Ferroelectric Doping of Graphene for Flexible Transparent Electrodes

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ABSTRACT
Owing to its excellent optical transparency, electrical properties and mechanical strength, graphene shows great potential for the applications of flexible transparent electrodes. The sheet resistance of graphene can be engineered by non-volatile doping with a ferroelectric film of P(VDF-TrFE). The ferroelectric property of P(VDF-TrFE) is essential to the performance of this graphene-ferroelectric hybrid structure. This project studied how several processing parameters affect spin-coated P(VDF-TrFE) 70/30 copolymer, especially its ferroelectric performance. Aspects discussed in the thesis include grain and surface morphology, thickness, crystallinity and remnant polarization.
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CHAPTER ONE  INTRODUCTION

This chapter lays the background of this project. First, it introduces transparent conductive electrodes and how graphene fits into the picture. The next section explains sheet resistance of graphene and ways of enhancement. Then basics of P(VDF-TrFE) are introduced with a focus on its ferroelectric property. The following section explains how ferroelectric P(VDF-TrFE) reduces the sheet resistance of graphene and briefly introduces graphene-ferroelectric hybrid structure. Lastly, two objectives of this project are presented with a focus on the latter.
1.1 Transparent Conductive Electrodes (TCE)

1.1.1 TCE and materials

Transparent conductive electrodes (TCE) are an essential part of many modern electronic devices such as touch screens, flat panel displays, light-emitting diodes and solar cells. TCE allow light to pass through while functioning as an electrode. Two basic requirements for candidate materials are high electrical conductivity and optical transparency [1,2,3].

Currently, the dominant material for transparent electrodes is indium tin oxide (ITO) with sheet resistance ~10 Ω/□ for a transmittance of ~85% [1]. Despite ITO’s excellent performance in optoelectronic devices, people have been looking for its replacement due to several drawbacks. Firstly, resource of indium is limited and it is becoming more expensive due to high demand [1,2,3]. Secondly, the deposition of ITO is costly and slow [4]. Last but not least, ITO’s brittle nature limits its use in flexible electronics.

Future electronic devices will require lightweight, flexible and large-scale transparent electrodes that can be produced at low cost [3]. Potential alternatives of ITO include graphene, carbon nanotubes and metal nanowires with their own advantages and disadvantages [2]. This project will focus on graphene.

1.1.2 Graphene as Flexible Transparent Electrodes

Graphene is a single layer of carbon atoms arranged in a honeycomb lattice (Figure 1). Graphene possesses exceptional properties that both facilitate studies on fundamental physics and allow numerous possible applications [5]. As an atomic layer, graphene displays high optical transmittance of 97.7% in the visible light spectrum. Carrier mobility of graphene is exceptionally high in nature, and it is still high at high carrier concentrations for both electric and chemical doping [5]. Due to the tight carbon-carbon bond, graphene is superior in endurance, and its excellent fracture strain makes it suitable for bendable and rollable devices.

Figure 1 Honeycomb structure of graphene [5]
Graphene was initially fabricated by mechanical exfoliation with a tape. Despite its high quality, the size of exfoliated graphene (~1000μm$^2$) is too small for common applications. A lot of efforts have been devoted to large-scale graphene fabrication. One promising direction is chemical vapor deposition (CVD). 30 × 30 inch graphene has been successfully produced in a roll-to-roll process$^{[6]}$. In this project, CVD graphene is used.

1.2 Engineering Sheet Resistance of Graphene

Sheet resistance of graphene can be engineered to meet the requirement for transparent electrode applications. The intrinsic Fermi level of graphene is at the Dirac point, where density of states is zero and conductivity at its minimum. In order to meet the requirements of TCE applications, conductivity of graphene needs to be engineered. Since graphene is a 2D material, it is more convenient to speak about sheet resistance than conductivity. Sheet resistance $R_s$ is inversely proportional to conductivity $\sigma$ by

$$R_s = \frac{1}{\sigma t} \quad (1)$$

where $t$ is the film thickness. Conductivity $\sigma$, carrier density $n$, electron charge $e$, carrier mobility $\mu$ are related by

$$\sigma = ne\mu \quad (2)$$

Sources affecting the carrier mobility of graphene include its quality, substrate, transfer and contamination. To minimize substrate-induced scattering, the substrate should have minimum charge impurities and be flat. Residues should be minimized during the transfer of graphene from copper to other substrate to avoid trapping of impurities. Also, all procedures should be conducted in a clean environment to avoid contamination.

Increase in conductivity is realized through increase of carrier density, which can be achieved by chemical doping or electric field doping.

In chemical doping, graphene can be p or n doped through surface transfer or substitutional doping. This method allows various chemical species to be introduced in graphene. However, chemical suffers from stability issues. Adsorbed chemicals could desorb from surface of graphene and they might also react with ambient molecules from the environment, such as oxygen or water. Also, it still remains a challenge to control the amount of dopants introduced into graphene$^{[7]}$. 

3
Electric field doping is the method adopted in this project. The ambipolar electric field effect of graphene allows continuous tuning of charge carriers between electrons and holes. Figure 2(a) shows schematic band structure of graphene with Fermi level below, at and above direct point, which corresponds to p-doped, undoped and n-doped graphene respectively. Since graphene has linear dispersion relation near Dirac point, induced charge density is linearly proportional to an applied gate voltage. Figure 3 shows a typical configuration for gated graphene. For example, if a positive (negative) gate-voltage $V_g$ is applied, graphene will be n-doped (p-doped) with electron (hole) concentration of $n = \alpha V_g$, where $\alpha$ is a constant depending on the dielectric. At zero gate-voltage, the conductivity reaches its minimum, and it decreases as the absolute value of gate-voltage increase (Figure 2(b)).

![Figure 2a) Schematic band structures of graphene with different gate voltage (see b)) and resulting positions of Fermi level; b) Typical conductivity as a function of gate voltage](image1)

![Figure 3 Typical structure of back-gated graphene with source and drain](image2)
To obtain the lowest possible sheet resistance it is desirable to apply a constant high electric field to induce charge carriers in graphene. However, it is difficult and impractical to sustain a gate voltage at all times. To this end, the dielectric (SiO$_2$) can be replaced by a ferroelectric film which is able to maintain an electric field and hereby a certain level of doping in graphene, even when the voltage is removed from the gate. Furthermore by using a ferroelectric polymer such as PVDF-TrFE we can create flexible, transparent devices allowing for a new generation of electronics.

1.3 Ferroelectricity of P(VDF-TrFE)
1.3.1 Ferroelectricity

Ferroelectric materials have spontaneous polarization that can be reversed repeatedly by an external electric field, and the polarization remains upon the removal of electric field (Figure 4) [9]. A hysteresis loop is observed if polarization is plotted applied electric field. Ferroelectric and paraelectric phase can exist in ferroelectric materials. The former behaves as non-polar dielectrics, whereas the latter displays disorder in dipole orientations. Several important characteristics of ferroelectric materials include Curie transition (transition between ferroelectricity and paraelectricity or between order and disorder at Curie temperature), domains (a microscopic region where polarization is homogenous), coercive field $E_C$ (critical electric field that turn polarized ferroelectric material to zero polarization), and remnant polarization $P_r$ (remaining polarization after removal of electric field).

Figure 4 A schematic diagram of the alignment of dipoles under an external electric field [9]
Research on ferroelectric materials started in the 1920s with the study of Rochelle salt\textsuperscript{[10]}. Some typical examples include ferroelectric ceramics based on titania such as BaTiO\textsubscript{3} and PbTiO\textsubscript{3}. Numerous efforts have also been spent on ferroelectric polymers. Compared to brittle ferroelectric ceramics, polymers are bendable and tolerant higher mechanical stress which makes them suitable for flexible electronic applications\textsuperscript{[11]}. In addition, ferroelectric polymers have advantages such as low-cost manufacturing, lightness, chemically stable and good resistance to degradation\textsuperscript{[12]}. Ferroelectric materials are useful for a wide range of applications\textsuperscript{[13]}. For example, the electric bistability makes ferroelectric materials useful for non-volatile memory devices such as ferroelectric random access memory and ferroelectric field effect transistors.

1.3.2 \textit{P(VDF-TrFE)}

Ferroelectricity of PVDF was discovered following studies on its piezoelectricity, pyroelectricity and nonlinear optical properties. Since then, a number of ferroelectric polymers have been found to possess ferroelectric properties\textsuperscript{[9]}. Among them, PVDF and its copolymers attract the most attention because of their large spontaneous polarization and chemical stability\textsuperscript{[14]}. PVDF has a mixture of crystalline and amorphous regions consisting repeating monomer units of –CH\textsubscript{2}-CF\textsubscript{2}– (Figure 6). Ferroelectricity arises in PVDF due to the large electronegativity between fluorine, carbon and hydrogen. PVDF can crystallize into 4
different conformations: \( \alpha \), \( \beta \), \( \gamma \) and \( \delta \). The \( \alpha \) and \( \beta \) phases are most commonly seen in practical situations. The \( \alpha \) phase has the lowest energy and exhibits no ferroelectricity as its molecules are arranged in a distorted TGTG’ configuration. Most interests in PVDF have been focused on the \( \beta \) phase because it has the largest dipole moment among all phases. To produce the \( \beta \) phase-PVDF, it is required that \( \alpha \) phase-PVDF be stretched to around 300% of its original length at a temperature of about 100°C.

![Figure 6 All-trans conformation of \( \beta \) phase-PVDF chain with carbon backbone](image)

For technical applications, TrFE (-CF\(_2\)-CFH) can be added into PVDF such that \( \beta \) phase can be achieved without stretching. TrFE increases the size of unit cell and inter-planar distance because a fluorine atom takes the place of smaller hydrogen atom. This resulted in a decrease of Curie temperature respective to its melting temperature. If the right amount of TrFE is added, P(VDF-TrFE) could display Curie transition before melting and so may crystalline into \( \beta \) phase directly without mechanical stretching. Also, the all trans \( \beta \) phase of P(VDF-TrFE) is more stable than PVDF as TrFE is introduced into PVDF chains \[^{15}\]. The properties of P(VDF-TrFE) are affected by the ratio of VDF/TrFE content. In this project, PVDF/TrFE ratio of 70/30 was used.

P(VDF-TrFE) shares similar properties with PVDF. Among its 4 phases, only the \( \beta \) phase is polar and it spontaneously polarizes in a direction parallel to the carbon-fluorine dipoles (Figure 7) \[^{14}\]. The focus of the project is on the \( \beta \) phase of P(VDF-TrFE) 70/30 copolymer.

![Figure 7a) A schematic of the crystal structure of \( \beta \) phase-P(VDF-TrFE) in plane ab, and b) the zig-zag chain along c axis](image)
1.4 Graphene-Ferroelectric Hybrid Structure

Carrier concentration in graphene can be tuned by electric field effect with a gate voltage. In order to maintain the electric field upon removal of the gate voltage, a ferroelectric film of β phase-P(VDF-TrFE) could be utilized as a gate. For example, as shown in Figure 8, if a negative gate voltage is applied, polarization in P(VDF-TrFE) film will point upwards. Graphene will be p-doped with holes. When the gate voltage is removed, the polarization remains due to the ferroelectric property of β phase-P(VDF-TrFE). Thus, graphene remains p-doped and a low sheet resistance is maintained. It has been shown that on-volatile doping with P(VDF-TrFE) can achieve a carrier density of up to $3 \times 10^{13}/\text{cm}^2$ \cite{16}.

Figure 8 Schematic of doping in graphene P(VDF-TrFE) hybrid structure

It has been shown that the transparency of the stack is above 90%, satisfying the requirement for TCE applications \cite{1,16}. The optical transmittance of a graphene-P(VDF-TrFE) hybrid structure and pure P(VDF-TrFE) thin film from visible to UV wavelength is shown in Figure 9.

Figure 9 Optical transmittance of a graphene-P(VDF-TrFE) stack and pure P(VDF-TrFE) thin film from visible to UV wavelength \cite{16}
In reality, sheet resistance of graphene increases gradually over time. Figure 10 shows the increase of sheet resistance over a period of 24 hours for a graphene-P(VDF-TrFE) transparent electrode. Such degradation of sheet resistance may be caused by an interfacial layer between and P(VDF-TrFE) created accidentally in the transfer of CVD graphene from copper to the substrate. An improvement in graphene transfer and interface engineering could alleviate the problem \[^{16}\]. However, the increase of resistance over time could not be avoided.

![Figure 10 Increase of sheet resistance over a period of 24 hours for a graphene-P(VDF-TrFE) transparent electrode \[^{16}\]](image)

A voltage could be applied at a certain time interval to reset the sheet resistance, as shown in Figure 11. This voltage should be large enough to allow a full polarization. A typical polarization field is around 100V/μm. From \(V = E \times d\), where \(V\) is voltage, \(E\) is electric field and \(d\) is the thickness of P(VDF-TrFE) film, 50V is needed for a film thickness of 500nm. To make the application portable and energy-friendly, a low reset voltage is desired. This requires a uniform P(VDF-TrFE) film as thin as possible.

![Figure 11 Reset sheet resistance of graphene in graphene P(VDF-TrFE) hybrid structure with a periodic voltage \[^{17}\]](image)
1.5 Objectives
This project is under the group’s main goal of achieving low and stable sheet resistance of graphene. Several projects are being carried out in the group towards the same end, such as investigation of sheet resistance of large-scale graphene by bar-coating and transfer and doping of graphene with P(VDF-TrFE).

1.5.1 Ultrathin P(VDF-TrFE) Film
The initial objective of this project is to produce ultrathin P(VDF-TrFE) film by spin-coating. The incentives are described in the previous section. Such film should be ideally around 30nm corresponding to an operation voltage of around 3V.

The thickness requirement was achieved, however, it was not possible to incorporate such film in a functional graphene P(VDF-TrFE) hybrid structure at current experimental setup due to leakage current stemming from pin-holes.

This led to a change of research direction which is the second objective of the project. However, the main goal still remains, which is to achieve low and stable sheet resistance of graphene.

1.5.2 Ferroelectric Phase In P(VDF-TrFE)
A high remnant polarization is desired since higher carrier density could be induced in graphene. Since β phase is responsible for the ferroelectricity of P(VDF-TrFE), the amount of β phase in P(VDF-TrFE) film directly affects the remnant polarization.

The objective is to investigate how variations in different parameters affect the ferroelectric phase of spin-coated P(VDF-TrFE) film. The parameters involved are annealing temperature, concentration of P(VDF-TrFE) in solvent, solvent and substrate.
CHAPTER TWO  MATERIALS AND METHODOLOGY

In this chapter, materials, processing methods and characterization methods are intruded. The first section introduces the chemicals and substrates used. The next section explains important experimental procedures involved in the project such as spin-coating, annealing and thermal evaporation. The last section explains how spin-coated P(VDF-TrFE) are characterized with different experimental techniques including AFM, XRD and hysteresis measurements.
2.1 Materials

2.1.1 Chemicals

Chemicals used in this project were P(VDF-TrFE) 70/30 copolymer powder from Piezotech, Dimethylformamide (DMF), cyclohexanone and acetone.

2.1.2 Solutions

5 wt% P(VDF-TrFE) in DMF, acetone and acetone/DMF (1:1 by volume) were prepared by completely dissolving the right amount of P(VDF-TrFE) in respective solvents on a magnetic stirrer for no shorter than 4 hours. 3 wt%, 10 wt% and 15 wt% P(VDF-TrFE) in DMF were made with the same recipe but different amount of P(VDF-TrFE). 5 wt% P(VDF-TrFE) in cyclohexanone was prepared by completely dissolving P(VDF-TrFE) in cyclohexanone at 60°C on a magnetic stirrer for 5 hours.

The default solution concentration was 5 wt% and the default solvent was DMF unless otherwise stated.

2.1.3 Substrates

Au/SiO₂ was prepared by thermal evaporation of 3nm Cr and 80nm gold on bought SiO₂/Si wafer. Graphene on Cu was prepared by standard chemical vapor deposition of CH₄ at 1000°C. Graphene on SiO₂/Si was prepared by transferring graphene from Cu to SiO₂/Si with PMMA.

The default substrate was Au/ SiO₂.

2.2 Processing

2.2.1 Spin-Coating

Before spin-coating, all substrates were kept clean and heated on a hotplate for 10 minutes to remove water molecules. Substrates were spin-coated in nitrogen environment in two steps: 1) 500rpm for 5 seconds to spread the solution and 2) spin-coat at a certain speed for 60 seconds. The default spin-coating speed in the second step was 2000rpm.

The spin-coater used (SPIN 150 from Polos) is shown in Figure 12, and nitrogen enters through the black tube on the lid.
2.2.2 Annealing

To enhance the crystallinity of P(VDF-TrFE), post-spin-coat annealing is necessary. The standard annealing temperature in the group is 135ºC, and this was the default annealing temperature in this project unless otherwise stated. The standard annealing time is 20 hours. Due to the large number of samples involved and the availability of the oven, the default annealing time was 2 hours unless otherwise stated.

2.2.3 Thermal Evaporation

Gold contacts were deposited with thermal evaporator through a metal stencil mask. 3nm chromium was deposited before depositing 80nm gold to enhance adhesion. Cr boat and Au boat were not close to each other at the bottom of the chamber. As Cr and Au travel across the chamber to land on the substrate at the top of the chamber, a misalignment could not be avoided, especially for chips near the edge of sample holder (Figure 13 a)). To minimize error in effective contact area, contact areas were determined individually for every chip with ImageJ (Figure 13 b)).
2.3 Characterization

2.3.1 AFM

P(VDF-TrFE) films were observed with Atomic Force Microscopy (AFM) in tapping mode. AFM belongs to the family of scanning probe microscopy. Surface topography is generated by monitor and regulation of the localized mechanical interaction between the probe and the surface. A laser beam is reflected from the cantilever beam, whose deflection and vibration is sensed by a photodiode array. The tapping mode of AFM is useful for non-destructive imaging for soft materials. The cantilever beam is activated by a piezoelectric driver close to its resonant frequency. When the tip-sample distance changes the oscillation amplitude of the tip is affected and a feedback system will move the tip closer or further from the sample to keep the oscillation at a constant amplitude. The data from the feedback system then creates a mapping of the sample topography.

The AFM used is Dimension Fastscan from Bruker. The software Nanoscope Analysis was extensively used to observe and process AFM images.

2.3.1.1 Thickness

The thickness of P(VDF-TrFE) film was obtained by measuring height difference with AFM. Scratches were made by a tweezer on P(VDF-TrFE) films to expose the substrate (Figure 14 left)), then the height difference between the substrate surface and film surface was measurement with AFM, usually at a scale of 20μm × 20μm.

For thicker films, such as P(VDF-TrFE) film cast by 15% P(VDF-TrFE) in DMF, scratches created thick and broad edges that the true thickness could not be obtained with AFM (Figure 14 right)). In this case, the P(VDF-TrFE) films (with top contacts) were treated by oxygen plasma to remove P(VDF-TrFE) and expose the substrate between contacts such that devices were isolated. Height of P(VDF-TrFE) film was obtained by subtracting the thickness of top contacts from the contact-substrate distance measured by AFM.
2.3.1.2 Grain morphology and Roughness

P(VDF-TrFE) grains were observe by AFM at 1μm × 1μm. Since Nanoscope Analysis is not suitable for selection of grains and area measurements in non-uniform samples, grain sizes were obtained by outlining grains on AFM images with ImageJ (Figure 15). Length and width of grains were measured from the depth profile in Nanoscope Analysis (Figure 16). On every chip, 4 grains were measured to minimize anomaly.

Surface of P(VDF-TrFE) film was observed also at 10μm × 10μm and 30μm × 30μm. Surface roughness was measured from 10μm × 10μm AFM images.
2.3.2 XRD

X-ray diffraction (XRD) was used for the identification of ferroelectric phase in P(VDF-TrFE) film. Wavelength of X-ray (0.5 Å ~ 2.5 Å) is on the same order of magnitude as the lattice spacing of most crystalline materials. When a sample is irradiated with incident X-ray at a range of angles, a characteristic diffraction pattern is produced from its crystal structure. This is because constructive interferences of reflected X-ray only happen at specific directions. The condition is expressed as the Bragg’s Law, as shown schematically in Figure 17.

\[ 2d \sin \theta = n\lambda \]

Where \( d \) is the lattice spacing and \( n \) is an integer.

In the XRD pattern of spin-coated P(VDF-TrFE) 70/30 copolymer, a characteristic peak occurs at around \( \theta_0 = 20^\circ \) that represents the ferroelectric \( \beta \) phase\textsuperscript{[14]}. XRD characteristic
peaks for other phases in spin-coated P(VDF-TrFE) 70/30 copolymer were seldom mentioned in a lot of studies, thus their specific positions were unclear from literatures.

X-ray diffraction analysis was carried out with Philips X’Pert XRD. Cu-Kα radiation ($\lambda_{K\alpha 1} = 1.540598 \text{Å}, \lambda_{K\alpha 2} = 1.544426 \text{Å}, \lambda_{K\alpha 1}/\lambda_{K\alpha 2} = 0.500$) was the source at the generator voltage of 40 kV and tube current of 30 mA. The scan range was $15^\circ - 30^\circ$ with a step of $0.02^\circ$ at a rate of 0.7 second per step. The software Origin 8.6 was used for data processing.

XRD patterns were fitted with Gaussian function. P(VDF-TrFE) is a semi-crystalline poly that contains various amount of amorphous phase. To offset the broadening of peak due to the amorphous phase, the ratio of peak height ($H$) versus full width at half maximum ($FWHM$) was used to evaluate the amount of crystallinity. XRD patterns shown in section 3.2 were smoothed with adjacent-averaging with a window of 10 (0.2°).

### 2.3.3 Electrical Measurements

Polarization-Voltage hysteresis loops were obtained by Precision Multiferroic tester. The probe station is shown in Figure 18. Values of coercive field and remnant polarization were obtained from the hysteresis loop as shown in Figure 5 in section 1.3.1.

![Figure 18 The probe station used in the project](image)
In this chapter, experimental results are presented and discussed. It is divided into two sections corresponding to the two objectives of the project with a focus on the latter. The reason for changing the objective is explained. Nevertheless, findings on thickness in section 3.1 are useful in explaining results in section 3.2. In section 3.2, the effect of annealing temperature, solution concentration, solvent and substrate were discussed.
3.1 Ultrathin P(VDF-TrFE) Film

3.1.1 Spin-Coat Speed and Thickness

Spin-coating speed was varied from 1000rpm to 5000rpm and the resulting thickness is shown in Figure 19. The solution used in this section was 10% P(VDF-TrFE) in DMF. The thickness decreased with increasing speed and it started to saturate at 4000rpm. The grain size also varied with different speed. The grain size increased with increasing spin-coat speed until 3000rpm when it started to decrease. The length and width were monitored and it was found that with increasing speed, the length increased while thickness decreased and grains became more elongated (Figure 20).

![Figure 19 Thickness as a function of spin-coating speed](image)

![Figure 20 Length and width of P(VDF-TrFE) grain as a function of spin-coating speed](image)
The fact that thickness started to saturate at higher spin-coating speed suggested that varying spin-coating speed is not going to produce ultrathin film from 10% P(VDF-TrFE).

3.1.2 Concentration and Thickness

Lower concentration of P(VDF-TrFE) in DMF were tested and the resultant thickness is shown in Figure 21. Generally, concentration decreased with more dilute solution used. At a concentration of 2%, film thickness was around 50nm. As the concentration was lowered down to 2%, the film did not stay on the substrate (Figure 22).

![Figure 21 Thickness as a function of concentration](image)

Figure 21 Thickness as a function of concentration

![Figure 22 P(VDF-TrFE) in DMF did not stay on SiO2 substrate at a concentration of 2%](image)

Figure 22 P(VDF-TrFE) in DMF did not stay on SiO2 substrate at a concentration of 2%

By decreasing the concentration, thinner film could be obtained. However, before the target thickness of 30nm was achieved, the poor adhesion stopped the attempts at lower concentrations below 2%.

3.1.3 Solvent and Thickness

Different solvents were attempted for 5% P(VDF-TrFE) solution. The thickness of P(VDF-TrFE) film cast from cyclohexanone, DMF, acetone and acetone/DMF is shown in Figure 23.
At the same concentration, cyclohexanone gave the least thickness of around 160nm. Thus cyclohexanone was tested for lower concentrations. A 3% solution resulted in a film thickness of 112nm. At 1%, 25nm-thick P(VDF-TrFE) film was achieved.

At this thickness, unlike that cast by 2% DMF, P(VDF-TrFE) stayed on the substrate. However, a number of deep pin holes were found on the film, as shown by the depth profile in Figure 24. The current experimental setup requires a top gate to polarize the P(VDF-TrFE) film. Au/P(VDF-TrFE)/Au devices with 1% P(VDF-TrFE) in cyclohexanone failed at polarization due to high leakage currents, which was due to the pin holes found in the film. The film could be polarized instead with corona poling, which does not require a top gate. However, it was not feasible with the current experimental setup.

Figure 23 Thickness of P(VDF-TrFE) film cast from cyclohexanone, DMF, acetone and acetone/DMF

Figure 24 Depth profile of P(VDF-TrFE) film cast from cyclohexanone at a concentration of 1%
3.2 Ferroelectricity of P(VDF-TrFE)

3.2.1 Annealing Temperature Test

Figure 25 shows the surface of as-cast and annealed P(VDF-TrFE) films at different temperatures observed by AFM at size 1μm × 1μm. The grain size of P(VDF-TrFE) displayed a growing trend for films annealed at increasing temperatures. As-cast films were constituted of small granules sized around 0.0005μm², which were more than 100 times smaller than those annealed at 140°C. Figure 26 shows how grain sizes changed with annealing temperature. At 150°C and 170°C, the grain structures could not be clearly observed, thus grain size was not measured for films annealed at these temperatures. Changes in grain shape were also observed. From 135°C onwards, it was clear that, as the grains grew larger, they started to elongate. At 150°C, the grains further grew into intercrossed needle-like shapes, resulting in a porous surface.
Figure 25 AFM images of P(VDF-TrFE) films (a) as-cast, annealed at (b) 100 °C, (c) 125°C, (d) 130°C, (e) 135°C, (f) 140°C, (g) 150°C and (h) 170°C at $1\mu$m × $1\mu$m
Figure 26 Grain size of P(VDF-TrFE) films annealed at different annealing temperatures

Figure 27 shows AFM images of as-cast and annealed P(VDF-TrFE) films at 10μm × 10μm. Root-mean-square (RMS) roughness of P(VDF-TrFE) film was plotted against annealing temperature (Figure 28).
Figure 27 AFM images of P(VDF-TrFE) films (a) as-cast, annealed at (b) 100°C, (c) 125°C, (d) 130°C, (e) 135°C, (f) 140°C, (g) 150°C and (h) 170°C at 10μm × 10μm
Figure 28 Surface RMS roughness of P(VDF-TrFE) film at annealing temperatures

XRD patterns of P(VDF-TrFE) films annealed at different temperatures are shown in Figure 29. H/FWHM ratio is plotted against annealing temperature in Figure 30. It is clear that annealing could enhance crystallinity. Crystallinity increased with increasing annealing temperature till 135°C, then it decreased slightly at 140°C. At 150°C, there was an abrupt rise of crystallinity. 170°C witnessed a decrease of crystallinity, which was still a lot larger than that below 150°C.

Figure 29 XRD patterns of P(VDF-TrFE) films annealed at different annealing temperatures
The electrical performance of P(VDF-TrFE) films annealed at different temperatures was evaluated. Polarization-voltage hysteresis loops were obtained by voltage sweeps from -30V to 30V. 30V was chosen as the maximum polarization voltage, since it was large enough for a full polarization yet not causing any breakdown for any P(VDF-TrFE) films involved in this test.

Remnant polarization is plotted as a function of annealing temperature in Figure 31. As-cast films did not display a remnant polarization. From 100°C to 135°C, with increasing annealing temperature, remnant polarization increased accordingly and peaked at 140°C. At 150°C and 170°C, remnant polarization dropped to values similar to those at 130°C and 135°C.
As the grain sizes of as-cast films were very small, AFM images at 10μm × 10μm suggests that the surface roughness was mainly contributed by the uneven distribution of materials during spin-coating. When the annealing temperature increased to 100°C and 125°C, surface roughness increased only slightly due to the formation of larger grains. At 130°C and 135°C, even larger gains were formed such that it overcame some of the roughness due to the initial uneven distribution of materials. At 140°C, P(VDF-TrFE) grains were 10 times larger those at 135°C, which was reflected as an increase in surface roughness. When annealed at 150°C and 170°C, grain-like structures disappeared and turned into intercrossed needles, and large pores started to form on the surface. This caused the sudden leap in roughness. The drastic change in morphology at annealing temperatures of 150°C and 170°C agrees with the melting temperature of P(VDF-TrFE) at around 150°C, where the copolymer re-crystallized during the cooling process.[14,18]

In the XRD pattern, the sharp peak at around 2θ=20°is assigned to (100) and (200) reflection from the ferroelectric β phase.[14,19] With Bragg’s equation, the inter-planer spacing was calculated to be around 4.5 Å, which agrees with earlier studies.

Linking the results from XRD and electrical measurements, the increase of remnant polarization till 135°C could be explained by higher content of ferroelectric phase in P(VDF-TrFE) films. The amount of ferroelectric phase peaked at 135°C, while remnant polarization peaked at 140°C. According to several previous studies, ellipsoidal grains indicate a preferable orientation of P(VDF-TrFE) chains parallel to the substrate, which is the desirable orientation for vertical polarization.[19] While the amount of ferroelectric phase is important for the switching behavior of P(VDF-TrFE) films, its crystal orientation also plays a role. Thus, with a slightly lower content of β phase than 135°C, an advantageous crystal orientation could result in a larger Pr for 140°C. At 150°C and 170°C, although crystallinity reached its highest, remnant polarization decreased to lower values. This could be caused by the large pores that started to form in the films at around and above the melting temperature. The pores would decrease the effective touching areas with the top contact and the substrate, resulting in smaller remnant polarizations.

3.2.2 Concentration Test

AFM images of P(VDF-TrFE) films cast by solutions of different concentrations are shown at 1μm × 1μm (Figure 32) and 10μm × 10μm (Figure 34). No obvious difference was observed in grain morphology from the images. As concentration increases, the surface
became rougher with small hills, especially for higher concentrations. This observation was confirmed with measurement of RMS roughness shown in Figure 34. Also shown is the relative roughness (roughness/thickness). It was found that relative roughness decreased with increasing concentration.

Figure 32 AFM images of P(VDF-TrFE) films cast from different concentrations: a) 3%, b) 5%, c) 10% d) 15% at 1μm × 1μm
Figure 33 AFM images of P(VDF-TrFE) films cast from different concentrations: a) 3%, b) 5%, c) 10% d) 15% at 10µm × 10µm

Figure 34 RMS roughness of P(VDF-TrFE) films cast from different concentrations

XRD patterns of P(VDF-TrFE) films cast from different concentrations are shown in Figure 35. It is clear from the figure that the peak intensity increased with concentration.
Positive remnant polarizations for 5% and 10% films were $7.4 \pm 0.1 \mu C/cm^2$ and $7.27 \pm 0.04 \mu C/cm^2$. Considering the error, remnant polarization for both films could be considered the same. Tests for 3% films failed due to large leakage currents. Also, remnant polarization and coercive field were not obtained for 15% films. The films were still not fully polarized with a drive voltage of 199V, which was the largest available voltage for the current experimental setup.

As the concentration of solution increases, the thickness increases accordingly (section 3.1). Increase in grain size with concentration means that grains would be larger in thicker films. This agrees with a study done by Mao et al., who proved it for different annealing temperatures [14].

Consideration of both absolute roughness and relative roughness has practical values. In the case of P(VDF-TrFE) films, a large absolute roughness could affect the effectiveness of top contact to be deposited on top. A large relative roughness indicates a small effective thickness, which means that the deposition of P(VDF-TrFE) is not effective and caused waste of material. The absolute roughness and relative roughness behaved oppositely with increasing concentration (thickness). As film decreased in thickness, relatively roughness became more significant. With reference to section 3.1, this implies that it would be difficult to obtain homogeneous ultrathin film of thickness 30nm by spin-coating.
While peak intensity (amount of β phase) clearly increased with concentration, 5% and 10% films had similar remnant polarization. This means that thickness did not affect remnant polarization, which is expected. The increase of peak intensity was caused by increase of film thickness. The penetration depth of XRD is 2µm, while all films were thinner than 1.5 µm. As film thickness increased, more materials would be probed by the x-ray, thus causing a rise in peak intensity. The result from this section would be useful for the subsequent test on solvent, as it helped to decouple the effect of film thickness from the solvent.

3.2.3 Solvent Test

Figure 36 shows the surface of P(VDF-TrFE) films cast by 5% P(VDF-TrFE) in different solvents at 1µm × 1µm. It can be observed that grains cast from acetone were rounder in shape. The length versus width ratio of P(VDF-TrFE) grains are shown in Figure 37. In order of decreasing length/width ratio and taking into account the errors, cyclohexanone > DMF ≈ acetone/DMF > acetone.

Figure 36 AFM images of P(VDF-TrFE) film cast by 5% P(VDF-TrFE) in different solvents: a) acetone, b) acetone/DMF, c) cyclohexanone and d) DMF at 1µm × 1µm
Surface of P(VDF-TrFE) films cast by different solvents were observed with AFM at 10µm × 10µm (Figure 38). RMS roughness is shown in Figure 39. Cyclohexanone cast films were significantly rougher than those by other solvents, and their relative roughness was as high as 15%. The films cast in acetone were the smoothest among all solvents at a small scale of 10µm × 10µm. However, at a macroscopic view, there were visible ripples on the film, especially for areas not at the center (Figure 40). Also, the film was thinner by over 100nm in the central circle.
Figure 38 AFM images of P(VDF-TrFE) films cast by different solvents: a) acetone, b) acetone/DMF, c) cyclohexanone and d) DMF at 10µm × 10µm

Figure 39 Roughness of P(VDF-TrFE) film cast by different solvents
Figure 40 Surfaces of P(VDF-TrFE) film cast by P(VDF-TrFE) in acetone left) not at the center right) at the center

XRD patterns are shown in Figure 41. Figure 42 plots H/FWHM of P(VDF-TrFE) films cast by different solvents and films cast in DMF at different concentrations.

Figure 41 XRD patterns of P(VDF-TrFE) films cast by different solvents

Figure 42 H/FWHM of P(VDF-TrFE) films cast by different solvents and films cast in DMF at different concentrations
Positive remnant polarization of P(VDF-TrFE) films cast by DMF, acetone and DMF/acetone is shown in Figure 43. Taking the error bar into consideration, the difference between different solvents was not drastic. Remnant polarization of films cast by acetone was slightly larger than the other two solvents, and those by acetone/DMF showed the lowest remnant polarization. Measurement error was most significant for acetone. For acetone cast films, all devices involved in the electrical measurement were located in the central circle, because the waves in non-central areas (Figure 40 left) made it unsuitable for Au/ P(VDF-TrFE)/Au structure. Attempts to measure electric properties of cyclohexanone cast films failed due to large leakage currents.

![Figure 43 Remnant polarization of P(VDF-TrFE) films cast by different solvents](image)

As discussed in the section about annealing temperature, an ellipsoidal shape indicates a chain orientation favorable to ferroelectric application. Of all solvents, P(VDF-TrFE) grains cast by cyclohexanone were the most elongated, suggesting a good chain orientation. With similar values of H/FWHM, films cast by 5% P(VDF-TrFE) in cyclohexanone were thicker by about 100nm than those by 5% P(VDF-TrFE) in DMF. Thus P(VDF-TrFE) cast by cyclohexanone induced larger crystallinity than DMF for the same thickness. Good chain orientation and crystallinity of cyclohexanone cast films suggest its bright prospect as a solvent. However, polarization of cyclohexanone cast films was not realized. Failure of the electrical measurement could be caused by two reasons. First, gold might diffuse into the polymer film, as the thickness was only 160nm, similar to films cast by 3% P(VDF-TrFE) in DMF, which also failed the electronic tests due to its thickness. Second, the appearance of
pinholes means that gold could make its way to the gold substrate during thermal evaporation. Although electrical measurements were not realized, working devices of cyclohexanone cast films have been successfully made\textsuperscript{[20]}. There might be some problems with the preparation of P(VDF-TrFE) in cyclohexanone solution. It is worthwhile to do further studies on solution preparation.

Films cast by 5\% P(VDF-TrFE) in acetone/DMF were around the same thickness as those by DMF, but the H/FWHM of acetone/DMF was noticeably larger than DMF. Thus acetone/DMF induced larger crystallinity in P(VDF-TrFE) than DMF for the same thickness. Although remnant polarization of acetone/DMF cast films was slightly lower than the other two solvents, it showed the most stable results as indicated by the small error.

Films cast by 5\% P(VDF-TrFE) in acetone displayed the largest crystallinity among all solvents, even larger than 15\% P(VDF-TrFE) in DMF which was more than 3 times thicker. The large crystallinity was reflected in its remnant polarization. The boiling point of acetone is 56°C, very low compared to the boiling point of DMF (153°C) and cyclohexanone (156°C). During spin-coating, acetone evaporated quickly while the droplet in the center spread towards the edge, thus leaving waves on the surface. The inhomogeneity in film surface could cause inaccuracy in the measurement of top contact area, which could induce the relatively large error observed in remnant polarization. Although the remnant polarization of acetone cast films was slightly larger than other solvents, it is not suitable as a solvent for P(VDF-TrFE) for the purpose of producing homogeneous film by spin-coat. Further studies could be done to optimize the processing of P(VDF-TrFE) in acetone.

3.2.4 Substrate Test

Figure 44 shows the surface of P(VDF-TrFE) films on gold, graphene/Cu and transferred graphene/SiO\textsubscript{2} at 1µm × 1µm. No obvious difference was observed in grain morphology. Figure 45 shows the films at 10µm × 10µm. Considering the errors, the roughness on different substrates was found such that Au ≈ SiO\textsubscript{2} > graphene / Cu > graphene/ SiO\textsubscript{2} (Figure 47). Unlike other substrates, graphene/Cu was flexible and easily bended. It was difficult to
make graphene/Cu smooth without doing damage to the graphene on top (Figure 46).
Figure 45 AFM images of P(VDF-TrFE) film on different substrates: a) Au, b) graphene, c) graphene/SiO$_2$ and d) SiO$_2$ at 10µm × 10µm

Figure 46 Graphene/Cu of size 1cm × 1cm
XRD patterns of P(VDF-TrFE) film on different substrates are shown in Figure 48. H/FWHM is shown in Figure 49. P(VDF-TrFE) film on graphene/SiO$_2$ displayed the largest crystallinity, while that on SiO$_2$ displayed the smallest. Crystallinity of P(VDF-TrFE) film on gold and graphene/Cu had similar values.
It is not advisable to spin-coat directly on graphene/Cu as purchased because of its flexibility and resultant large-scale roughness.

Among all substrates, P(VDF-TrFE) seems to work best on graphene/SiO₂. Prior to spin-coating the substrate, roughness of graphene/SiO₂ and SiO₂ is similar, with the former smaller than the latter by 0.2 nm \(^{21}\). Thus the smoothness of P(VDF-TrFE) on graphene/SiO₂ was mostly caused by graphene rather than the difference in roughness of two substrates. H/FWHM value of P(VDF-TrFE) film on graphene/SiO₂ is significantly higher than on other substrates. Thus crystallinity of P(VDF-TrFE) was enhanced on graphene/SiO₂. It would be interesting to do further studies on why P(VDF-TrFE) worked well with graphene/SiO₂, and its possible applications.

The enhancement of crystallinity by graphene was not found for graphene/Cu. H/FWHM of P(VDF-TrFE) on graphene/Cu was similar with that on gold. As for SiO₂, it is an insulator with considerably fewer free charge carriers than copper and gold. The dipoles in P(VDF-TrFE) remained mostly unaffected by the substrate in this case.

Figure 49 H/FWHM of P(VDF-TrFE) film on different substrates
SUMMARY AND FUTURE WORK

In this project, efforts have been spent on two objectives with an emphasis on the latter. In the first part of the project, different spin-coating speed, concentration of P(VDF-TrFE) in DMF solution and solvents were varied to achieve ultrathin film of 30nm. Thickness was found to saturate at high spin-coating speed and dilution of P(VDF-TrFE) in DMF solution led to poor adhesion of P(VDF-TrFE). Both methods were not able to produce film of the target thickness. A solvent, cyclohexanone, was found to produce 25nm-film at a solution concentration of 2%. However, the problem of pinholes could be overcome with the current experimental setup.

In the second part, ferroelectricity of P(VDF-TrFE) was probed with varying processing parameters, including annealing temperature, solution concentration, solvent and substrate. Results such as grain and surface morphology, crystallinity and remnant polarization were used to monitor the change in ferroelectric property. For 5% P(VDF-TrFE) in DMF, the optimum annealing temperature was found to be 140°C. For P(VDF-TrFE) in DMF, a better solution concentration was 5%. For P(VDF-TrFE) in different solvents, DMF showed both high polarization and relatively low error. For P(VDF-TrFE) spin-coated on different substrates, it was found that graphene/SiO2 could greatly enhance the crystallinity of P(VDF-TrFE).

This project finds a number of directions for future studies. With reference to results from the first part of the project, one such direction is to try to polarize ultrathin films with pinholes with corona poling, and investigate the performance of graphene-ferroelectric hybrid structure. If low sheet resistance of graphene is achieved, it will show promise in low-operation voltage graphene-ferroelectric hybrid structure.

The results from the substrate test suggests that graphene could possibly enhance the β phase crystallinity of P(VDF-TrFE) especially for P(VDF-TrFE) on graphene/SiO2. Another interesting direction would be to confirm if graphene would increase the ferroelectric property of P(VDF-TrFE), is it dependent on the substrate that graphene sits on or the transfer method.
REFERENCES


[17] Used with permission, Reset sheet resistance of graphene in graphene P(VDF-TrFE) hybrid structure with a periodic voltage, graph from Prof. Ozyilmaz’s group in National University of Singapore.


