentally. Figure 4.7 shows the current measured for the first and second pulses of a sample switched at 250 MV m\(^{-1}\) (Voltage =330 V). Figure 4.7a shows the total current pulses and Fig. 4.7b zooms to a region where the current is dominated by the leakage current. As seen in Fig. 4.7b the data only puts a clear upper limit on the leakage current which is about 1 μA. This value leads to a calculated bulk conductivity of \(\sim 7 \times 10^{-9} \text{ S m}^{-1}\). As will be shown in section 4.7 this bulk conductivity is too low to lead to the screening of the polarization at the time scales investigated in this experiment. But the compensation of the bound charge by a screening charge is still a plausible explanation of the 2 regime polarization growth seen in Fig. 4.1. The screening charge does not have to be free charge that comes from the bulk conductivity, but can be generated locally at the amorphous-crystalline interface and can be localized to that region. For this model it will be assumed that the polarization charge is screened somehow but the mechanism of screening is not investigated.
Initially, as an electric field is applied across the material to reverse the polarization, the local field experienced in each ferroelectric region is roughly the same. We assume that each ferroelectric region is a single ferroelectric domain and the time it takes for one region to completely reverse its polarization after polarization reversal has been nucleated is much less than the time it takes for one region to nucleate such a polarization reversal. As a consequence of this assumption each of the ferroelectric regions will switch according to statistical laws of nucleation covered in Appendix B. At some instant one of the regions will reverse its polarization, and if the time it takes for the the screening charge to reorient to compensate the polarization is much longer than the time it takes for a region to reverse its polarization the bound and free charge distribution in the ferroelectric will look like that in Fig 4.8.
Figure 4.8. Schematic of the instant when one ferroelectric region switches. The red and blue arrows represent the polarization direction of the ferroelectric regions. The red plus and minus symbols represent the bound polarization charge and the green plus and minus symbols represent the free charge. Notice if the ferroelectric is fully compensated internally the charge at the interface is double the polarization charge.

After a region switches the local fields in the un-switched and switched ferroelectric regions change dramatically. The new local electric field ($E'_\text{local}$) inside the region that switched its polarization is now the old local field ($E_{\text{local}}$) minus the field produced by uniformly polarized sphere. If the polarization charge is fully compensated at the interface the totally charge at the interface is $2P$. However, the screening charge could be less than $P$ and in this thesis will be denoted as $\rho_{\text{screen}}$. The total charge at the interface is then $P + \rho_{\text{screen}}$ and $E'_{\text{local}}$ in the switched ferroelectric region is equal to

$$E'_{\text{local}} = E_{\text{local}} - \frac{P + \rho_{\text{screen}}}{3\varepsilon_0}.$$

Taking into account the free charge that hasn't had time to react to the changing polarization the total surface charge is then

$$\sigma_{\text{total}} = P + \rho_{\text{screen}}.$$
The field created by this surface charge outside of this sphere is equivalent to the field produced by a dipole at the center of the sphere with the magnitude

$$|P_{\text{sphere}}| = \frac{4}{3} \pi R^3 (P + \rho_{\text{screen}}),$$

where $R$ is the radius of the sphere. The electric field produced at a distance $r$ from this sphere is

$$E_{\text{dipole}} = \frac{1}{4\pi \varepsilon_0 r^3} [3 (\vec{p} \cdot \hat{r}) \hat{r} - \vec{p}],$$

with $\rho = P_{\text{sphere}}$. The new local electric field at each of the un-switched regions will be the old local field at this region minus the field produced by the effective dipole at the center of the switched region. The problem quickly becomes intractable if all the local electric fields are calculated in this manner. It is useful to take a mean field approach. The field produced in the un-switched ferroelectric regions by the switched ferroelectric regions is a result of the bound charge and the screening charge can be written as

$$E_{\text{bound}} = \frac{\alpha P}{\varepsilon_0 \varepsilon_r},$$

and

$$E_{\text{free}} = \frac{\alpha \rho_{\text{screen}}}{\varepsilon_0 \varepsilon_r},$$

where $\alpha$ takes into account the interaction of the mean polarization with the un-switched regions and the direction the electric fields is opposite of that of the applied field. As described above the screening charge and bound polarization charge add initially after a ferroelectric region has switched and subtract after a period of time. To differentiate between these two situations $\rho_{\text{screen}}$ will be used.
designate the free charge that adds to polarization and $\rho_{\text{screen}+}$ will be used to designate the free charge that subtracts from the polarization. The new local electric field in a un-switched ferroelectric region due to the polarization of the switched regions is

$$E'_{\text{local}} = E_{\text{local}} - \alpha \frac{(P + \rho_{\text{screen}+} - \rho_{\text{screen}^-})}{\varepsilon_0 \varepsilon_r}. \quad (\text{Eq. 4.7})$$

Considering that the interval between the fast polarization switching and slow polarization switching is significant $\sim 10^{-4}$ seconds it is assumed that at the time immediately following the fast polarization reversal the free charge has not had enough time to reorient themselves during the fast polarization growth and assuming that $\rho_{\text{screen}}$ is some multiple of $P$, $\rho_{\text{screen}+} = C \ast P$ and $\rho_{\text{screen}^-} = 0$. As a consequence $E'_{\text{local}}$ experienced by un-switched regions in the fast regime is totally dependent on the polarization of the switched regions.

$$E'_{\text{local}} = E_{\text{local}} - \alpha \frac{(1+C)P}{\varepsilon_0 \varepsilon_r}.$$ 

Three assumptions are now made, first the field that all ferroelectric regions experience before any switching occurs is constant, secondly that all un-switched ferroelectric regions experience the same field (as a result of the switched regions and the applied field) at any given time (mean-field approximation), and lastly that $E'_{\text{local}}$ at the time the fast polarization reversal stops defines $E_{\text{min}}$. The expression for $E'_{\text{local}}$ can be rearranged to be

$$E_{\text{min}} - E_{\text{applied}} = -\alpha \frac{(1+C)P}{\varepsilon_0 \varepsilon_r},$$

= 74
According to the relation above, the difference between the minimum switching field and the local initial field will be linear in the polarization with a y-intercept of 0. Figure 4.9 shows polarization value at the end of the polarization reversal in the fast regime vs \( E_{\text{applied}} \). The slope of this line is \( \frac{(1+C)\cdot \alpha}{\epsilon_0 \epsilon_r} \) and the y-intercept is \( E_{\text{min}} \) as shown in Eq. 4.8. It should be noted that in the literature the term “minimum switching field” and the term “coercive field” are sometimes used interchangeably. In fact by definition the two fields are different:

1. The minimum switching field is the smallest field needed to initiate polarization reversal

2. The coercive field is the field at which the polarization is 0 in a hysteresis curve.

From the definitions the minimum switching field is a better way to compare ferroelectric samples since unlike the coercive field, it is not inherently frequency dependent.

The data for a representative sample is shown in Fig. 4.9. By fitting the data it becomes possible to model the polarization reversal in PVDF by using a lumped parameter \( \lambda = \frac{(1+C)\cdot \alpha}{\epsilon_0 \epsilon_r} \). This is useful since reliable values for the relative permittivity, interaction term, and the amount of polarization that is screen internally are not readily available in the literature.
After a given amount of time if there is mobile charge in the material that can screen the polarization the \( E_{\text{local}}' \) becomes

\[
E_{\text{local}}' = E_{\text{local}} - \alpha \frac{(P + \rho_{\text{screen+}} - \rho_{\text{screen-}})}{\varepsilon_0 \varepsilon_r}.
\]

Assuming the polarization is totally screened internally, after a sufficient amount of time has passed \( \rho_{\text{free+}} = 0 \) and \( \rho_{\text{free-}} = P \) resulting in

\[
E_{\text{local}}' = E_{\text{local}}.
\]

In the next section the expression for the local fields inside a TMSC PVDF film will be used with the concepts of NLS model in section 4.3 and the probability of formation of growth nuclei per germ nuclei per unit time discussed in section 4.2 to develop a model that describes switching in TMSC PVDF.
4.6 Switching In TMSC Films

As mentioned earlier both the standard KAI and NLS models cannot account for the fast and slow polarization regimes (shown in Fig 4.1 and reproduced in Fig 4.10 below for convenience) since in both models the reversed polarization grows continuously (only one regime is predicted) until reaching a saturation value that is dependent on the applied electric field. Von Seggern and Fedosov also observed two different polarization switching regimes in PVDF, but as discussed earlier did not explain or study the switching in detail as is done in this dissertation.

Figure 4.10. Plots of the polarization switching curves at 266K for different applied fields (250, 225, 200, and 175 MV m\(^{-1}\)). The inset shows characteristic curves for the KAI and NLS models. Notice how the experimental data shows two regimes of distinct polarization growth behavior while the NLS model and KAI model only predict one.

The nearly exponential growth of polarization in the Fast Regime suggests that the polarization growth in this regime is functionally similar to that predicted
by the NLS model. In general, nucleation limited models start with defining the probability of nucleation per number of nucleation sites per unit time. This probability $p$ is generally written as a function of the driving potential and an energy barrier as

$$p = K \exp \left( - \frac{\text{Energy Barrier Height}}{\text{Driving Potential}} \right),$$

where $K$ is a rate constant that depends on both the temperature and driving potential. In the original formulation of the NLS model, a distribution of energy barrier heights was assumed to exist in the material. Furthermore, the NLS model predicts that the saturation polarization will increase as a function of the driving potential (in this case the applied field). This is because the energy barrier height distribution is assumed to be wide and that the driving potential is such that only a fraction of the regions can be nucleated in the time of the experiment. As the driving potential increases the fraction of regions that can be nucleated increases. The NLS model also predicts that the polarization will grow at a constant exponential rate as discussed in section 4.3 and that this rate increases as the driving potential increases because $p$ increases. Both these characteristics are characteristics of the experimentally observed TMSC polarization reversal in the fast regime seen in Fig. 4.9. However, a distribution of energy barrier heights alone does not completely explain the TMSC data because once the polarization is saturated there is no mechanism for the continued polarization growth in the slow regime.
Since the local electric field ($E'_{\text{local}}$) provides the driving potential for polarization reversal, a distribution in $E'_{\text{local}}$ will yield similar results to a distribution in the barrier heights. As shown in Eq. 4.7 the local electric field experienced by an un-switched ferroelectric region is reduced as the mean field polarization increases. $E'_{\text{local}}$ increases back to its original value as the mean polarization is screened by mobile charge (also shown in Eq. 4.7), over a certain amount of time. This distribution in time of the local driving potential explains the two regime polarization growth: as the polarization grows $E'_{\text{local}}$ is lowered, eventually dropping below the minimum switching field of the ferroelectric regions which causes the polarization to stop increasing. Mobile charge is then rearranged at the ferroelectric/non-ferroelectric boundaries to screen the polarization of the switched ferroelectric regions thus increasing $E'_{\text{local}}$ in the un-switched ferroelectric regions. This increased $E'_{\text{local}}$ allows the un-switched ferroelectric regions to switch polarization, again lowering $E'_{\text{local}}$ and continuing the process. It should be noted that the origin of this mobile charge or if this charge is only mobile at the ferroelectric/non-ferroelectric interface was not investigated. Its existence was inferred both from typical properties of other polymeric films and from its ability to screen the polarization.

The experimentally observed switching of TMSC films can now be understood qualitatively in the following way:

1. PVDF TMSC films consist of ferroelectric regions in a non-ferroelectric matrix. These regions are single domain.
2. The crystallinity and the microstructure are such that the domain walls in a ferroelectric region cannot propagate from one ferroelectric region to another.

3. The time it takes for a ferroelectric region to reverse its polarization after reversal has been nucleated is much faster than the time it takes to nucleate polarization reversal.

4. The probabilistic nucleation of a ferroelectric region is dependent on the local electric field.

5. The local electric field is dependent on the overall extent of polarization reversal in the film and the rate at which bound charge resulting from the polarization reversal can be screened by the screening charge.

The constant exponential growth of the polarization in the fast regime suggests that polarization growth during this stage is not strongly dependent on the local electric field since a constant exponential growth suggests a constant probability of nucleation per number of nucleation sites per unit time. The rapid decrease in polarization growth rate at the end of the fast regime suggests that near the minimum switching field polarization growth rapidly decreases. These two observations lead to the conclusion that the effect of the local electric field on the polarization growth is much stronger when the local field is close to the minimum switching field than otherwise. This observation is incorporated into the model as an extra sigmoidal term that weights the probability of nucleation per number of nucleation sites per unit time by
\[ \text{sig}(a) = \frac{1}{1 + e^{-a(Local \ Field - Minimum \ Field)}} \]

where \( a \) is a parameter that describes how quickly the sigmoidal term goes to 0 as the minimum field is approached.

Figure 4.10 shows that there is a latency from when the field is applied to when switching occurs of about \( 4 \times 10^{-5} \) s. This latency is not affected by the applied voltage and is an orders of magnitude longer than the specified rise time of the instrumentation amplifier and the RC time constant of the circuit. These observations suggest that the latent time is an intrinsic property of the material. Although this observation is interesting, other experiments would need to be carried out to make an accurate statement about why this latency time exists. In the following model, switching is not allowed to occur until after the latency delay time.

4.7 Building a Switching model

In the interest of simplicity, the polarization of each microscopic region will be taken to be normal to the film surface and have the same energy barrier height for nucleation. This simplification allows for a simple derivation of the probability of nucleation and does not take away from the generality since the model can be modified to take into account each orientation, if we had greater computational power. The probability of nucleation per number of nucleation sites per unit time is modeled after the probability derived in Appendix B and is taken to be

\[ p = K \exp \left( -\frac{E_{\text{activation}} \cdot \text{pol}}{E_{\text{local}} \cdot \text{pol} \cdot \cos(\theta)} \right) \cdot \text{sig}(a), \]
where \( pol \) is the the dipole moment of a nucleation center. Since all the dipole moments of the ferroelectric regions are normal to the film surface and the applied electric field is normal to the surface \( p \) can be simplified to

\[
p = K \exp \left( -\frac{E_{\text{activation}}}{E_{\text{local}}} \right) \times \text{sig}(a). \tag{Eq. 4.9}
\]

\( E'_{\text{local}} \) is determined by Eq 4.7.

In the fast regime it is assumed that the mobile charge cannot rearrange itself to screen the polarization thus making \( \rho_{\text{free-}} = 0 \). \( E_{\text{activation}}, a, \) and \( K \) will be taken as fitting parameters. \( E_{\text{local}} \) is the applied electric field. The minimum switching field used in \( \text{sig}(a) \), and is determined using the method in the previous section.

Because the ferroelectric regions cannot grow in this model, analogies can be made to the original Avrami derivation of phase transformations dominated by nucleation. \(^6\) The number of ferroelectric regions that are able to be switched is taken as the number of initial germ nuclei. The number of switched ferroelectric regions is taken as the number of growth nuclei. The number of ferroelectric regions that switch in \( \Delta t \), \( \Delta N_{\text{switch}} \) is

\[
\Delta N_{\text{switch}} = N_{\text{un-switched}} \times p \times \Delta t. \tag{Eq. 4.10}
\]

The the macroscopic polarization \( P \) is

\[
P = \text{pol} \times N_{\text{switch}}.
\]

The probability, \( p \), is dependent on \( E'_{\text{local}} \) as shown in Eq. 4.9 which in turn is dependent on the macroscopic mean field polarization, \( P \), as shown in Eq. 4.7.
The coupled equations are solved iteratively in Matlab. Using a short time step the number of regions that switch is calculated, followed by a recalculation of the local electric field and this process is repeated until a specified time. The time step $\Delta t$ is chosen to be small enough such that the polarization and the local electric field do not change dramatically in an interval $\Delta t$.

For a better understanding on how the fitting parameters mentioned above effect the model, 3 plots are presented below. Figure 4.11a shows how varying the activation field alters the switching dynamics. $\text{Sig}(a)$ is set to 1 so as to emphasize the dependence on the activation field clearly. Decreasing the activation field increases the rate at which the polarization reaches its saturation value. Figure 4.11b shows the effect of changing $K$, the rate constant, on the model (once again $\text{sig}(a)$ function is set to 1). Lowering $K$ has a similar effect as increasing the activation field.

In the following chapter data will be shown that shows that lowering the temperature (changing the activation field and $K$) while keeping the driving potential constant has a similar effect to lowering the driving potential while keeping the temperature constant (changing $K$ but not the activation field). Unfortunately, the effect of $K$ and the activation field are not mutually exclusive. Experimentally the polarization grows at a specific slope and to maintain this slope in the model an increase in the activation field needs to be accompanied by an increase in $K$. The effect of the sigmoidal term and the parameter $a$ is shown in Fig. 4.11c. The center of the sigmoid is the minimum switching field and the parameter $a$ controls how fast the polarization growth stops around the this field.
Figure 4.11. The effect of varying the model parameters on the resulting polarization curves.

To simulate the fast polarization regime in the TMSC switching data we set $\rho_{\text{screen}}$ to zero and we use $\text{sig}(a)$ to stop the polarization growth upon reaching the minimum switching described earlier. The parameter $a$ in the sigmoidal is set to $2.5 \times 10^{-6}$ because as shown in the Fig. 4.11c this value effectively stops the polarization growth at the minimum switching field. Figure 4.12 shows the effect of changing the activation field and $K$ together. The model shows that as we increase the activation field (and $K$) we start to see the growth of the polarization in the fast regime become less exponentially constant at increased applied fields.
Figure 4.12. Plots showing the simulated polarization growth (line) and the experimental data (points) for different applied fields as a function of activation field.

As seen from Fig 4.12 the model reproduces the experimental data for the fast polarization growth regime better when the activation field is 1000 MV m\(^{-1}\) than 100 MV m\(^{-1}\). By letting the applied field also be varying parameter (possibly due to parasitic resistance) the model is improved as shown in Fig 4.13.
Figure 4.13. Plots showing the simulated polarization growth (line) and the experimental data (points) for different applied fields (in MV/m) as a function of activation field when the applied field is allowed to be a fitting parameter.

The discussion above shows that the switching of ferroelectric regions in TMSC PVDF films cause the local field to decrease and approach the minimum switching field thus slowing the polarization growth. The polarization growth in the fast regime is well-described by this model. The model surmises that the polarization growth in the slow regime is caused by an increase of the local electric field experienced by the un-switched ferroelectric regions due to the rearrangement of mobile charge in the sample. The screening charge is introduced into the model as the $\rho_{\text{screen}}$ term in

$$E'_{\text{local}} = E_{\text{local}} - \lambda(P - \rho_{\text{screen}}),$$

and is equal to

$$\rho_{\text{free}} = \int_0^t \sigma(E_{\text{applied}} - E'_{\text{local}}) dt,$$

in the case where the mechanism of the generation of the free charge is the conductivity of the films. $\sigma$ is a conductivity term that describes how fast the mobile charge can screen the polarization. When running the code this integral is solved iteratively to allow for easy integration into the previous model. Setting $\sigma$ to $8 \times 10^{-7}$ S m$^{-1}$ the model produced the data seen in Fig 4.14.
Figure 4.14. Shows the model results when a field dependent conductivity is introduced. Introducing a bulk conductivity reproduces the two regimes of switching but does not describe the slow regime well.

Introduction of the screening charge through the conductivity does reproduce the two regime switching as expected, however the growth of the polarization is inconsistent with the experimental data in the slow regime. This suggests that the screening charge does not originate from the conductivity of the material. The large mismatch in the simulation of the fast and slow polarization growth regimes and the experimental data suggest that the kinetics of polarization switching in the two regimes are different and should be modeled differently.

The electric field driving the polarization growth in the slow regime is assumed to be close to the minimum switching field. This is supported most strongly in the data collected at an applied field of 175 MV m\(^{-1}\), which is a few percent above the calculated minimum switching field of 165 MV m\(^{-1}\). At 175 MV m\(^{-1}\) there is an initial fast regime where the polarization grows and causes E'local to quickly drop...
below the minimum switching field as indicated by the data. This shows that at 175 MV m\(^{-1}\) the polarization grows faster than it can be screened. In the slow regime \(E'_{\text{local}}\) does not drop below the minimum switching field as indicated by the continuous growth of the polarization in the slow regime. As a consequence of these two observations the polarization growth in the slow regime has to occur slower than it can be screened, which happens when the driving field is close to the minimum switching field. As discussed earlier (and supported by the rapid decrease in polarization growth at the end of the fast regime) the polarization growth near the minimum switching field behaves much differently than at fields just a few percent larger. This supports modeling the slow regime and fast regime differently. This also supports modeling the growth of the polarization in the slow regime using a constant \(E'_{\text{local}}\) (or driving potential).

The Avrami equation described earlier in this chapter for nucleation and growth at constant driving potential can be written as follows:\(^7,^8\)

\[
1 - X = \exp(-At^n),
\]

where \(X\) is the degree of crystallinity (polarization) and \(A\) and \(n\) are constants. While this equation functionally describes the polarization growth dynamics, current understanding attributes a physical basis to the \(A\) and \(n\) parameters only in very limited systems as mentioned earlier. By taking the natural log of both sides and then taking the log of both sides we end up with

\[
\log[-\ln(1 - X)] = n\log(t) + \log(A). \tag{Eq. 4.11}
\]
If the slow regime polarization growth can be described using the generalized Avrami equation a plot of the $\log[-\ln(1-X)]$ vs $\log(t)$ should yield a straight line. $X$ is replaced with the polarization value that has been normalized to the maximum polarization at that given electric field. The data are plotted in Fig. 4.15 below. It should be noted that the model of polarization switching in the fast regime was also modeled using Avrami nucleation, but in the fast regime physical parameters (electric field, nucleation rate constant, etc.) were used to model the data.

![Avrami plots](image)

Figure 4.15. Avrami plots of the polarization growth versus time with the linear fits. The behavior of the polarization in slow region is approximately linear in the Avrami plots.

The data show that the polarization growth in the slow regime is linear in the Avrami plots and is suitable to be modeled using the generalized Avrami equation. This is also consistent with the conclusion above that the polarization is
driven at a constant field in the slow regime. (Note that the polarization growth in the fast regime deviates from a straight line as expected since the driving field is changing considerably). Fitting the experimental data from the slow regime polarization growth the Avrami model yields a straight line with slope $n$, and an intercept of $\log(A)$. Values for $n$ and $A$ are shown in the table below. Data from $2 \times 10^{-4}$ seconds to 0.01 seconds was used for this fit.

<table>
<thead>
<tr>
<th>E (MV/m)</th>
<th>n or slope</th>
<th>intercept</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>175</td>
<td>0.519</td>
<td>1.119</td>
<td>13.15225</td>
</tr>
<tr>
<td>200</td>
<td>0.491</td>
<td>1.459</td>
<td>28.77398</td>
</tr>
<tr>
<td>225</td>
<td>0.219</td>
<td>0.909</td>
<td>8.109611</td>
</tr>
<tr>
<td>250</td>
<td>0.118</td>
<td>0.64653</td>
<td>4.431288</td>
</tr>
</tbody>
</table>

Table 4.2. The fit values for the Avrami constants

This model also explains data gathered by other researchers studying polarization reversal in ferroelectric polymers. Most of the previous work on ferroelectric switching in thin film polymers is done using PVDF-TrFe because it is very difficult to produce high quality thin film samples of the homopolymer as discussed in previous chapters. The copolymer is usually annealed to have very high crystalline content (>90%). The high crystal content of these films suggest that ferroelectric domains are large. For large ferroelectric domains are large polarization reversal is dominated by domain wall motion and not nucleation. The relevant local electric field in this case is the field caused by molecular dipoles at the domain wall interface. A sample with large ferroelectric domain will not show two regime switching since the electric field at the domain wall (due to the
geometry of the domain wall) is relatively constant with a constant applied field. This situation is best modeled using a nucleation and growth (not just nucleation) model with a constant driving force such as the Avrami model.

Films that have charges that can rearrange quickly will not show a two regime polarization growth because the polarization can be screened faster than it can grow. In Fig 4.16 polarization growth is simulated using a conductivity of $0$, $10^{-7}$, and $10^{-5}$ S m$^{-1}$. The simulation shows that even at relatively low conductivities, free charge can screen polarization faster than it can grow. Although rarely reported in the literature the conductivity of thin polymer films (especially when loaded with inorganic materials) can be high enough such that two regime polarization switching is masked. In this case the Avrami model can be used since the driving field is relatively constant (since the polarization is being effectively screened as fast as it can grow).
Figure 4.16. Plots of the simulated polarization growth for different conductivities of the screening charge. Notice how a bulk conductivity of $10^{-9}$ S m$^{-1}$ doesn’t screen the internal polarization in the time of the experiment but a conductivity of $10^{-5}$ S m$^{-1}$ screens the polarization fast enough that the two regimes are not resolved.

The lack of two-regime polarization switching polycrystalline oxides provides further insight for switching in thin homopolymer films. Although the origins of the screening charge were not investigated, the lack of the two-regime polarization switching in oxides suggest the the screening charge originates at the amorphous/crystalline polymer interface, because this interface is not present in polycrystalline oxides. Further evidence that the screening charge is a consequence of the interface is that the leakage current in the double wave experiment cannot be distinguished from the noise meaning that the highest value for the bulk conductivity is less than $7 \times 10^{-9}$ S m$^{-1}$ (Fig. 4.7). A conductivity this slow would not allow for the polarization to be screened within the timeframe.
of the experiment and suggests that the screening charge is confined to the amorphous/crystalline interface.

4.8 Conclusions

In conclusion the model developed here shows that variations in the local electric field caused by polarization growth explains the experimental observation of two regime polarization growth. Internal compensation of the polarization in the ferroelectric regions has significant consequences for PVDF applications. As the amount of polarization that is internally compensated increases the interface compensation charge decreases. An example of device that uses this interface charge to operate is a ferroelectric transistor. The charge accumulated at the transistor channel and ferroelectric layer modulate the conductivity of the channel. If the charge at the transistor channel and ferroelectric channel changes over time due to internal compensation of the polarization in the ferroelectric the channel will have a time dependent conductivity. This behavior is useful to know for ferroelectric transistor design. Further research needs to be done to clarify how much of the polarization is internally screened. Another consideration is the origin of the screening charge. If the screening charge is generated by an electrochemical reaction at the interface between ferroelectric and non-ferroelectric regions the interface would undergo significant change during switching and could lead to the eventual breakdown of the film.

The model also shows that the films need to be of high dielectric quality while still providing some screening mobile charge for two regime polarization switching to be observed. The presence of mobile screening charge has not
been shown to exist in oxide ferroelectrics yet the polarization of the oxides is stable. This suggests that the depolarization field can be screened far away from ferroelectric domains. Studies of composites of ferroelectric oxides in amorphous polymer matrices with varying conductivities has the potential of elucidating the effect of screening charge and the depolarization field in films with ferroelectric and non-ferroelectric phases.

Homopolymer PVDF films are less crystalline than PVDF-TrFe films. This lowered crystallinity changes the kinetics of polarization reversal from being dominated by domain wall motion to being dominated by nucleation. Since domain wall motion occurs roughly at the speed of sound, switching times are longer in nucleation dominated switching. The switching time is an important parameter for device design. For example in a typical memory device the speed of polarization switching determines how fast a bit can be written and is usually desired to be fast. Slow polarization growth may be favorable in devices where one wants to control the amount of polarization, such as multi-state memory.

The concept of a minimum switching field was defined in the development of the switching model. This is better suited to compare ferroelectrics than the coercive field because it is not frequency dependent. This minimum switching field will be found to vary with the structural phase of PVDF as shown in the next chapter. In the slow regime the polarization data is shown to follow Avrami like behavior and the constants $n$ and $A$ are extracted. With further investigation, $n$ and $A$ could be shown to correlate with other aspects of the material. Ultimately,
understanding the polarization switching of TMSC PVDF films will lead to better device design.
References


Chapter 5 Effect of Microstructural Phase on the Ferroelectric and Dielectric Properties of PVDF

Abstract

Using TMSC, high quality ferroelectric PVDF films are deposited onto Au surfaces. The films are heat treated to produce films with polymer chains that have different structural phases. The structural phase of the polymer films is analyzed using Fourier transform infrared spectroscopy. Atomic force microscopy is used to study the difference in the surface morphology of PVDF samples of different crystalline compositions. Polarization and dielectric impedance spectroscopy measurements are used to study the structural phase dependence of the ferroelectric and dielectric properties of PVDF samples.

5.1 Introduction

As seen in Fig 1.1 (Chapter 1), PVDF can exist in three ferroelectric crystalline phases at room temperature and atmospheric pressure. These three crystalline phases, the $\beta$-, $\gamma$-, and the $\delta$-phase, have different unit cells that are a result of the polymer chain conformation. The $\beta$-phase has an all trans conformation, the $\gamma$-phase has a trans-trans-trans-gauche conformation, and the $\delta$ phase has a trans-gauche conformation. It should be noted that spin cast PVDF does not exist as a single crystal and that crystallites often have chains with varying degrees of the $\beta$, $\gamma$, and the $\delta$ conformations as a consequence. In this thesis, the variation in composition of the amount of $\beta$, $\gamma$, and the $\delta$ conformations is referred to as the variation in the structural phase. Differences in the ferroelectric and dielectric properties are expected with variation in the structural phase compositions since
material properties such as the melting point (α and β ~170 °C, γ ~180 °C), unit cell, and dipole moment of the unit cell vary with chain conformation. However, owing to the difficulties in producing pore-free thin PVDF films, it the effect that the compositional phase has on the ferroelectric and dielectric properties has been difficult to actually determine.

This chapter begins with using FTIR to study the structural phase compositions of 3 PVDF films prepared using the TMSC process but annealed at different temperatures. The FTIR data will be used to show that simple hot plate annealing can be used the vary the structural phase composition of PVDF. In section 5.3, impedance spectroscopy will be used to study the dielectric relaxation of the amorphous regions in these 3 PVDF films. It will be shown the the dielectric relaxation is the same regardless of annealing which confirms that differences seen in the polarization reversal is attributed to the crystalline regions and not the amorphous regions. Polarization reversal is studied in section 5.4. It will be shown that switching in PVDF thin films follows a universal behavior when changes in temperature and variations in the structural phase composition are properly accounted for.

5.2 Composition and Morphology of Annealed Samples

PVDF samples were spin coated onto Au coated substrates using the TMSC method at room temperature and 20% relative humidity. The infrared spectra of the as cast sample (referred to as As-Cast) is shown in Fig 5.1. Table 5.1 shows the FTIR absorption peaks used to identify the structural phase of the PVDF films (remember that the α and δ phases will have the same FTIR peaks).
Table 5.1. Location of characteristic absorptions features in PVDF and the corresponding structural phases

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>762</td>
<td>α</td>
</tr>
<tr>
<td>840</td>
<td>β,γ</td>
</tr>
<tr>
<td>976</td>
<td>α</td>
</tr>
<tr>
<td>1210</td>
<td>α</td>
</tr>
<tr>
<td>1234</td>
<td>γ</td>
</tr>
<tr>
<td>1274</td>
<td>β</td>
</tr>
</tbody>
</table>

Figure 5.1. FTIR spectra of the As-Cast PVDF sample. Notice the absence of characteristic absorption features at 762 cm\(^{-1}\) and the strong absorption features at 1234 cm\(^{-1}\) and 1274 cm\(^{-1}\).

The data show that the As-Cast sample consists of the γ and β phases. A sample was annealed at 175 °C overnight (labeled AN-175C). The temperature was chosen to be above the melting point of the β-phase but below the melting point of the γ-phase. The time was chosen so that the maximum amount of the film would convert to the γ-phase. The infrared spectra is shown in Fig. 5.2.
Figure 5.2. FTIR spectra of the PVDF sample annealed at 175 °C (AN-175C). Notice that the 1234 cm\(^{-1}\) has been enhanced and the shoulder peak at 1274 cm\(^{-1}\) reduced.

The data shows that the absorption at 1234 cm\(^{-1}\) has increased and the absorption at 1274 cm\(^{-1}\) has decreased dramatically. Osaki et al. suggested that any imperfect γ-phase films will contain long all trans sections that are identified as the β-phase absorptions in the infrared spectra. By annealing the PVDF films at 175 °C the amount of these trans sections in the films is reduced greatly as seen in Fig. 5.2.

The As-Cast film and the film annealed at 175 °C allow for the study of the effect of decreasing the number of trans bonds in the polymer chain. To study the effect of increasing the number of trans-gauche bonds a sample is annealed at 185 °C for 30 s (labeled as AN-185C). The temperature is chosen to be just above the melting point of γ-phase (which has the highest melting point of all PVDF phases). The time is chosen such that the film is converted to the non-ferroelectric α-phase without allowing the formation of overly large (~50 μm) α
crystallites. Very large crystallites increase the surface roughness and can degrade the dielectric strength of the film, making the study of dielectric properties more difficult. The infrared spectra in Fig 5.3 show that the AN-185C sample consists of mostly the α-phase.

![FTIR spectra of the sample annealed at 185 °C.](image)

Changes in the polymer conformation lead to changes in the unit cell and expected changes in the surface morphology. AFM micrographs at 2 x 2 and 10 x 10 microns are shown in Fig 5.4. The AFM micrographs show a drastic change in morphology for the As-Cast, AN-175C and AN-185C samples. The As-Cast sample has a morphology that consists of tightly packed globular structures as seen in the 2 x 2 μm micrograph. The root mean squared (rms) roughness calculated from the 10 x 10 μm micrograph of the As-Cast sample is 8.55 nm. The AN-175 sample has a worm-like morphology as seen in the 2 x 2 μm micrograph and an rms roughness of 15.46 nm calculated from the 10 x 10 μm
The change in morphology was not studied in detail, but a plausible explanation is as follows. The change in morphology occurs due to the melting of β and α crystallites at 175 °C leaving only γ crystallites. These small γ crystallites act as nucleation surfaces for the polymer chains in the melted phase to attach to. In general, polymer crystallites form in lamellar structures and under certain conditions crystallize in a preferred direction (this is clearly seen in the well-studied solution crystallization of poly(ethylene) \(^6\)). It is possible that annealing at 175 °C causes the crystallite to elongate in one direction (due to the preferred direction of crystallization) forming the worm-like morphology seen in the AFM micrographs. At 185 °C the film is just above the γ-phase melting point (and well above the melting point of the α and β phases). It is well documented in the literature that when melted PVDF is cooled to room temperature at a rate below 100 K s\(^{-1}\), α-crystallites are preferentially formed. \(^1\) The 10 x 10 μm AFM micrographs of the AN-185C sample show structures that are similar to the observed α-phase spherulites except that that are ~10x smaller and borders between crystallites are less defined, likely due to short annealing time. \(^5\) The rms roughness of the AN-185 sample is 22.6 nm calculated from the 10 x 10 μm micrograph.
Figure 5.4. AFM micrographs of as cast and annealed PVDF samples showing the differences in morphology between the as cast and annealed samples.

The FTIR spectra clearly show that the conformation of PVDF polymer chains can be controlled using a simple annealing process, as described in the literature. This change in conformation in the polymer chain leads to a change in the morphology as shown in the AFM micrographs. These changes in
morphology and conformation allow study of changes in the dielectric and ferroelectric properties of PVDF as function of chain conformation.

5.3 Dielectric Properties of PVDF with composition

Top contacts (0.75 mm x 0.75 mm squares) of Au are deposited onto the samples to make capacitor structures. The real and imaginary components of the impedance are measured using an HP4192A from 5 kHz to 1000 kHz. The impedance at lower frequencies could not be measured due to instrumentation sensitivity limitations. The real and imaginary components of the dielectric constant are calculated from the impedance measurements. Figures 5.5, 5.6, and 5.7 show the comparison of the real and imaginary dielectric constants as a function of temperature at different frequencies for As-Cast, AN-175C and AN-185C samples, respectively. In general poling slightly increases the real and imaginary components of the dielectric constant. This is due to increased alignment of dipoles with the electric field during poling. Because the data in Figs. 5.5-5.7 show that the dielectric properties of the sample only change slightly after poling, the dielectric spectra from the poled samples will be used in this chapter to discuss differences between the PVDF compositions.

The dielectric relaxation between 225 K and 350 K present in all the samples is identified as the β relaxation. The β relaxation is ascribed to the micro-Brownian motions of the chain segments in the amorphous regions. The dielectric relaxation that appears to begin around 400 K is identified as the α relaxation and is ascribed to motions in the crystalline phase of PVDF. Unfortunately, the experimental setup does not allow for this relaxation peak to
be fully resolved. Due to this limitation, the variation of the amorphous region dielectric properties due to different preparation methods is studied. While it is clear that polymer chain conformation changes the structure of the crystalline regions it is unclear whether crystalline regions or annealing have an effect on the amorphous regions.

Figure 5.5. The real and imaginary part of the dielectric constant as a function of temperature for 10 different frequencies for the As-Cast sample before and after poling, showing that there is no strong effect of poling on the dielectric constants.
Figure 5.6. The real and imaginary part of the dielectric constant as a function of temperature for 10 different frequencies for the An-175C sample before and after poling, showing that there is no strong effect of poling on the dielectric constants.
Figure 5.7. The real and imaginary part of the dielectric constant as a function of temperature for 10 different frequencies for the An-185C sample before and after poling, showing that there is no strong effect of poling on the dielectric constants.

Figure 5.8 shows the loss tangent as a function of frequency at 260 K, 270 K, 280 K, and 290 K for all three samples. The temperatures were chosen because the β relaxation loss peak is apparent at these temperatures. Yano has suggested that the magnitude of the loss peak of the β relaxation increased with the amount of amorphous material in PVDF. According to this interpretation, samples that are annealed have an increased amount of amorphous material. The magnitude of the loss peak is related to how much energy is lost to the material at a particular frequency. This can change with the number of dipoles contributing to the loss as Yano has suggested but could also be due to a fundamental difference in molecular makeup of the dipole moment contributing to
this relaxation. If there is a difference in local structure in the amorphous region the activation energy of the β relaxation should be drastically different. The difference in activation energy would lead to difference in the Arrhenius plots of the different phases. Using the data from Figs 5.5-5.7 the loss tangent was calculated at 10 different frequencies. The maximum of the loss tangent vs temperature at the given frequency gives the relaxation temperature for a given relaxation time (frequency). The Arrhenius plots for the three different samples are plotted in Fig. 5.9. The data show that the activation energy of the β relaxation is very similar for all three samples. This supports the suggestion of Yano that the difference in magnitude of the loss tangent is indeed caused by relative amounts of amorphous content in the samples. This suggests that the As-Cast sample is the most crystalline sample of all three.
Figure 5.8. Loss tangent versus frequency for all samples at various temperatures

As the data in Figs. 5.5-5.7 show, a large part of the real dielectric constant is due to the amorphous regions. The real part of the dielectric constant at
temperatures above the glass transition (~240 K) is the highest for the film with the largest amorphous content (AN-185C) and is the least high for the most crystalline film (As-Cast) as shown in Fig. 5.10. This is because the dipoles in the amorphous phase can at least partially relax at frequencies above 1000 Hz and at temperatures above the glass transition as indicated by the β relaxation in Figs. 5.5-5.7. The dipoles in the crystalline phase cannot relax at the frequencies and temperatures investigated as indicated by the absence of the α relaxation in Figs. 5.5-5.7. Since AN-185C has the most amorphous content of the samples it has the most number of dipoles in the amorphous phase that can contribute to the dielectric constant at the frequencies and temperatures investigated and therefore will have the largest real dielectric constant above the glass transition temperature.
Figure 5.9. Real part of the dielectric constant vs frequency for the As-Cast and annealed samples.
5.4 Dependence of Polarization Reversal Dynamics on Temperature

Polarization reversal in the annealed and non-annealed TMSC samples were studied using the method described in Chap. 4. The polarization versus time is behavior is determined for all three samples as function of temperature and applied electric field. All samples were poled at 300 MV m\(^{-1}\) before polarization measurements were performed. This chapter will show that switching in PVDF thin films follows a universal behavior when changes in temperature and variations in the structural phase composition are properly accounted for.

Fig 5.10-5.12 show the polarization growth behavior for the As-Cast, AN-175C and AN-185C samples at 300 K, 266 K, and 233 K. Reliable data for an applied field of 250 MV m\(^{-1}\) could not be acquired for samples at 300 K.
Figure 5.10. Polarization growth versus time behavior at 300 K for all three samples.

Figure 5.11. Polarization growth behavior at 266 K for all three samples.
In general nucleation is temperature dependent since the temperature determines the distribution of energy of the nucleation sites. If the nucleation of the polarization reversal in TMSC films follows a simple Arrhenius type dependence on the temperature (Appendix B), the probability of nucleation per number of nucleation sites per unit time is of the form (Appendix B, and Chap. 4)

\[ p = K \exp \left( -\frac{E_{\text{activation}}}{E_{\text{local}} + E_{\text{pol}}} \right), \]  

(Eq. 5.1)

where \( \text{pol} \) is the the dipole moment of a nucleation center. Using the data from the temperature dependent polarization reversal, the following discussion shows that an Arrhenius-type temperature dependence on the nucleation of polarization reversal explains the temperature dependence of the polarization reversal data.

Figure 5.12. Polarization growth behavior at 233 K for all three samples.

115
As discussed in Chap. 4 the polarization versus time plots show two distinct regions: the slow regime, and the fast regime. Again, as described in Chap. 4 the point at which the polarization growth slows at the end of the fast regime is where the local electric field and the minimum switching field are equal (by definition if the local electric field is higher than the minimum switching field the polarization will continue to grow). Figure 5.13a shows the applied field vs the polarization state of the sample at the end of the fast regime for 233 K, 266 K and 300 K for the As-Cast sample. Since data points at the same sample polarization at the end of the fast regime exists for all three temperatures, the variation in the minimum switching field can be found as described below without knowledge of the absolute minimum switching field. And because the local field at the end of the fast regime is the minimum switching field we can extract the temperature dependent behavior of the polarization reversal.

At the time when the polarization growth stops in the fast regime the relationship between the applied field and minimum switching field is (derived in Chap. 4)

\[ E_{\text{applied}} = \alpha \frac{(1+C)p}{\varepsilon_0 \varepsilon_r} + E_{\text{min}}. \]  

(Eq. 5.2)

It is assumed that \( \alpha \frac{(1+C)}{\varepsilon_0 \varepsilon_r} \) is not strongly temperature dependent and can be written as a constant, \( \lambda \). A new variable is defined as

\[ \frac{k \Delta T}{p_{\text{pol}}} = \Delta E_{T_2-T_1}. \]

As the temperature goes from \( T_1 \) to \( T_2 \), the minimum switching field at \( T_2 \) is written as
\[ E_{\min, T_2} = E_{\min, T_1} + \Delta E_{T_2 - T_1}. \]  
(Eq. 5.3)

The minimum field at \( T_2 \) can be written this way because we are assuming that the absolute minimum switching field doesn’t vary with temperature but the variation in the probability of nucleation with temperature is determined by the \( kT \) term in Eq. 5.1.

At the different temperatures Eq. 5.2 becomes

\[ E_{\text{applied}} @ T_1 = \lambda P_{T_1} + E_{\min, T_1}, \]

and

\[ E_{\text{applied}} @ T_2 = \lambda P_{T_2} + E_{\min, T_1} + \Delta E_{T_2 - T_1}. \]

When the polarization state is the same at \( T_2 \) and \( T_1 \), \( P_{T_2} = P_{T_1} \), the above equations are combined to give the relation

\[ E_{\text{applied}} @ T_2 - \Delta E_{T_2 - T_1} = E_{\text{applied}} @ T_1, \]

which is rearranged to give

\[ E_{\text{applied}} @ T_2 - E_{\text{applied}} @ T_1 = \Delta E_{T_2 - T_1}. \]

\( \Delta E_{T_2 - T_1} \) is found experimentally from the difference in the applied electric field at equivalent polarization states as based on the derivation above. Regardless of variation in the structural phase, the experimental value for \( \Delta E_{T_2 - T_1} \) for \( T_2 \) equal to 300 K and \( T_1 \) equal to 266 K is 55 MV m\(^{-1}\) and for \( T_2 \) equal to 266 K and \( T_1 \) equal to 233 K is 60 MV m\(^{-1}\). The probability of nucleation per number of nucleation sites per unit time is equal when the polarization states are equal due to the
number of nucleation sites remaining constant and the time elapsed during the fast regime is approximately constant, therefore the equality

\[ K_{@T_1} \exp \left( -\frac{E_{\text{activation}@T_1}}{E'_{\text{local}@T_1} + \frac{kT_1}{\text{pol}}} \right) = K_{@T_2} \exp \left( -\frac{E_{\text{activation}@T_2}}{E'_{\text{local}@T_2} + \frac{kT_2}{\text{pol}}} \right) \]  \hspace{1cm} (\text{Eq. 5.4})

is true. Assuming that the activation field \( E_{\text{activation}} \) and the rate constant \( K \) are temperature independent Eq. 5.4 becomes

\[ E'_{\text{local}@T_1} + \frac{kT_1}{\text{pol}} = E'_{\text{local}@T_2} + \frac{kT_1}{\text{pol}} \]

The resulting equation after rearranging the terms and assuming that the difference in the local fields is that same as the difference in the applies fields is

\[ k\Delta T = \text{pol} \cdot \Delta E_{T_2 - T_1} \]

Taking \( \text{pol} \) to be 2.1 D (the dipole moment of the VDF monomer), \( \Delta T \) to be 33 K (from experiment), and the average value of \( \Delta E_{T_2 - T_1} \) to be 57.5 MV m\(^{-1}\), it is found that

\[ k\Delta T = 2.84 \ast 10^{-3} \text{ eV}, \]

and

\[ \text{pol} \ast \Delta E_{T_2 - T_1} = 2.39 \ast 10^{-3} \text{ eV}. \]

This result supports the hypothesis that the probability of nucleation has an Arrhenius type temperature dependence as shown in Eq. 5.1.

Fig 5.13b shows \( (E_{\text{applied}} + \Delta E_{T_2 - T_1}) \) versus the polarization state for the As-Cast sample. The same procedure is used to produce plots of the \( E_{\text{applied}} \)
\( +\Delta E_{T_2-T_1} \) versus the polarization state for the As-Cast, AN-175C and AN-185C samples shown in Fig. 5.14a-c.

Figure 5.13. a) Applied electric field versus Polarization state at the end of the fast regime b) \((E_{\text{applied}} +\Delta E_{T_2-T_1})\) versus the polarization state at the end of the fast regime showing the universal temperature behavior of polarization at the end of the fast regime for the As-Cast sample.
Figure 5.14. \( (E_{\text{applied}} + \Delta E_{T2-T1}) \) versus the polarization state at the end of the fast regime showing the universal temperature behavior of polarization at the end of the fast regime for the As-Cast, AN-175C and AN-185C samples.

The deviation of the data in Fig. 5.13 from the linear behavior from Eq. 4.7 is presumably due to the limitations of the assumptions used to derive Eq. 4.7. For polarization states that are a small fraction of the total possible polarization there are three effects that lead to this deviation: 1. The mean field approach for the local field is not valid since only a small part of the sample is switched and the actual ferroelectric regions experience differing local fields. 2. At small polarization values, the coupling factor vary due to reason 1. 3. In deriving of Eq. 4.7, the dipole moments of the ferroelectric regions were assumed to be normal to the film surface. This is generally not true and effects from the distribution of the orientations of the ferroelectric regions will affect the polarization state. At
polarization states that are close to the maximum polarization state, Eq. 4.7 fails because the polarization value cannot grow larger than the maximum and that the effect of the distribution of the orientations of the ferroelectric regions will be more evident.

5.5 Dependence of Polarization Reversal Dynamics on Structural Composition

Earlier in this chapter it was shown that $\Delta E_{\min T_2-T_1}$ represented the change in electric field needed to change the potential driving the polarization growth. It was also shown that for a given structural phase the $(E_{\text{applied}} + \Delta E_{T_2-T_1})$ versus the polarization state at the end of the fast regime follows a universal behavior (Fig. 5.13). It is hypothesized that a term similar in function to $\Delta E_{\min T_2-T_1}$ exists for the change the driving potential to keep the probability of nucleation the same for different structural phases. This is because a change in the structural phase would change the energy barrier height for nucleation. Such a term will be represented by $\Delta E_{\min S_2-S_1}$. The following argument will show that this is indeed likely.

For all samples, polarization states lower than about $\sim 0.02 \text{ C m}^{-2}$ deviate from linearity with $(E_{\text{applied}} + \Delta E_{T_2-T_1})$, as seen in Fig. 5.14. The highest polarization state following linearity varies by sample and is $0.06 \text{ C m}^{-2}$ for the As-Cast sample, $0.05 \text{ C m}^{-2}$ for the AN-185C sample and is taken to be $0.06 \text{ C m}^{-2}$ for the AN-175C sample. By only considering the data between these two limits, the sample minimum switching field is found using the approach used in Chapter 4 is
used to extract the different minimum switching fields for the different samples. While it is clear that the minimum field extracted at using this method is only valid when the mean field approach is valid, the difference in the minimum switching field should apply regardless of the actual minimum field. The data show that in reference to the minimum switching field of the As-Cast sample, the AN-175C sample has a $\Delta E_{\min S_2-S_1}$ of 20 MV m$^{-1}$ and the AN-185C sample has $\Delta E_{\min S_2-S_1}$ of 40 MV m$^{-1}$. As illustrated in Fig. 5.14b, when the $(E_{\text{applied}} + \Delta E_{\min T_2-T_1} - \Delta E_{\min S_2-S_1})$ versus the polarization state is plotted, the data show that curves lie on top each other until they start to deviate due to differences in the maximum polarization. The physical meaning of $\Delta E_{\min S_2-S_1}$ lies in the energy needed to nucleate polarization reversal for different structural compositions. The behavior of $\Delta E_{\min S_2-S_1}$ suggest that it is easier to nucleate polarization reversal in samples that have long trans sections.

Figure 5.14. a) $(E_{\text{applied}} + \Delta E_{\min T_2-T_1})$ versus the polarization state before being adjusted for different minimum switching fields b) $(E_{\text{applied}} + \Delta E_{\min T_2-T_1} - \Delta E_{\min S_2-S_1})$ versus the polarization state. Universal behavior is demonstrated for polarization reversal when the appropriate adjustments are made to the applied field.
The data in Fig. 5.14 also show that maximum polarization for the AN-175C sample is the highest among the samples. This is not expected from the dielectric relaxation data showing that the As-Cast sample has the highest crystallinity. Furthermore, the As-Cast sample contains the highest amount of the β-phase which has the largest dipole moment per volume of all the three phases and has the smallest minimum switching field. A possible reason for this is that the ferroelectric regions in the As-Cast sample can orient with the poling field to a higher degree than the annealed sample due the trans-trans-trans-gauche conformation or the morphology seen in the AFM micrographs.

As the discussion above and Fig. 5.14 suggest, when comparing different compositions of PVDF it is more useful to compare samples where the “driving field” defined as \((E_{\text{applied}} + ΔE_{\text{min}T_2-\text{T}_1} - ΔE_{\text{min}S_2-S_1})\) is similar. For example all samples have a data point where the polarization state is \(.03 \text{ C m}^{-2}\). Table 5.2 shows the temperature, applied field, and driving field at those data points for each sample (the reference temperature is 233 K and the reference structure is the As-Cast sample). The data in Table 5.2 show that data collected at different applied fields and temperatures can have similar driving fields and Fig. 5.15 shows the polarization growth for all three samples at two similar “driving fields”.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp (K)</th>
<th>Applied Field (MV m(^{-1}))</th>
<th>Driving Field (MV m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Cast</td>
<td>233</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>AN-175C</td>
<td>266</td>
<td>200</td>
<td>240</td>
</tr>
<tr>
<td>AN-185C</td>
<td>266</td>
<td>225</td>
<td>245</td>
</tr>
</tbody>
</table>

Table 5.2. The values of the temperature, applied field and driving field for all three samples at a polarization state of \(~.03 \text{ C m}^{-2}\). The table shows that the driving field is approximately equal for a similar polarization state while the temperature and applied field vary.
Figure 5.15. Polarization growth curves for similar driving fields for all samples at different applied fields and temperatures. The applied field and the temperature at which the data was collected for the plots are:
Plot a. As-Cast T=233 K E_{app} = 250 MV m^{-1}; An-175C T=266 K E_{app} = 200 MV m^{-1}; An-185C T=266 K E_{app} = 225 MV m^{-1}. Plot b. As-Cast T=233 K E_{app} = 200 MV m^{-1}; An-175C T=233 K E_{app} = 225 MV m^{-1}; An-185C T=233 K E_{app} = 250 MV m^{-1}.

The data in Fig. 5.15 show that, upon properly accounting for the “driving field” defined above, the initial polarization growth is similar. Polarization growth deviates from this common behavior in the slow regime between the AN-175C sample and the other two samples. This can be explained by the larger maximum polarization that the AN-175C sample can achieve at a given driving field. In other words, in the slow regime the growth rate of the polarization is initially determined by the probability of nucleation per nucleation site per time, but
towards the end of the slow regime polarization growth is determined by the maximum polarization.

To determine the variation in polarization growth in the slow regime due to the variation in structural phase composition, the slow regime growth can be fit to Eq. 4.11 and the Avrami constants extracted.

Figs. 5.16-5.18 show the Avrami plots of all the samples at 233 K, 266 K and 300 K. A line is fit sing the data from the Avrami plots in the slow regime between $2 \times 10^{-4}$ and $3 \times 10^{-3}$. The slope is the $n$ constant in Eq. 4.11 and the intercept is related to the $A$ constant in Eq. 4.11. Figure 15.19 shows $n$ and the intercept as a function of driving field discussed above.
Figure 5.16. Avrami plots of the As-Cast, AN-175C, and AN-185C samples at 233 K. Notice the linearity of the growth from $2 \times 10^{-4}$ s to $2 \times 10^{-3}$ s suggesting that the polarization reversal follows an Avrami type behavior.

Figure 5.17. Avrami plots of the As-Cast, AN-175C, and AN-185C samples at 266 K. Notice the linearity of the growth from $2 \times 10^{-4}$ s to $2 \times 10^{-3}$ s suggesting that the polarization reversal follows an Avrami type behavior.
Figure 5.18. Avrami plots of the As-Cast, AN-175C, and AN-185C samples at 300 K. Notice the linearity of the growth from $2\times10^{-4}$ s to $2\times10^{-3}$ s suggesting that the polarization reversal follows an Avrami type behavior.

Figure 5.19. Avrami constants plotted as a function of driving field defined earlier in this section showing that the polarization reversal behavior in the slow regime is similar for all samples when the temperature and structural phase variation is properly accounted for.
The data show that generally $n$ goes from a value of around 0.5 to 0.6 and decreases as a function of the driving field. Although the Avrami constants in general do not have a physical interpretation some authors under specific criteria have found that $n$ can be related to the dimensionality of the problem and $A$ ($\log(A)=\text{intercept}$) to the probability of nucleation. \textsuperscript{9,10} With more investigation it may be possible to correlate the Avrami constants found here to physical parameters of the system.

5.6 Conclusions

This chapter used simple annealing techniques to vary the structural phase of TMSC PVDF films to study the change in dielectric and ferroelectric properties of TMSC PVDF as a function of structural phase.

FTIR was used to confirm the structural phase composition of each sample. The As-Cast sample had a mix of the $\beta$ and $\gamma$ phases. The sample annealed at $175^\circ \text{C}$ had an increased content of $\gamma$ phase compared to the As-Cast sample and a decreased amount of $\beta$-phase. The sample annealed at $185^\circ \text{C}$ showed a large amount of the $\alpha$-phase and decreased amounts of the $\gamma$ and $\beta$-phases. The morphology of all three samples was investigated using AFM. The AFM showed large variations in sample morphology dependent on the crystalline phase.

Impedance spectroscopy was used to determine the real and imaginary parts of the dielectric constant over a large range of frequencies and temperatures and to verify that the amorphous regions in all the samples were similar. Samples were poled at $300 \text{ MV m}^{-1}$. Poling did not have a significant effect on the
impedance data. The dielectric relaxation noticeable in the frequency/temperature range was identified as the β-relaxation, which is due to the amorphous region in PVDF. The dielectric relaxation peak showed that the As-Cast sample had the highest crystalline fraction. Arrhenius plots showed that the activation energy of the relaxation was the same for all samples.

Polarization versus time curves were obtained using the double-wave method. A model was developed to account for the variation of the polarization reversal as a function of temperature and structural phase composition. Experimental data was used to show that the variation of the polarization reversal with temperature is likely due to a $kT$ term in the probability of nucleation. Experimental data also showed that variations in the structural composition lead changes in the probability of nucleation of polarization reversal. When the temperature and structural composition of the sample was taken into account, it was shown that switching in TMSC films follow a universal behavior.
References


Chapter 6 Summary and Future Work

Abstract

Major ideas and findings discussed in this thesis are summarized. Future work based off the findings of this thesis is suggested.

6.1 Summary of Work

The work in this dissertation primarily focused on the processing of polyvinylidene fluoride (PVDF) thin films via spin coating and thermal annealing. This work found that a primary cause for defects in spin coated films of PVDF solutions was vapor induced phase separation (VIPS). Using Flory-Huggins theory as a guide this work developed a temperature modulated spin coating process to deposit high quality ferroelectric thin film PVDF. This was the first demonstration of a general and easily implemented process to produce ferroelectric thin film PVDF on polar and non-polar substrates. The remnant polarization of these films were shown to be among the highest reported PVDF thin films deposited by any method. The phase composition of the films was manipulated by simple thermal annealing techniques. The dielectric and ferroelectric properties of the films were studied as a function of composition.

Chapter 1 introduced PVDF as a material and the problems posed trying to deposit it by traditional thin film techniques, such as spin coating. Potential applications for thin film PVDF were briefly discussed and the outline of the thesis was presented.
Chapter 2 investigated the cause of large pore defects present in spin coated PVDF. A humidity controlled spin coater was used to coat PVDF solutions onto reflective substrates in different relative humidity conditions. Small angle laser scattering (SALS) was used to study the formation of these pore defects in-situ. Scanning electron microscopy was used to study the final morphology of spin coated films. The morphology also supported a phase separation process. The scattering data in combination with the SEM micrographs suggested that the pore defects were caused by VIPS via spinodal decomposition. This was in contrast to the hypothesis that defect formation was caused by slow evaporation of the solvent. This understanding of the origins of the morphology of spin coated PVDF films allowed for the design of a process to mitigate these defects.

Chapter 3 summarizes the thermodynamics of VIPS using Flory-Huggins theory. It was argued that by varying the temperature, a solution that has undergone phase separation via spinodal decomposition can remix. This understanding is used to develop a process that modulates the temperature during spin coating to mitigate defects caused by VIPS and allowing the film to crystallize into one of the ferroelectric crystal phases of PVDF. This is the first process that has been shown to deposit high quality ferroelectric thin films of PVDF via spin coating on polar and non-polar substrates at relative humidities ranging from 20 to 80%. This contribution to the field allows for the repeatable, facile deposition of high quality PVDF thin films for device applications and simplifies the ongoing study of the fundamental properties of PVDF.
Chapter 4 develops a ferroelectric switching model for PVDF thin films. The model is developed using concepts of nucleation and local electric fields. It is shown that switching in PVDF occurs in two regimes: a fast regime and a slow regime. The model shows that a possible cause for the switching to occur in two regions is that the local electric field changes dramatically as a function of time. Initially, the local field decreases due to the polarization growing through a nucleation process. Then it increases due to the slow screening of local polarization gradients. The polarization growth in the fast regime is modeled using Avrami nucleation theory in which the electric field is varied in time. The fast regime is well-described by the model. The model fails to accurately reproduce the behavior of the second regime. This is thought to be due to the way the screening charge is produced. The polarization growth in the second region is shown to be consistent with Avrami nucleation, but uses non-physical parameters for the model, whereas the parameters in fast regime are shown to be representative of the nucleation probability.

Chapter 5 used simple annealing techniques to vary the phase content of TMSC PVDF films to study the change in dielectric and ferroelectric properties for the different phases of ferroelectric PVDF. FTIR was used to confirm the phase composition of each sample. The as cast sample had a mix of the β and γ phases. The sample annealed at 175 °C had an increased content of γ phase compared to the as cast sample and a decreased amount of β-phase. The sample annealed at 185 °C showed a large amount of the α-phase and decreased amounts of the γ and β-phases.
The morphology of all three samples was investigated using AFM. The AFM showed large variations in sample morphology dependent on the crystalline phase. Impedance spectroscopy was used to determine the real and imaginary parts of the dielectric constant over a large range of frequencies and temperatures. Samples were poled at 300 MV m\(^{-1}\). Poling did not have a significant effect on the real and imaginary parts of the dielectric constant.

The dielectric relaxation noticeable in the frequency/temperature range was identified as the β-relaxation, from the amorphous PVDF regions in the films. The dielectric relaxation peak showed that the As-Cast sample had the highest crystalline fraction. Arrhenius plots showed that the activation energy of the relaxation was the same for all samples.

Polarization growth versus time curves were obtained using the double-wave method. The polarization growth data showed that the sample with the highest amount of β-phase had the lowest minimum switching electric field and the sample with the largest amount of α-phase had the highest minimum switching field. These observations suggest that the all trans β-phase is the easiest to switch. The sample annealed at 175\(^{o}\) C had the highest polarization value of all the samples this suggest that the ferroelectric crystallites in this sample were able to orient with the applied electric field to a higher degree.

A model was developed to show that the temperature dependence of polarization reversal in all samples followed an Arrhenius-type behavior. The model was used to also show there is a difference in the energy needed to
reverse polarization in PVDF that depends on the structural phase of polymer chains in the film. All three samples showed similar switching kinetics after accounting for the temperature and structural phase.

6.2 Future Work

The ability to consistently produce high quality ferroelectric PVDF allows for the investigation of many different phenomena and the fabrication of many devices. Three of these ideas will be discussed here.

Solution Blended PMMA/PVDF composites

Although solution blended PMMA/PVDF compositions have been reported, they have had to be annealed at high temperatures or melted and cooled to improve the morphology of the film.\(^1, 2\) This annealing increases the crystallinity of the PVDF in the sample and improves the morphology of the film.\(^1, 2\) However, it is of technological interest to produce purely amorphous PVDF films for use, for instance, in energy storage applications because purely amorphous PVDF should not have a large amount of hysteresis, but still have a relatively large dielectric constant. The literature has shown that PMMA decreases the crystallinity of cast PVDF but this effect is diminished during high temperature annealing.\(^1, 2, 3\) Using the TMSC process a high quality film of PMMA/PVDF can be deposited without the need for high temperature annealing to improve the morphology. Such films should be investigated for the ability to store large amounts of energy with low losses.
Studying the properties of PVDF-Metal interfaces

In thin films, the interfaces can account for a large part of the dielectric behavior. Chapter 2 showed that the TMSC method can be used to deposit ferroelectric PVDF on a variety of different substrates. This allows for the in depth study on the effect of the interface on the dielectric and ferroelectric properties of PVDF.

Mechanical Properties of the Different Phases and Direct Measurement of the Pyroelectric Coefficient

The dielectric and ferroelectric properties of the different phases of PVDF were studied in this thesis and were shown to be similar for all 3 ferroelectric phases. Pei and Zheng suggest through DFT calculations that the Young’s modulus of PVDF can vary by a factor of 2 between the three different phases. Newsome and Andrie have shown experimental evidence that the measured pyroelectric coefficient is dominated by secondary (piezoelectric) effects. A lower Young’s modulus should lead to higher thermal expansion coefficient and therefore a larger pyroelectric coefficient. A study of the mechanical properties of the different phases along with the direct measurement of the pyroelectric coefficient is needed to show this.
6.3 Conclusion

The work presented in this dissertation has shown a robust, facile and repeatable process for the deposition of thin film ferroelectric PVDF. This process now can be used to produce films used to study various physical phenomena and devices. In this dissertation, the dielectric and ferroelectric properties of different compositions of PVDF were analyzed. Different PVDF structural phases lead to different switching characteristics that can be described by a change in the amount of energy needed to nucleate polarization reversal in the sample. The temperature behavior of the polarization reversal showed an Arrhenius behavior. When properly accounting for the structural phase and temperature switching in TMSC PVDF follows a universal behavior.

The understanding of processing of PVDF developed in this dissertation could lead to significant opportunities for the incorporation of ferroelectric PVDF in microelectronics and photonics. Finally, this dissertation puts forth a significantly different view of the dynamics of ferroelectric switching that may help in achieving PVDF’s full potential.
References


Appendix A: Methods

PVDF Films

PVDF powder with a melt viscosity of 28,000-34,000 poise was purchased from Polysciences Inc. The PVDF powder was dissolved in dimethylsulfoxide (DMSO) purchased from EMD Millipore to form a 12% solution by weight. The solution was deposited onto substrates by spin coating in a modified WS-650MZ-23NPP Laurell spin coater. The humidity was controlled in the spin coater from 20% to 80% relative humidity using a home built PID humidity controller. Temperature modulation of the substrate/film was accomplished by using a halogen bulb placed 7.5 cm above the spin coater chuck. Substrates consisted of Si-wafers covered with a native oxide (assumed to be SiO$_2$), aluminum (with native oxide, assumed to be Al$_2$O$_3$), or Au. The thickness of all films were in the range $1.3 \pm 0.2 \mu$m as measured by and AlphaStep profilometer.

Hotplate Annealing

To anneal PVDF samples a hotplate was heated to the specified temperature. Once the specified temperature was reached an half an hour was allotted to allow the temperature to stabilize. The films were then placed on the substrate for the time specified in the text.

Ferroelectric Testing

The double–wave method was used to measure the ferroelectric polarization switching in PVDF capacitors. A voltage pulse of one period of a sine wave was
used to set the polarization state of the PVDF films. Then a ½ period voltage pulse was used to switch the film; the current resulting from this voltage pulse has contributions from the ferroelectric switching, capacitive current, and leakage current. A second ½ period voltage pulse in the same direction is then applied across the film; the current resulting from this pulse has contributions from the capacitive current and leakage current. The current from these two pulses is subtracted from each other to give only the current from the ferroelectric switching. This current is integrated to give the polarization versus time behavior. For the hysteresis curves a triangle waveform was used with a period of .5 seconds for the polarization growth behavior a square pulse was used with 1 s period.
Appendix B: Nucleation Theory

Much of the following discussion on classical nucleation theory is developed from Crystal Growth for Beginners. When the chemical potentials of two infinite phases are in equilibrium the phases are in equilibrium and there is no thermodynamic driving force for one phase to transform in another phase. When the chemical potential of two infinite phases not in equilibrium the difference in chemical potential is the driving force for the transformation from one phase to another. In a constant temperature system a vapor phase can transform into a crystal phase with small deviations in pressure. Initially, the change in the chemical potential ($\Delta \mu$) is the difference between the chemical potential of the vapor phase and the crystalline phase Eq. 1.

$$\Delta \mu = \mu_v (P) - \mu_c (P).$$  \hspace{1cm} (Eq.1)

If $P$ is a pressure that is a small deviation from the equilibrium pressure $P_0$ (the chemical potential of both phases were equal) then we can write the change in chemical potential as the following where $\nu$ is the density of the phase.

$$\Delta \mu = (\mu_v (P) - \mu_v (P_0)) - (\mu_c (P) - \mu_c (P_0)),$$

$$\approx \int_{P_0}^{P} \frac{\partial \mu_v}{\partial P} \, dP - \int_{P_0}^{P} \frac{\partial \mu_c}{\partial P} \, dP,$$

$$= \int_{P_0}^{P} (\nu_v - \nu_c) \, dP,$$

$$\sim \int_{P_0}^{P} (\nu_v) \, dP,$$

If the vapor can be treated as an ideal gas the density ($\nu_v$) = $kT/P$ and then the change in chemical potential is...
\[ \Delta \mu = kT \ln \left( \frac{P}{P_0} \right). \]

One can do similar derivations for other systems as long as there is a way to express the change in chemical potential. When considering finite phases the surface area between the two phases has to be taken into account. For example for a liquid drop formed in a bulk vapor phase the Gibbs free energy at constant pressure and constant temperature is

\[ \Delta G = \mu_v dn_v + \mu_l dn_l + \sigma dS \]

If the system is in thermodynamic equilibrium (\( \Delta G = 0 \)) then we find the there is a finite difference in the chemical potentials of the two phases that does not drive a phase transformation but was used in creating a new surface separating the two phases.

In a system that is in thermodynamic equilibrium at a temperature >0K there will be fluctuations in the local composition (and Gibbs free energy). For example in a volume of liquid in thermodynamic equilibrium kept at constant pressure and temperature there will be microscopic fluctuations in the density throughout the volume. Since the liquid phase is the stable phase (\( \mu_l < \mu_s \) or \( \mu_v \)) these fluctuations in density will always decay back to macroscopic density of the liquid phase. If we lowered (raised) the temperature of the liquid to the point where the solid phase (vapor phase) had a lower chemical potential then the density fluctuations that lead to a transformation to the lower chemical potential phase will grow eventually converting the entire liquid into a solid (vapor).
To illustrate the idea of homogenous nucleation we will follow the example from Crystal Growth from Beginners of a liquid droplet forming in the bulk vapor phase. Initially the Gibbs free energy of the system is

\[ G_1 = n_v \mu_v. \]

A liquid drop formed in the system will have a Gibbs free energy of

\[ G_2(n_l) = n_l \mu_l + 4\pi r^2 \sigma. \]

In a closed system the molecules that form the liquid drop come from the initial molecules that were in the vapor phase. The Gibbs free energy of the system can be written as

\[ G_{sys} = (n_v - n_l) \mu_v + n_l \mu_l + 4\pi r^2 \sigma. \]

The change in the Gibbs free energy is therefore \( G_{sys} - G_1 \)

\[ \Delta G_{sys} = n_l \mu_l + 4\pi r^2 \sigma - n_v \mu_v. \]

or

\[ \Delta G_{sys} = -n_l (\mu_v - \mu_l) + 4\pi r^2 \sigma. \]

This relation shows us that the change in the Gibbs free energy is the difference between the thermodynamic potential of the droplet with a number of molecules and the same number of molecules in the vapor phase. The relation also makes clear the concept of a critical radius. The volume of a droplet (and the number of molecules in it) are related to radius of the droplet. For a spherical liquid droplet the number of molecules in the droplet is \( 4\pi r^3 / v \) with \( v \) being the volume of one molecule. The change in the Gibbs free energy can be written as

\[ \Delta G_{sys} = - (4\pi r^3 / v)(\mu_v - \mu_l) + 4\pi r^2 \sigma. \]
Written in this form it is easy to see that when $\mu_v > \mu_l$ that there is a maximum in the Gibbs free energy at some critical radius and the free energy decreases as the radius of the droplet becomes bigger than the critical radius. In the case where $\mu_v < \mu_l$ the Gibbs free energy increases as the vapor droplet forms and grows meaning that droplet formations in thermodynamically prohibited. The change in the Gibbs free energy of the system at the critical radius is zero however this equilibrium is not a stable equilibrium any small increase or decrease to the volume of the droplet will cause the droplet to grow or shrink without a thermodynamic barrier. It should be noted that the previous derivation did not take into account the effect that a surface would have on the formation of a droplet (homogenous nucleation vs heterogeneous nucleation). Although the formulation will not be derived here in general a surface that the liquid wets lowers the the change in the free energy to form a nucleus (droplet of the critical radius).

Formation of droplets with a radius equal to the critical radius (nucleation) is a random process, and we can use statistical analysis to find the rate the these nuclei form. Derivation of the nucleation rate follows that presented in Crystal Growth for Beginners. This derivation adopts the following assumptions

1. The growing droplets preserve a constant geometrical shape which coincides with the equilibrium one.
2. Clusters of molecules of size $N$ where $N$ is larger than the number of molecules in a droplet with a critical radius are removed from the system and replaced by $N$ single molecules. This is to ensure that the difference in chemical potential between the two phases is kept constant.

3. The nucleation process is considered as a series of bimolecular reactions

$$A_n + A_1 \rightleftharpoons A_{n+1}.$$  

The reaction rate $w_{n+}$ is the rate the reaction proceeds to the right and $w_{n-}$ is the rate the reaction proceeds to the left. Generally, the change of the concentration, $Z_n(t)$, of clusters with the size $n$ in time is given by

$$\frac{dZ_n(t)}{dt} = w_{n-1}^+ Z_{n-1}(t) - w_n^- Z_n(t) - w_n^+ Z_n(t) + w_{n+1}^- Z_{n+1}(t),$$

by introducing a flux of clusters through size $n$,

$$J_n(t) = w_{n-1}^+ Z_{n-1}(t) - w_n^- Z_n(t),$$

the change in concentration of clusters becomes

$$\frac{dZ_n(t)}{dt} = J_n(t) - J_{n+1}(t),$$

in the steady state the change in concentration of clusters is zero and

$$J_n(t) = J_{n+1}(t) = J_0.$$  

The result is that the steady state rate of formation of clusters of size $n$ does not depend $n$. To find the steady state formation of clusters that are of the size $N$ where $N$ is the critical size we write down the flux of clusters from size $n=1$ to size $n=N$. 

145
\[ J_0(t) = w^+_n Z_n(t) - w^-_{n+1} Z_{n+1}(t) \]

... \[ J_0(t) = w^+_{N-1} Z_{N-1}(t) - w^-_{N} Z_N(t). \]

Because of assumption number 2 we know that \( Z_n = 0 \) and then the equation for the flux through \( N \) is

\[ J_0(t) = w^+_{N-1} Z_{N-1}(t). \]

Following Crystal Growth for Beginners we use the method of Becker and Doring and multiply each equation by a ratio of rate constants, sum up the equations and with some algebraic manipulation the the flux of clusters through \( N \)

\[ J_0(t) = Z_1 \left[ \sum_{n=1}^{N-1} \frac{1}{w^+_n w^-_1 w^+_2 \ldots w^+_n w^-_{n-1}} \right]^{-1}. \]

This flux is the general expression for the nucleation rate in the steady state and is only dependent on the initial concentration and the rate constants for adding and subtracting molecules from clusters. In the special case when the addition of a molecule to a cluster is due to collisions the rate constant for growth is

\[ w^+_{n-1} = \frac{P}{(2\pi mkT)^{1/2}} \sigma_{n-1}, \]

where \( P/(2\pi mkT)^{1/2} \) is the number of collisions per unit area and \( \sigma \) is the surface area of a cluster of size \( n-1 \), with \( P \) being the vapor pressure available in the system. The rate constant for the removal of a molecule from the cluster is

\[ w^-_n = \frac{P_n}{(2\pi mkT)^{1/2}} \sigma_{n-1}, \]
Where $P_n$ is the vapor pressure of a cluster of size $n$. In equilibrium conditions $J_0$ is zero and we find the equilibrium concentration of clusters of size $N$ to be

$$n_N = n_1 \exp\left(-\frac{\Delta G_N}{kT}\right).$$

To find the steady state nucleation rate we convert the sum in the equation for the flux of clusters though size $N$ with an integral, use the appropriate rates for addition and subtraction of a molecule from a cluster and find that the nucleation rate is

$$J_0 = \omega^* \Gamma Z_1 \exp\left(-\frac{\Delta G}{kT}\right),$$

where $\Gamma$ is

$$\Gamma = \left(\frac{\Delta G}{3\pi kTN^2}\right)^{1/2},$$

and is called the Zeldovich factor. Assuming that $n_1$ is equal to $Z_1$ we can right the nucleation rate as

$$J_0 = \omega^* \Gamma Z_1 n_N.$$