Characterization and applications of piezoelectric polymers

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Technical Report No. UCB/EECS-2015-253
http://www.eecs.berkeley.edu/Pubs/TechRpts/2015/EECS-2015-253.html

December 18, 2015

Characterization and applications of piezoelectric polymers

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Research Project

Submitted to the Department of Electrical Engineering and Computer Sciences, University of California at Berkeley, in partial satisfaction of the requirements for the degree of **Master of Science, Plan II**.

Approval for the Report and Comprehensive Examination:

Committee:

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* * * * * * *

Professor Kristofer S. J. Pister
Second Reader

Abstract

Mechanical and electrical properties characterizations as well as some of applications for piezoelectric polymer polyvinylidene fluoride (PVDF) are reported here. A package level piezoelectric sensor with transient mode was designed as a main application of PVDF polymer as acoustic sensor. The PVDF sensor can detect acoustic signal outside of the package with acoustic sensitivity of -48.7 dBV/pa in our design. Upon triggering, both PVDF sensor and contents of package can be destroyed preventing reverse engineering of its content. For this application, a thermal transient condition and a footstep sound detection were studied. With the package temperature of 180°C, it takes around 300 seconds to destroy PVDF sensor on package. Maximum sound detection distance with footstep was about 20cm with gain of 100. X-ray diffraction (XRD) patterns were used to analyze the crystallinity of PVDF. Spin coated PVDF-TrFE, copolymer of PVDF, shows β-phase with XRD peak value of 20.2° which matches well with commercially purchased β-phase PVDF film without any poling process. XRD pattern of electrospun PVDF-TrFE sample is reported here. It shows XRD peak value of 20.47°. A heart rate of 67 bpm was measured using a commercial PVDF sensor that shows the possible biomedical application of piezoelectric polymer PVDF.

Acknowledgement

At first, I want to thank my advisor, Professor Ana C Arias, for supporting me throughout my graduate school years. I think that past few years were the hardest times of my life in terms of financial and personal problems. I honestly do not think that I could finish Masters degree without her kind support and patience with me. Without you I would never experience true nature of the research field. I really appreciate everything, Ana.

Next, I want to thank Dr. Kristopher J Pister for kindly be my second reader for this report. I first met him back in 2011 during my undergraduate class in circuit class. I really appreciate his enthusiasm towards electrical engineering that makes me start enjoying the field. As a result, I ended up pursuing graduate school in electrical engineering. Thank you, Professor Pister.

At last, I want to thank my mother. About ten years ago, you told me “we are moving to US next year”. When I first heard that, I did not know how to react to that sentence. I did not speak or properly learn any English at that time, so I thought you were joking with me mom. It has been eight years that we left everything behind and came to this foreign country. Many hard and terrible things happened but I overcame because of your love and support. Thank you and love you, mom.

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1 Introduction

Piezoelectric materials convert energy between mechanical and electrical domains. Piezoelectricity is the accumulation of charges in response to applied stress to the material [1]. Traditionally, certain ceramics and crystals commonly used as piezoelectric materials are quartz, Lead zirconate titanate (PZT), and Barium titanate [1]. These solid materials show good piezoelectric property, but it cannot be used in biomedical applications due to its rigid, and high acoustic impedance characteristics of piezoelectric crystals. However, previous studies found that such as polymers like Poly vinyl carbonate (PVC), Nylon 11, and polyvinylidene fluoride (PVDF) also show piezoelectricity and are light weight and flexible. Especially, PVDF have been shown as a good candidate material for sensors because of its piezoelectric voltage constant around $216\frac{V/m}{N/m^2}$ [1, 2]. PVDF's piezoelectric voltage constant is about 20 times higher than PZT ($6.6\frac{V/m}{N/m^2}$)[1, 2] and 40 times higher than Barium titanate ($10\frac{V/m}{N/m^2}$)[1, 2]. PVDF polymer shows much lower density and acoustic impedance than piezoelectric crystals [1,2], which enables its usage for biomedical or acoustic sensing. This research is mainly focused on the characterization of material properties of PVDF polymer, its applications as an acoustic sensor, and different fabrication technique to deposit PVDF polymer.

1.1 Piezoelectricity

A piezoelectric material will accumulate electrical charges when mechanical stress is applied. This is called piezoelectric effect, while conversion of the electric field to mechanical strain is called reverse piezoelectric effect. Before understanding various coefficients of piezoelectricity for solid piezoelectric material, the direction of material due to the anisotropic nature of piezoelectric material must first be defined. Typical piezoelectric coefficients are denoted as A_{ij} where i denoted as the direction of the

electrical measurement, and j denotes the direction of the mechanical movement [7]. Figure 1 shows the typical dimensions of piezoelectric material for defining the piezoelectric constants. For example, d_{31} is a piezoelectric constant that measures electrical value in poling direction "3" in Figure 4 by mechanical stress applied in the width direction "1" in Figure 1. Some of the important piezoelectric constants regarding this study are following:

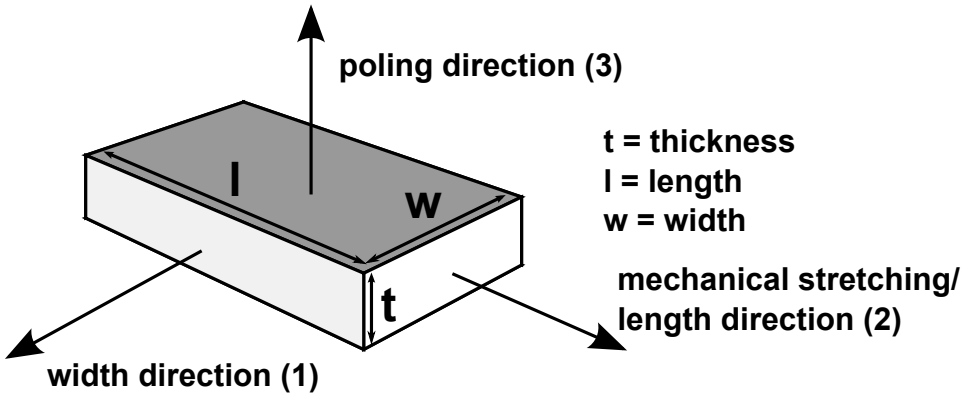

Figure 1: Schematic representation of dimensions in piezoelectric material

Piezo strain constant: d_{3j} ($\frac{C/m^2}{N/m^2}$) represents the piezoelectric effect in the film. This constant indicates how much charges can be accumulated in 1 m^2 when 1 Pa of pressure is applied along the "j" axis. Typical values of d_{33} for PVDF and its copolymer are between 20 and 30 $\frac{C/m^2}{N/m^2}$ [1,2].

Piezo stress constant: g_{3j} ($\frac{V/m}{N/m^2}$) represents the electric field induced in "3" direction by a stress of 1 Pa is applied along the "j" axis. It is often called piezo voltage constant and the typical g_{33} values for PVDF polymer are around 200 to 300 $\frac{V/m}{N/m^2}$ [1,2].

1.2 Piezoelectric polymer

Although the idea of piezoelectric polymers was introduced about 40 years ago [9], piezoelectric polymers have only gained attention in early 2000 from research society due to possible biomedical applications [14, 15]. Traditionally, solid piezoelectric like ceramics were used in various applications such as medical, aerospace, consumer electronics, and even automotive industry. However, as it is shown in Table1, piezoelectric polymer PVDF is lightweight, flexible, has low acoustic impedance and high piezoelectric constant, making it a good candidate for acoustic or biomedical sensors. Typical acoustic impedance value for PVDF is around $2.7\times10^{6}kg/m^{2}\bullet s$ [2] that matches well with body ($1.6\times10^{6}kg/m^{2}\bullet s$) or water ($1.4\times10^{6}$ $kg/m^{2}\bullet s$) [21]. However, the crystallinity of the PVDF polymer will be a major factor on the piezoelectric constant of polymers. Typical piezoelectric polymers have a crystalline region that has an internal dipole moment. These dipole moments are randomly oriented without any mechanical or electrical poling process [18, 19], and the net dipole moment is zero in this condition. This type of structure is called α-phase PVDF film that has no piezoelectric response. The α-phase PVDF film is commonly used as insulating material because of its low thermal conductivity, low density, and high chemical and heat resistance [2]. With post processes such as mechanical stretching and electrical poling under a high electric field, crystalline regions inside the bulk PVDF film will align in electric field direction [2]. The PVDF structure with this morphology is called β-phase film. It has been shown that the higher β-phase portion of PVDF film shows a higher piezoelectric constant as sensor material. Typically, around 90~95% of β-phase portion shows a strong piezoelectric response for PVDF polymer [17, 20]. Copolymers of PVDF such as PVDF-tetrafluoroethylene (PVDF-TrFE) show higher crystallinity due to its chemical structure, resulting in better piezoelectric response. Upon application of post processes to the PVDF film, the β-phase PVDF film retains its morphology unless there are severe changes in temperature to the film. The maximum operating temperature for the β-phase PVDF film is 80°C and 110°C for the β-phase PVDF-TrFE film [2].

Table 1 Material property of common piezoelectric materials [1][2]

Material property	*Units*	*PVDF*	*Nylon 11*	*PVC*	*PZT*	*Barium Titanate*
Density	g/cm^3	1.78	1.15	1.45	7.5	5.7
d_{31} piezoelectric Constant	pC/N	23	0.26	0.7	1200	1700
g_{31} voltage constant	V•m/N	216	2.5	6.6	10	5
Acoustic impedance	10^6 kg/m^2•s	2.7	2.9	3.27	30	30

1.3 Piezoelectricity in semi crystalline polymers

A PVDF film without any post processes such as mechanical stretching or electrical poling results in the alpha phase PVDF structure that has a zero net dipole moment in the crystalline region, as show in Figure 2. This type of crystalline structure has no piezoelectric characteristic, because the α-phase PVDF crystalline regions will align such that all dipole moments cancel each other. On the other hand, the β-phase PVDF structure of PVDF has Fluorine on the one side and Hydrogen on the other side, as shown in Figure 3. This will form a net dipole moment in a stacked direction inside the β-phase PVDF crystalline regions. When stress is applied to this stacked polymer chain region illustrated in Figure 4, it will change the local dipole distributions and induce an electric field in the stack. The induced electric field accumulates the charges at both the top and bottom of the film, demonstrating the principle of piezoelectric effect. Various studies show ways to increase the β-phase portion in the film by mechanical or electrical poling. [2] Figure 5 shows the whole polymer structure with aligned β-phase crystalline regions inside. A copolymer of PVDF, PVDF-TrFE, shows a higher temperature range of use, a slightly higher piezo strain constant, and a higher portion of β-phase morphology with just thermal annealing process [5, 13]. PVDF-TrFE is a good candidate material for piezoelectric polymer sensor because it can achieve high portion of β-phase morphology without poling process.

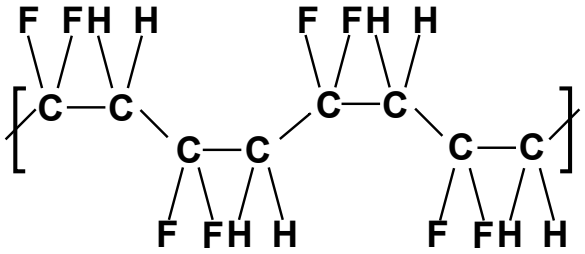

Figure 2: Chemical structure of α-phase PVDF structure

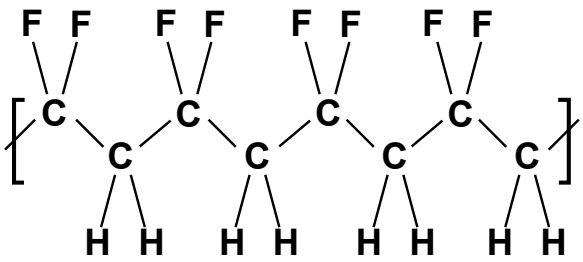

Figure 3: Chemical structure of β-phase PVDF structure

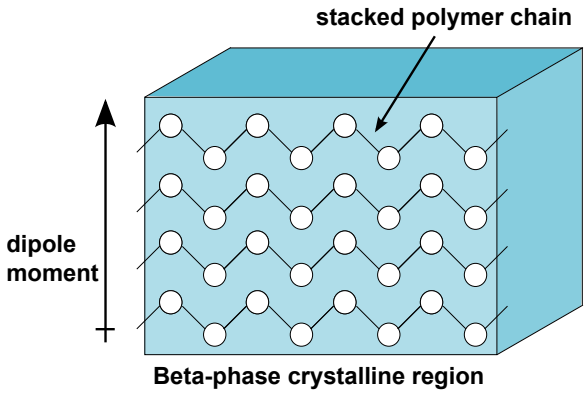

Figure 4: Schematic illustration of beta-phase crystalline region

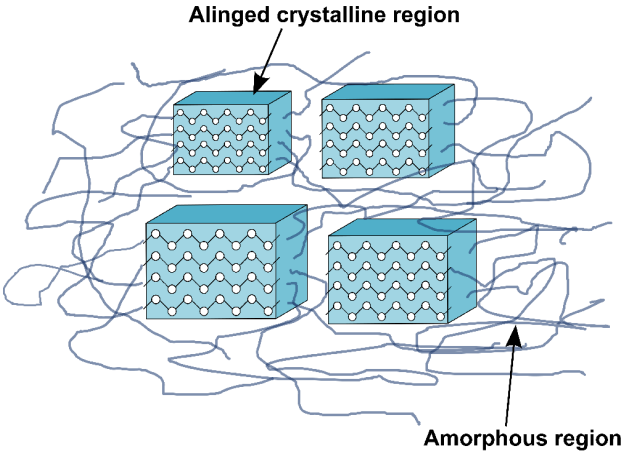

Figure 5: Schematic illustration of poly crystalline structure of PVDF polymer

1.4 Acoustic sensitivity

Since our main application of the PVDF polymer is an acoustic sensor, we need to define the acoustic sensitivity of the microphone. Acoustic sensitivity measurement is typically measured by a 1kHz sine wave sound signal with 94 dB sound pressure level (SPL) that is equivalent to 1Pa of pressure [6]. With this input signal, we measure the output signal (usually an analog signal like voltage) to get the sensitivity of the sensor. Although we compare the 1kHz signal with 94 dB for microphone sensitivity, the frequency response of audible range (up to 20kHz) is measured for comparison. The microphone linearity curve, output voltage with respect to logarithmic scale of an input acoustic pressure, is often measured in order to verify the sensor characteristics as a microphone. The sensitivity of an analog microphone is defined in the unit of dBV, decibel with respect to reference voltage of 1V, as follows:

$$Sensitivity_{dBV} = 20 \times \frac{(Sensitivity_{mV/Pa})}{(Output_{AREF})} \quad [6]\ (1)$$

where $Sensitivity_{mV/Pa}$ is the measured output voltage in mV with input signal of 94 dB (1Pa), and $Output_{AREF}$ is 1000 mV/pa. This study focuses on both the acoustic sensitivity of PVDF and its copolymer and the microphone linearity curve of the sensor.

1.5 Electrospinning of piezoelectric polymers

Besides mechanical stretching and electrical poling, there is another interesting method to achieve high percentage of β-phase PVDF film: a far field electrospinning process. In recent studies [3][4], this technique has received much attention from many research groups because it is a unique method for generating nanofibers of polymer material. Electrospun nanofibers are useful for wearable biomedical applications because of their flexible and stretchable nature of material. Figure 6 shows schematic illustration of the far field electrospinning setup. The equipment of electrospinning process consists of three parts: a grounded collector, high dc voltage source, and syringe with controlled flow. With enough high voltage applied to the tip of a syringe needle, the polymer solution becomes charged, and electrostatic repulsion balances with the surface tension of the liquid. At this point, a stream of liquid breaks out from the tip of the syringe. Once the steam is emitted from the surface, charges inside the stream migrate to the surface and cause nanofibers to accelerate. These surface charges also cause electrostatic repulsion, which bends the fibers into fluctuation in air as shown in Figure 6. Electrospun nanofibers can be either collected by a planar collector or rotating collector. The sample collected by a planar collector shows random orientation in Figure 7(a) while rotating collector samples show a linearly aligned orientation as shown in Figure 7(b). The electrospinning process is useful for piezoelectric polymer PVDF because it can provide both effects of mechanical stretching and electrical poling simultaneously [12]. Fabricating β-phase PVDF nanowire requires specific control over both electrospinning and solution parameters. In this study, solution of 25 weight percent of PVDF-TrFE in

DMF:acetone with 7:3 in volume was used as polymer solution. Electrospinning voltage was 15kV with 10.5cm of distance between the needle and the collector, and the collector was placed on the rotating cylinder in order to achieve alignment of nanofibers. Figure 8 shows the picture of electrospun PVDF-TrFE nanofiber sample by rotating collector.

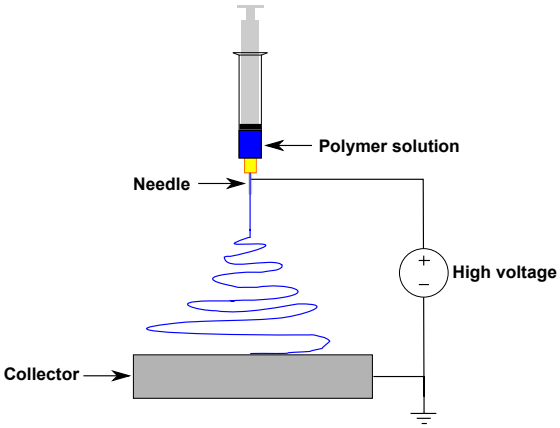

Figure 6: Schematic illustration of far field electrospinning process

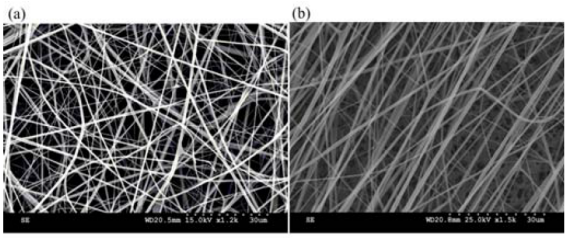

Figure 7: SEM images of electrospun sample collected by (a) planar collector and (b) rotating collector [3]

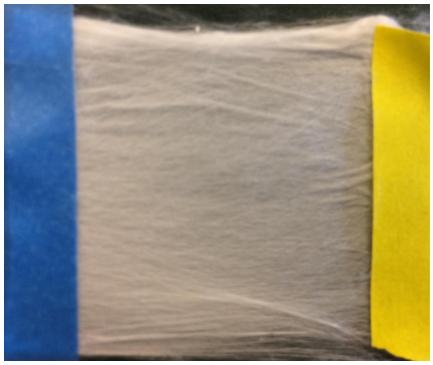

Figure 8: Picture of electrospun PVDF-TrFE nanofiber

1.6 Package level piezoelectric sensor design

Recovering all hardware devices from the battlefield is a difficult task. This results in unwanted waste in the environment and possible reverse engineering of critical technologies by unauthorized persons. Vanishing programmable resources (VAPR) is a project that is looking for electronic systems that can disappear through triggering upon

command. The main contribution in this research is achieving package level acoustic or vibration sensors that can detect the surrounding environment without affecting other parts of the package elements. Figure 9 shows the design of the proposed package design. The volume of the whole package is $1cm^3$ that has two chambers inside. The bottom chamber contains the xenon difluoride (XeF_2) and sealed with barrier layer. A silicon chip sits on top of this barrier layer. In normal operating mode, both polymer-based sensor and silicon chip inside the package should be stable. Upon triggering however, silicon chip will be etched from released XeF_2 by destroying barrier layer. Also the PVDF sensor in the upper chamber should be significantly damaged in order to prevent both reverse engineering and creating environmental waste. PVDF was chosen as a sensor material due to its mechanical and chemical stability with relatively low melting point of 180°C. Two transient mechanisms were considered in order to destroy the PVDF sensor: destroying film by heat from a chemical reaction and directly applying joule heating to the film. The chemical reaction of silicon with XeF_2 creates a large amount of heat during reaction. In order to implement transient mode with chemical reaction, the first design includes the sensor with applied silicon powder on the back, then release the XeF_2 gas to destroy the sensor. We chose the thermal transient mode achieved by joule heating as final design. In order to implement transient mode with joule heating, thin metal traces was used as electrode in design. Because thermal transient mode does not depend on other transient mode using XeF_2, we have independently controlled transient mode for package sensor.

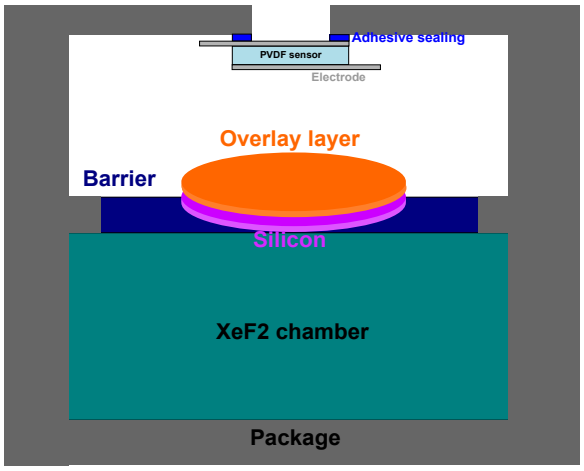

Figure 9: Schematic illustration of overview package of VAPR project

2 Experimental details

2.1 Materials

Commercial β-phase PVDF film was purchased from Measurement Speciality (USA). This commercial film has a deposited silver layer on both top and bottom of the film. PVDF-TrFE copolymer powder with 70/30% mol ratio was purchased from Piezotech (France). For solvent, N,N-dimethylformamide (DMF) and acetone were purchased from Sigma Aldrich (USA). The solution was prepared with DMF/acetone (7:3 by volume) and stirred at 120° C for around two hours with PVDF-TrFE powder. In this study, 15 wt% of PVDF-TrFE solution was used for a spin coated film. The spin condition was at 1000 RPM for 60 seconds. For electrospinning process, 25 wt% was used for the electrospinning process with rotating cylinder at 3000 RPM. 3D printed plastic holder in Figure 10 was used for reliable electrical contacts with measurement circuit. It has opening in the middle that is designed for active sensor area that are exposed to acoustic signal. Two crocodile clips with one insulated side were used for both electrode sides of the film. With these crimping connectors, it solved the problem of electrical short of top and bottom electrodes.

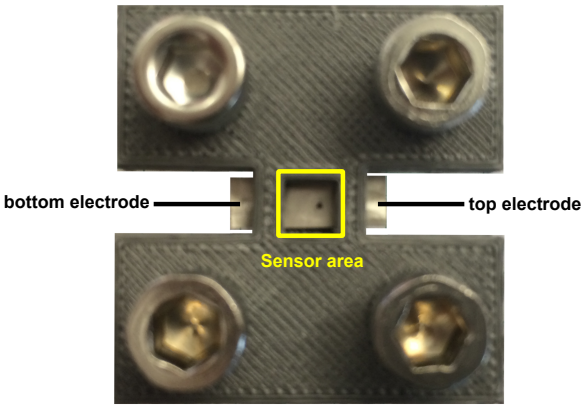

Figure 10: Picture of assembled plastic holder with PVDF film inside

2.2 Acoustic measurement setup

The acoustic measurement setup is shown in Figure 11. An arbitrary function generator from Agilent (USA) was used to create a 1kHz sine wave signal. This signal is fed to an audio power amplifier from Steward audio (USA) then connected to the internal speaker of an anechoic chamber. The anechoic chamber was from Bruel & Kjaer (UK), and it was used to produce an accurate reference signal inside the box and to exclude all noise sources from outside when performing acoustic measurements. The input sound source was calibrated at 94dB with a sound level meter on the spot where the PVDF sensor is placed. The output signal from the PVDF sensor is connected to an impedance adaptor circuit in order to enhance the acquired signal. This signal is then connected to a digital oscilloscope from Analog Devices (USA). The post processing of a fast Fourier transform (FFT) was used in the range of 1Hz to 20kHz to get the final data. The β-phase PVDF film was cut into 5mm by 5mm in size and fixed with a 3D-printed plastic holder to get an acoustic sensitivity measurement.

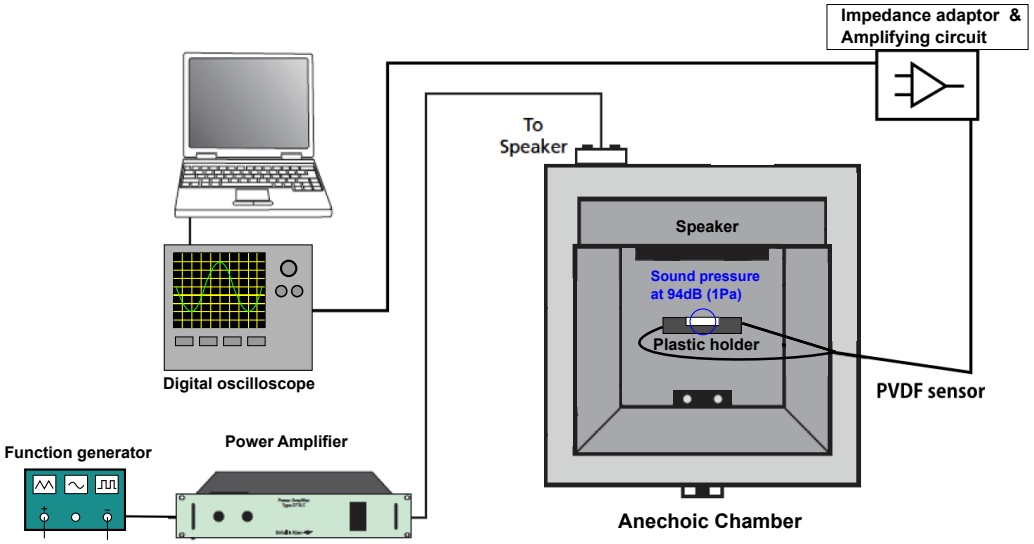

Figure 11: Schematic illustration of acoustic measure setup

2.3 Acoustic measurement circuit

For voltage measurement from a PVDF polymer sensor, it needs to measure the voltage between two electrodes on the top and bottom of the film. If we think of the PVDF sensor as a passive circuit element, it can be represented as a capacitor with fixed capacitance value. If we need force (voltage) with respect to time measurement, the RC constant with R as an input resistance should be sufficiently larger than the sampling period of the measurement. [7] A typical charge amplifier can be used, but without sufficiently high input resistance in parallel, only part of the signal will be obtained by the circuit. One of the most common ways to solve this problem is using an additional circuit called the impedance adaptor. Figure 12 shows the schematic view of the impedance adaptor. For the acoustic sensitivity measurement, a gain of 1 ($\frac{R_2}{R_1} = 1$) and R_{in} value of 1 GΩ was used in comparison to other types of microphone sensitivities. The reason for having a high input impedance stage is shown in Figure 13 [7]. Ideally, infinite input resistance will capture all the output voltage from the applied pressure to the sensor. The RC time constant with a 5mm by 5mm active sensor area (C=66pF) with an input resistance of 1 GΩ is 66ms for our measurement setup.

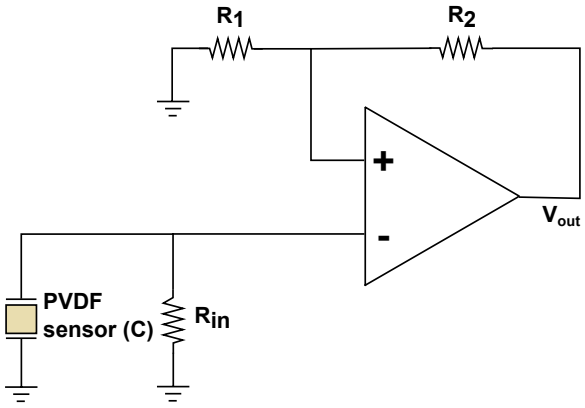

Figure 12: Circuit diagram of impedance adaptor

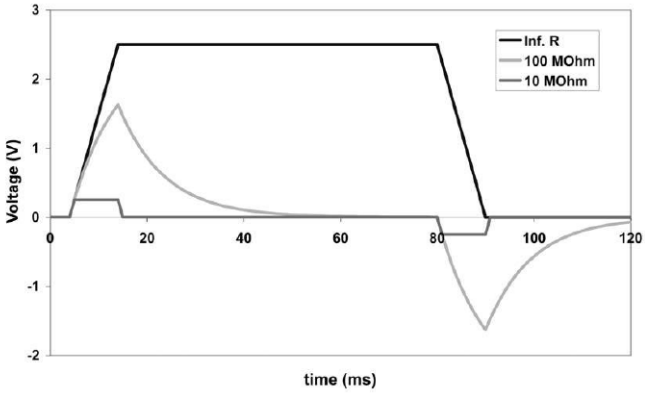

Figure 13: Graph of measured voltage signals depending on input impedance [7]

3 Results

3.1 Piezoelectric material properties

In order to understand better about crystalline structures in the PVDF film, a X-ray diffraction (XRD) pattern was analyzed [11]. XRD is a rapid analytical technique used for phase identification of a crystalline material. X-ray diffraction equipment consists of three parts: an X-ray tube, a sample holder, and an X-ray detector. X-ray was generated with specific wavelength (Cu was used as target material) to produce monochromatic X-ray beam. This X-ray beam is directed on the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded with respect to rotating angle. For a smooth surface like continuous film, XRD pattern with low noise floor will be measured. For a rough surface, we can still obtain the information about crystallinity of sample with higher noise floor due to random reflections of X-rays on the surface. At first, three different types of films were measured: commercially purchased α-phase PVDF film, commercially purchased β-phase PVDF film, and a spin coated PVDF-TrFE film with annealing. Figure 14 shows the XRD patterns of three different phases of PVDF film: α-phase, β-phase, and γ-phase as a reference [20]. Figure 15(a), 15(b) and 15(c) show the XRD patterns of α-phase, β-phase, and spin coated PVDF-TrFE in the same order. When we look at Figure 15(a), it shows the XRD pattern of an α-phase PVDF film. The measured peaks are at 17.75°, 18.45°, 19.9° and 26.00° that match really well with peak values of 17.66°, 18.30°, 19.90° and 26.56° from reference [20]. Figure 15(b) and 15(c) show two strong peaks at 20.6° and 20.2° respectively. These diffraction peak values match well with 20.26° from references [8,11,20]. This XRD pattern shows that spin coated PVDF-TrFE will have β-phase crystallinity without any mechanical or electrical poling. Figure 15(d) shows the XRD pattern of an electrospun PVDF-TrFE sample. It shows a distinct peak at 20.47° like the β-phase film but with a much higher noise floor due to its rough surface of nanofibers. From this data, we can see

the electrospinning process has similar effects of mechanical and electrical poling to the crystallinity of PVDF.

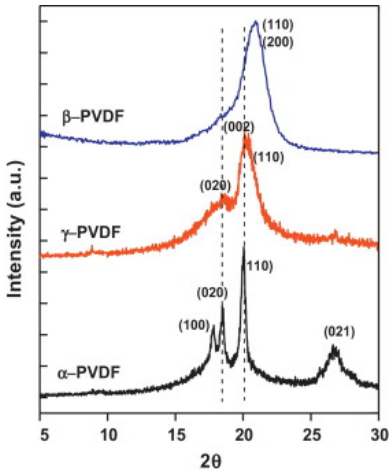

Figure 14: XRD patterns of α,β,and γ-phase PVDF film [20]

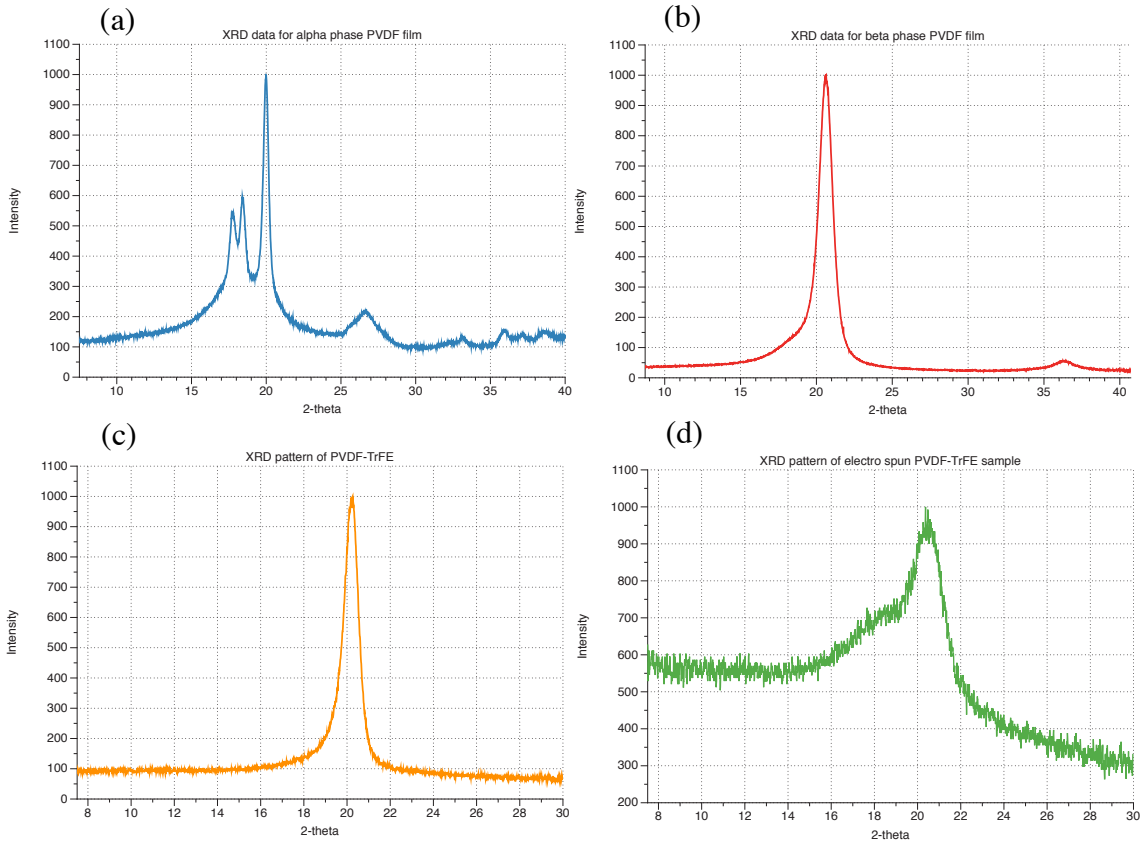

Figure 15: XRD patterns of commercial α-phase film (a), commercial β-phase film (b), spin coated PVDF-TrFE film (c), electrospun PVDF-TrFE film (d)

3.2 Thermal transient

As we discussed in Section 1.6, the thermal transient mode of the PVDF sensor film was studied in this section. A β-phase PVDF film with a 28um thickness sample was cut into 1cm by 1cm in size, and taped on the glass slide holder. A prepared sample was placed in the oven with a temperature range from 180°C to 350°C. The deformation time is defined here as the time until there is no further deformation of the PVDF film by visual inspection. Figure 16 also shows the exponential fit of the measured deformation time with respect to temperature. Because our data fit into an exponential decay function with respect to temperature, the deformation reaction rate follows the Arrhenius equation, $k \propto e^{\frac{-E_a}{T}}$ where k is reaction rate, E_a is activation energy, and T is temperature. Because of the limited amount of energy from the battery package, a temperature of 180°C and deformation time of 300 seconds was chosen as the thermal transient condition. Also, thorough energy calculation was conducted in order to destroy the sensor film by joule heating. With the assumption of battery capacity of 5mAh and 1.5V, the sensor film can be destroyed with about 15.5% of the total battery power.

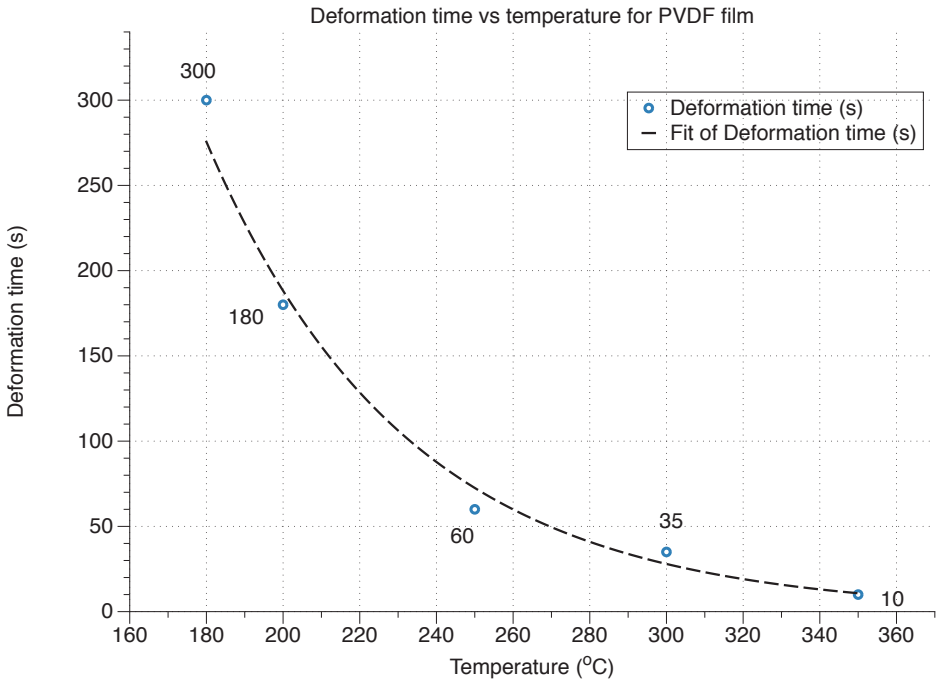

Figure 16: Plot of deformation time with respect to temperature

3.3 Sound detection

Because PVDF film was used on the package to detect sounds, one of the important parameters for our sensor is the detection distance and sensitivity comparison to other microphones. Figure 17 shows the sound detection setup. Two different acoustic sensors, 28μm thick β-phase PVDF film in plastic holder and commercial electret microphone, were placed toward sound source from four different distances. The acoustic signal of the PVDF sensor was measured through an impedance adaptor with a gain of 100, and it was compared with a commercial electret microphone with the same gain. Both sensors were facing toward the sound source, and the distance from the sound source ranged from 10cm, 20cm, 50cm, and 1m. The entire setup was placed in a quiet place (SPL around ~50 dB) with a concrete floor. Quiet footsteps were measured with a distance of 10cm and 20cm, and loud stomps were measured with a distance of 50cm and 1m in order to find the maximum detectable distance of the sensor. Table 2 shows the number of detected points, average output voltage, and standard deviation for detected signal in this experiment. At all four distances, a commercial electret microphone detects 100% of the sound source and shows less deviation in measured output. The PVDF sensor shows a large standard deviation in detection signals and a lower detection rate for longer distances. For example, average output voltage for PVDF sensor decreases from 1.35V (10cm quiet steps) to 0.11V (20cm quiet steps), while electret sensor changes from 1.46V(10cm quiet steps) to 1.34V (20cm quiet steps). The average output voltage decreases rapidly with respect to changes in distance. For the PVDF sensor, the maximum detectable distance with a loud stomp was around 1m. In order to use PVDF sensor in package level design, higher gain stage is needed to further increase the detection range.

Table 2 Number, average, and standard deviation of detected signal from sound detection measurement with two different microphone types

Measurements	*Number of detected points*	*Average output voltage*	*Standard deviation of output voltage*
PVDF, 10cm	9	1.35 V	0.75 V
PVDF, 20cm	9	0.11 V	0.07V
PVDF, 50cm	3	1.9V	0.66V
PVDF, 1m	8	0.79V	0.83V
Electret, 10cm	9	1.46 V	0.27 V
Electret, 20cm	9	1.34V	0.38V
Electret, 50cm	9	1.61V	0.013V
Electret, 1m	9	1.29V	0.20V

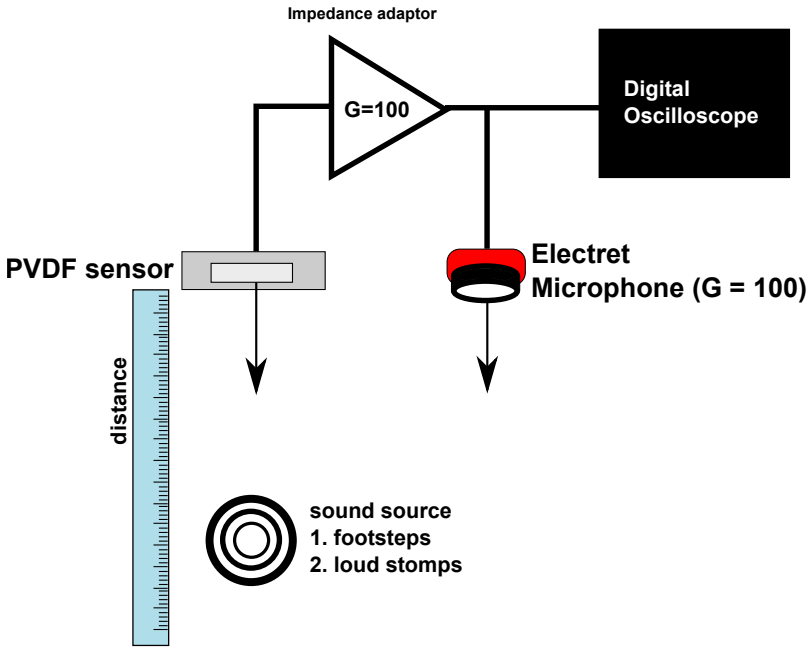

Figure 17: Schematic illustration of sound detection measurement setup

3.4 Acoustic property of β-phase PVDF film

An acoustic signal for commercial β-phase PVDF film in plastic holder was measured with the setup from Figure 11. Figure 18 shows the fast Fourier transform (FFT) of a measured 94 dB sine wave signal with 1 kHz frequency. Since FFT transforms signals from time domain to frequency domain, it is easier to analyze output value with

specific frequency. In our case, output signal with 1kHz frequency was analyzed for acoustic sensitivity. The opening of the plastic holder that are exposed to input sound signal for PVDF film was 5mm by 5mm in size. With a 1kHz signal, -58 dBV of output signal, which corresponds to 3.56 $mV_{peak\text{-}peak}$, was measured. From Equation (1), the measured acoustic sensitivity of the PVDF sensor film is -48.7 dBV/pa. Table 3 shows the comparison of acoustic sensitivities for different types of commercial microphones. This shows comparable acoustic sensitivity value compared to other types of commercially available microphones. Another important measurement was the microphone linearity curve as shown in Figure 19. This proves that our PVDF sensor behaves in a way so that output voltage is linearly increasing in logarithmic scale with respect to input acoustic pressure in dB. This means that our microphone exhibits an almost linear response up to 120 dB.

Table 3 Acoustic sensitivity comparison chart including commercial microphones

Microphone type	*Condenser*	*Electret*	*Dynamic*	*Moving coil*	*PVDF sensor (this work)*
Acoustic sensitivity	-37 dBV/pa	-45 dBV/pa	-56 dBV/pa	-54.5 dBV/pa	-48.7 dBV/pa

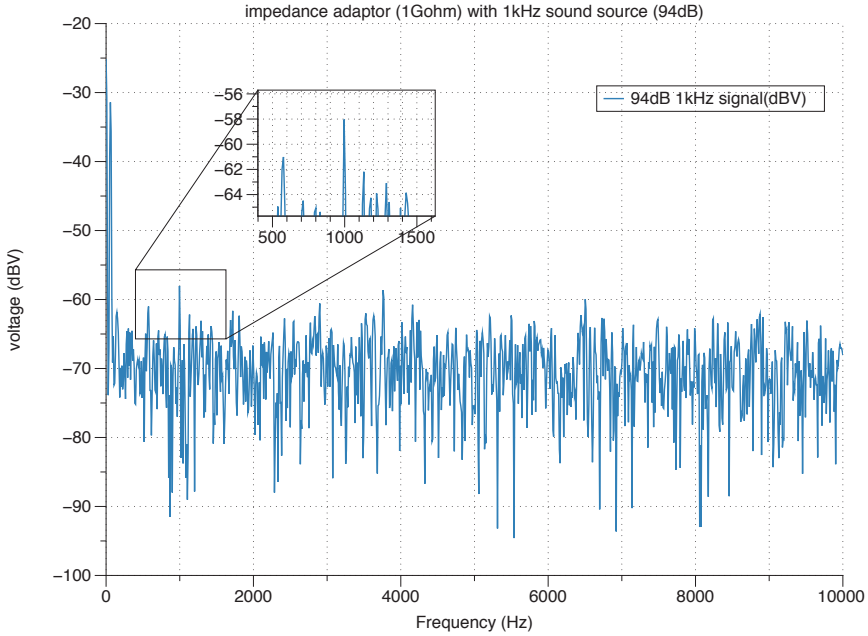

Figure 18: Plot of measured 1kHz sine wave signal with 94dB using FFT

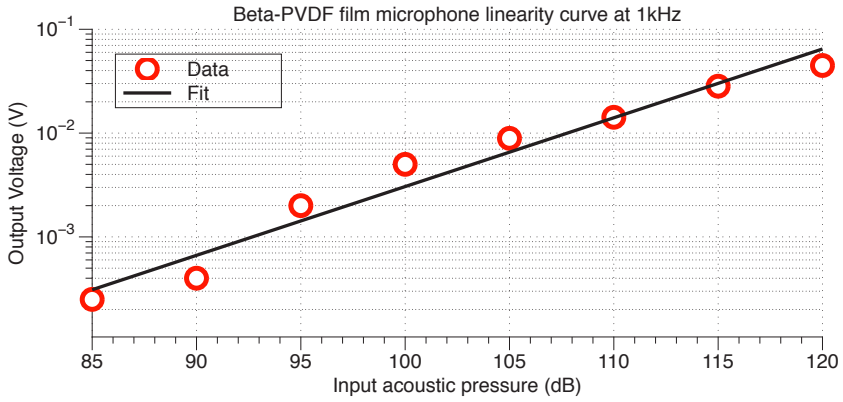

Figure 19: Plot of output voltage with respect to input acoustic pressure

3.5 Acoustic property of Electrospun PVDF-TrFE sample

An acoustic signal from the electrospun PVDF-TrFE sensor was also measured with the setup from Figure 11. Since the electrospun PVDF-TrFE sample was a bunch of nanowires in the same plane, fabricating the top and bottom electrodes was difficult due to electrical shortage problems. Typical fabricating techniques such as evaporating, blade coating, and inkjet printing were attempted, but all of them resulted in electrical shortage. In order to solve this problem, silver electrodes were deposited laterally 5mm apart. Because of the surface roughness of the electrospun sample, a silver paste was applied on the surface and dried at room temperature. With this sensor design, an acoustic sensitivity of -85.0 dBV/ Pa was measured. There are two reasons for this low sensitivity: a long average charge moving distance, and a different piezoelectric mode of the sensor. For the electrospun sensor, the average distance that charges have to travel is significantly larger compared to the sensor in Section 3.3. Another important factor for this result is that the electrospun sensor is in d_{31} (width) mode while β-phase film is in d_{33} (thickness) mode. The average piezo strain constant in width mode is around 2/3 of the thickness mode value. For future improvements, a new electrode design such as interdigitating electrode fingers can be used to reduce the average charge traveling distance for higher acoustic sensitivity.

3.5 Heart rate measurements

As previously mentioned, a biomedical application of the PVDF sensor was also studied. A commercial β-phase PVDF sensor was purchased from Measurement speciality (USA). It has two metal pins that are connected to the top and bottom of the electrodes, and the whole sensor is laminated with polymer film. The sensor is placed on the wrist near radial artery and fixed with a rubber band during measurement. Figure 20 shows the measured heart rate signal from the wrist, and we can estimate the heart rate from this data as 67 bpm. Although the signal is quite noisy, we can clearly see the heart rate pulses from this measurement. Two pulse signals are magnified from Figure 20 in Figure 21. As we can see from these graphs, the measured heart rate signal shows one big pulse and another small pulse right after that shows the characteristic of the heart sound signal S1 (Systole) and S2 (Diastole) respectively [10]. S1 sound results from mitral and tricuspid valve closure, and S2 sound results from aortic and pulmonic valve closure [16]. The superimposed noise signal is 60Hz from the measurement circuit. From this data, we can see the possible usage of the PVDF sensor as a heart rate monitoring device with further development.

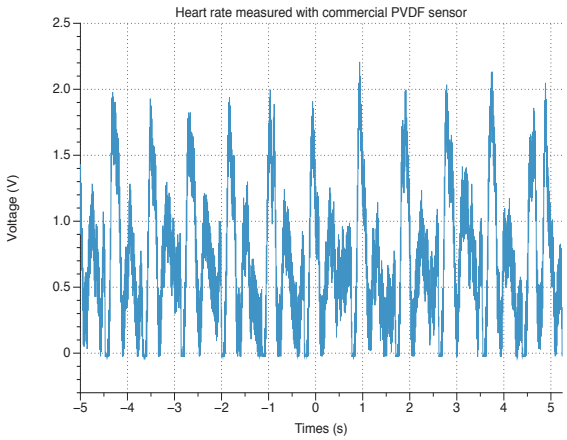

Figure 20: Plot of measured heart rate from the wrist

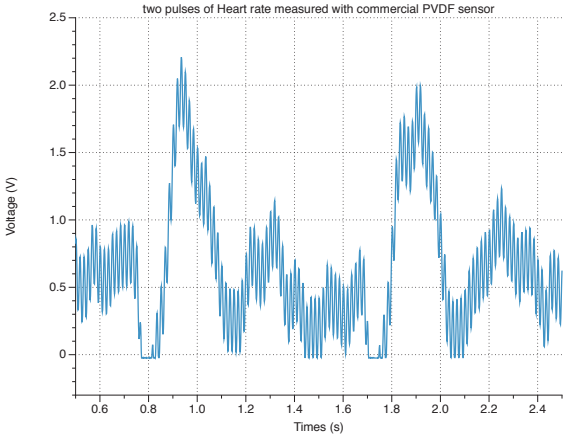

Figure 21: plot of two enlarged pulse signals from Figure 20

4 Conclusions

The main goal of this report is to characterize both mechanical and electrical properties of PVDF, and develop a package level acoustic sensor with transient mode. There are several results and findings during this work: Spin coated PVDF-TrFE with only thermal annealing shows β-phase crystallinity with XRD peak value of 20.2° which matches well with commercially polled β-phase film XRD peak value. The reference XRD peak value for commercially polled β-phase film is 20.26°. Electrospun PVDF-TrFE shows β-phase crystallinity with XRD peak of 20.47° that also matches well with commercial β-phase film XRD peak value. However, it shows much higher noise floor in XRD data due to rough surface. Using PVDF as acoustic sensor, Acoustic sensitivity of -48.7 dBV/pa was measured with calibrated setup. This value is comparable with other types of microphone that are expensive than PVDF sensor. For thermal transient mode, Joule heating was chosen to implement this function in design. With the temperature of sensor at 180°C, it takes around 300 seconds to destroy the PVDF sensor on package. With respect to sensing capability, PVDF sensor on package can detect footstep with the maximum distance of 20cm with gain of 100. However, PVDF sensor has higher standard deviation and lower detection rate compared to other type of microphone as distance increases. Finally, possible biomedical application of PVDF is reported. A heart rate of 67 bpm was measured using a commercial PVDF sensor on the wrist near radial artery.

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