All-Polymer Flexural Plate Wave Sensors

by

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Abstract

A novel all-polymer flexural plate wave (FPW) sensor from a piezoelectric polyvinylidene fluoride (PVDF) thin-film with poly-(3,4-ethylenedioxythiophene) poly-(styrenesulfonate) (PEDOT:PSS) interdigital transducer (IDT) electrodes has been fabricated and characterized. PVDF films are made piezoelectric by stretching and poling. X-ray diffraction measurements confirm the transition of the PVDF into its piezoelectric $\beta$-phase. Inks of PEDOT:PSS, dimethyl sulfoxide and Triton X-100 are deposited on the PVDF films by inkjet printing to produce the IDT patterns. The sensor operates using fundamental frequency, $f_0$, detection of Lamb waves propagating through the PVDF film. Upon the application of a time-varying voltage signal to the input IDT, acoustic waves are generated and measured using a laser Doppler vibrometer, as well as through an electric signal at the output IDT. The output signal is amplified, filtered and processed using an analog to digital converter, digital signal processor and a computer program. The measured fundamental frequencies range from 330 to 1600 kHz for devices with 18 and 125 $\mu$m thick PVDF substrates and 800 and 400 $\mu$m acoustic wavelengths. These values for fundamental frequency are well predicted by the device geometry using Lamb wave theory. The effect of mass-loading was characterized by inkjet printing layers of polyvinyl alcohol on the sensors and measuring the resulting frequency shift. The devices demonstrate a frequency shift, $\Delta f$, to mass loading, $m$, with a measured resonance frequency mass sensitivity of $\Delta f/(mf_0) = -55.9 \text{ cm}^2/\text{g}$. Temperature sensitivity was measured to be 1870 Hz/$^\circ\text{C}$. Sensors were also coated with a sensing layer of polyvinyl acetate and its response to toluene and acetone vapour concentrations was characterized.
Preface

Statement of Contributions

Much of this work was accomplished in collaboration with Christoph Sielmann. The equipment and procedures described in Section 3.3, Section 3.4 and Section 3.5 were designed jointly between Christoph and myself. The electrical measurement system described in Section 3.2 - including the driving waveforms, instrumentation amplifier circuit, Blackfin 506F digital signal processing unit, AD9262 16-bit analog to digital converter and LabView interface - was designed and configured by Christoph. The differential sensor design in Section 2.1.2 was also created by Christoph. The temperature, mass and vapour sensitivity experiments presented in Section 4.2, Section 4.4 and Section 4.5 were conducted jointly between Christoph and myself, however, Christoph performed most of the data post-processing. The following figures were also contributed by Christoph: Figure 3.5, Figure 4.5, Figure 4.6 and Figure 4.7.

The ink solutions and printing processes described in Section 2.3.2 were based on previous work by Gabriel Man [1]. Chou Fan contributed to the design and assembly of the gas test chamber in Section 3.5 and Lisheng Wang provided the X-ray diffraction measurements presented in Section 2.3.1.

List of Publications or Submissions

The work presented in Section 2.3.1, Section 2.3.2, Section 4.4 and Section 4.5 is also included in a submission entitled “Inkjet printed all-polymer flexural plate wave sensors”.
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List of Abbreviations

ABS  acrylonitrile butadiene styrene
ADC  analog to digital converter
BAW  bulk acoustic wave
BSA  bovine serum albumin
DAQ  data acquisition
DMSO  dimethyl sulfoxide
DSP  digital signal processing unit
EM   electromagnetic
FP   flexural plate
FPW  flexural plate wave
HSP  Hansen solubility parameters
IDT  interdigital transducer
LDV  laser Doppler vibrometer
LSER linear solvation energy relationships
MFC  mass flow controller
NDT  non-destructive testing
**PEDOT:PSS** poly-(3,4-ethylenedioxythiophene) poly-(styrenesulfonate)

**PPB** parts per billion

**PPM** parts per million

**PTFE** poly-tetrafluoroethylene

**PVA** poly-vinyl alcohol

**PVAC** poly-vinyl acetate

**PVDF** poly-vinylidene fluoride

**QCM** quartz crystal microbalance

**RED** relative energy difference

**SAW** surface acoustic wave

**SMO** semiconductor metal oxide

**TSM** thickness shear mode

**VOC** volatile organic compound

**XRD** x-ray diffraction

**ZNO** zinc oxide
I extend my sincere gratitude to my advisors, Dr. Konrad Walus and Dr. Boris Stoeber, for their continued guidance and support. Their enduring dedication has been a constant inspiration. I especially thank Dr. Walus for encouraging me to pursue a Master’s degree and for always offering advice on research and life related matters. I thank Dr. Stoeber for his thoughtful comments and attention to detail, which have greatly improved the quality of my work and research skills.

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Dedication

To Jessie,
my own true love.
Chapter 1

Introduction

Acoustic wave sensors have been studied extensively since the 1950s. They operate on the principle of a physical quantity (ie. mass, pressure, chemical concentration) modulating the dynamic deformations of a substrate which is electromechanically coupled to a measurement circuit. In this way, an electrical signal can be measured that is related to the physical quantity of interest. The most widely studied acoustic wave sensors include surface acoustic wave (SAW), flexural plate wave (FPW) delay lines, and bulk acoustic wave (BAW) (also known as thickness shear mode (TSM)) resonators [4]. These devices are shown schematically in Figure 1.1.

One of the most common applications of acoustic wave sensors is the detection and discrimination of volatile organic compound (VOC)s. To accomplish this, a selective polymer coating is applied to the sensor surface. The selective coating absorbs the VOC of interest, resulting in a density change. This change in density changes the speed of wave propagation through the device, resulting in a measurable change in frequency or phase in the electrical signal. In order to discriminate between several different types of VOCs, an array of sensors with different selective coatings is typically used. The joint response of the sensors can be used to determine the different concentrations of each VOC of interest.

1.1 Motivation

VOCs are a major type of indoor and outdoor air contaminant and there is increas-
Figure 1.1: Schematics of (a) a SAW sensor (b) a FPW sensor and (c) a BAW sensor
ing concern about their long term health and environmental effects. VOCs can contribute to chronic health problems and, even in low concentrations, can cause dizziness, headaches and fatigue and are associated with “sick building syndrome”. The British Columbia Air Action Plan describes VOCs as some of the main contributors to smog and the worst offenders against human and environmental health [5].

The current method of monitoring VOCs involves collecting samples at monitoring stations around the province and sending them to a central lab for gas chromatography mass spectroscopy analysis. This does not provide real-time data, making it difficult to detect fluctuations in VOC levels throughout the day.

In order to properly monitor sources and quantities of airborne VOCs, a distributed network of real-time sensors is highly desirable. To facilitate this, low-cost, real-time sensing systems with the ability to detect parts per billion (PPB) levels of different classes of VOCs are required. With sufficient gain by a gas pre-concentrator, an acoustic wave sensor could achieve this. Acoustic wave sensors based on crystalline piezoelectric materials such as quartz, lithium niobate and zinc oxide (ZNO) require photolithographic fabrication, which can be expensive. The development of a polymer-based acoustic wave sensor has the potential to provide sensors at a much lower cost.

1.2 Objectives

The primary goals of this research are to develop a low-cost, polymer-based sensing platform and investigate its performance in terms of mass and chemical vapour sensitivity. Specifically, the objectives of this work are to:

- develop a low-cost, novel FPW sensing platform using polymers,
- verify the presence and propagation of FPWs,
- compare the wave characteristics with Lamb wave theory,
- demonstrate mass sensitivity comparable to that of existing sensors,
- demonstrate vapour sensitivity for detection of parts per million (PPM) levels of VOCs.
A thin, piezoelectric poly-vinylidene fluoride (PVDF) film will serve as the membrane upon which flexural plate (FP) waves will be generated and propagated. The PVDF will first have to be converted to its piezoelectric $\beta$-phase using a stretching and poling process. The waves will be generated by an interdigital transducer (IDT) of poly-(3,4-ethylenedioxythiophene) poly-(styrenesulfonate) (PEDOT:PSS). The IDTs are then patterned onto the PVDF using drop-on-demand inkjet printing. For chemical vapour detection, a polymer sensing layer is also applied to the sensor surface.

The presence and propagation of FP waves will be verified using a laser Doppler vibrometer (LDV) to measure out-of-plane vibrations. This will also be verified electrically by receiving the acoustic signal at an output IDT. Lamb wave theory, as it applies to FPW devices will be described in this chapter. In the following chapters, predictions will be made based on this theory and compared to experimental results. The response of the sensors to mass loading, chemical vapours and temperature will also be characterized.

The work presented in this thesis will describe the procedures and methods used to fabricate and characterize PVDF FPW sensors. The remainder of this chapter will present the fundamentals of acoustic wave, and especially FPW, sensors and summarize the current state of the art regarding FPW and PVDF-based sensors. Chapter 2 details the procedures used to pole the PVDF, pattern the IDTs and apply polymer sensing layers. Chapter 3 will describe the experimental setups used to characterize the FPWs and mass and vapour sensitivities. The experimental results and discussion, comparing the theory to results, are presented in Chapter 4.

### 1.3 Acoustic Wave Sensors

SAW and FPW delay-line and BAW resonator sensors are widely used for applications in gravimetric sensing. Each of these sensors uses electromechanical coupling to determine the phase velocity of a certain acoustic mode via electronic measurements. The different acoustic modes and electrical measurement schemes offer distinct advantages.

An acoustic sensor operating in a delay line configuration has both input and output transducers. In the case of SAW and FPW delay lines, IDTs are used [6]. The
transducers consist of interdigital electrodes deposited on a piezoelectric substrate. The input IDT produces a periodic strain distribution in the piezoelectric substrate, with an acoustic wavelength defined by twice the center-to-center distance between adjacent IDT fingers, in response to an applied electric field. The strain waves propagate from the input to output where they produce an electrical signal at the output. The delay time between the input and output signals is determined by the phase velocity of the wave. The phase velocity can by modulated by mass loading of the medium between the input and output, providing a means of electrically measuring the change in mass. Delay line sensors are often used with an amplifier as a feedback oscillator in which phase velocity can be determined by measuring frequency rather than delay [7].

Resonator acoustic sensors, such as quartz crystal microbalance (QCM), are typically passive, one-port devices whose resonant frequency is determined by the geometry and the phase velocity in the medium [4]. The phase velocity, and hence, the resonant frequency can be modified by mass loading on the surface. This, again, provides a means of electrically measuring a change in mass. In all types of acoustic wave sensors, vapour sensing is accomplished by depositing a thin sensing layer which has some affinity to the vapours of interest. The most common interactions involve absorption of the vapours into polymer layers [8].

1.3.1 Characteristics of Acoustic Wave Sensors

Characteristic parameters of gravimetric acoustic wave sensors are operating frequency, mass sensitivity, vapour sensitivity and limit of detection. The operating frequency is important because there are practical limitations associated with accurately measuring high-frequency devices. BAW and FPW devices typically operate around 1-10 MHz, whereas SAW sensors operate at frequencies as high as 100s of MHz. Higher-frequency measurement electronics are inherently noisier and more expensive than low-frequency electronics. This means simpler and less-expensive support electronics may be used for BAW and FPW devices.

The mass sensitivity, \( S_M = \Delta f / (f_0 \Delta m) \), expressed in units of \( \text{cm}^2/\text{g} \), describes the normalized change in frequency (\( \Delta f / f_0 \)) in response to a change in mass per area (\( \Delta m \)). An analytical comparison of sensitivities of BAW, SAW and FPW sensors
was given by Wenzel and White [9]. The theoretical sensitivities of these devices, assuming the stiffness and tension are unaffected by mass-loading, are given by

\[ S_{BAW} = -\frac{2}{\rho \lambda}, \]  

(1.1)

\[ S_{SAW} = -\frac{K(\sigma)}{\rho \lambda}, \]  

(1.2)

\[ S_{FPW} = -\frac{1}{2\rho d} \]  

(1.3)

for BAW, SAW and FPW devices, respectively, where \( \rho \) is the substrate mass density, \( \lambda \) is the acoustic wavelength, \( d \) is the substrate thickness and \( K(\sigma) \approx 1 \) is a function of the Poisson’s ratio, \( \sigma \). In the cases of BAW and SAW devices, the sensitivity is an inverse function of the acoustic wavelength which means there is a tradeoff between sensitivity and operating frequency. This tradeoff does not exist in FPW devices since the sensitivity depends only on the density and the thickness of the substrate.

The vapour sensitivity describes the relative change in frequency in response to a given concentration of vapour and can be expressed in units of \((\text{Hz/MHz})/\text{PPM}\). The vapour sensitivity depends on the mass sensitivity, the thickness of the sensing layers and the ability of the sensing layers to absorb the vapour. The thickness of the sensing layer, \( d_s \), is typically measured as a frequency shift,

\[ \Delta f_s = S_M f_0 d_s \rho_s, \]  

(1.4)

using \( S_M \) to relate the two parameters. Vapour sensitivity is more practically determined experimentally by measuring the frequency change in response to vapour concentration, but it can also be established theoretically using the partition coefficient, which is the ratio of concentration of the vapour in the sorbent phase to its...
concentration in the gas phase (see Section 1.3.2). The relationship,

\[
\frac{\Delta f_v}{C_v} = \frac{\Delta f_s K}{\rho_s},
\]

holds for both SAW and FPW cases. The frequency response, \(\Delta f_v\), to the concentration of the vapour of interest, \(C_v\), depends on the thickness of the sensing layer (expressed in terms of the resulting frequency shift, \(\Delta f_s\)), the partition coefficient, \(K\), and the the density of the sensing layer, \(\rho_s\). This shows that, though the mass sensitivities are very different for SAW and FPW devices, the absolute vapour sensitivity can be the same, provided that the sensing layers are of a thickness that gives the same \(\Delta f_s\) in both cases.

The limit of detection refers to the absolute minimum concentration of a vapour that can be detected by the sensor. Equation 1.5 can be rearranged to solve for the limit of detection, \(C_{\text{min}}\)

\[
C_{\text{min}} = \frac{\Delta f_{\text{min}} \rho_s}{\Delta f_s K}
\]

where \(\Delta f_{\text{min}}\) is the minimum detectable frequency shift defined as the product of the noise floor (in Hz) and minimum signal-to-noise ratio (typically 3). Although the vapour sensitivities are identical in the case above, the frequency of operation in the FPW case is less than in the SAW case. This means the noise floor of the supporting electronics will be lower for FPW sensors than for SAW sensors. This again, demonstrates the tradeoff between sensitivity and operating frequency for a SAW sensor, while the sensitivity of a FPW sensor can be sustained while lowering its operating frequency to take advantage of lower detection limits.

### 1.3.2 Selective Coatings and Chemical Vapour Sensor Arrays

In order to detect and distinguish mixtures of chemical vapours, it is necessary to develop an array of sensors. Chemical sensor arrays offer the advantages of sensitivity to a broad range of analytes and the ability to identify individual analytes or groups of analytes. This is typically accomplished by using a number of sensors, such as acoustic wave or chemiresistor sensors. Each sensor is coated with a different sensing layer which is selective to a subset of the analytes and together they
are sensitive to the full range of analytes of interest. Using multivariate analysis techniques, several analytes can be detected and identified based on the combined response of all the sensors.

Chemical sensor arrays were first studied in 1986 and have since been explored using SAW [10], [11], TSM [12], FPW [13], microcantilever [14] and chemiresistor sensors for applications in air quality monitoring [15], wine discrimination [11], perfume quality control and breath characterization for disease detection [14].

Since acoustic sensors are mostly sensitive to mass changes, a wide variety of selective coatings can be used. Some common materials include polymers, chromatographic stationary phases, soot extracts and proteins [16]. Selective coatings should be selective and sensitive to the analytes of interest while reacting reversibly and reproducibly. Since real coatings will not be ideally selective, each coating response will overlap with others in the array. The goal is to find a set of coatings that will respond to all the analytes while minimizing the overlap between coatings and the total number of coatings used. This can be done by measuring the response of an overdetermined array of coatings to the analytes of interest and using techniques such as principle component analysis to narrow the array down to the minimum number of coatings that will span the entire set of analytes.

In order to initially select a set of selective coatings, it is necessary to use an appropriate model that predicts the sensitivity of the coatings to different analytes. The linear solvation energy relationships (LSER) are usually used for this. This model accounts for polarity, van der Waals and hydrogen bonding interactions between the coating and analyte [8]. Based on these interactions, the model predicts a value for the partition coefficient,

\[ K = \frac{C_s}{C_v} \]  

(1.7)

\( K \) relates the concentration of the analyte in the sorbent phase, \( C_s \), to the concentration in the vapour phase, \( C_v \). Using the partition coefficient, the sensitivity of a FPW sensor can be predicted as in Equation 1.5.

The LSER approach has been very successful at modeling coating-analyte interactions that are dominated by solubility interactions [16]. Its limitation, however, is that there is limited information available for the parameters necessary to define the
partition coefficient. An alternative model, with more comprehensive information available for its parameters, is the Hansen solubility model [17]. This approach does not predict the partition coefficient, but instead gives a relative energy difference (RED) which similarly describes the ability of a solvent to dissolve a solute. A RED < 1 usually means the polymer/vapours will dissolve. In this work, polymer/vapour pairs are selected using the Hansen solubility parameters (HSP) method. The partition coefficients of some of the relevant pairs have also been measured using QCMs [18].

1.3.3 Prior Art in Acoustic Wave Sensors

Acoustic wave sensors have been used for a wide variety of applications such as gravimetric sensing for chemical vapour detection and film thickness monitoring as well as force, acceleration and pressure sensing. BAW devices, such as the QCM, are most commonly used as film-thickness monitors [19], but have also been studied for applications in chemical and bio-sensing [20], [21], [22]. SAW devices have been used for bio-sensing [23], sensing of VOCs in air and water [24], [25] and force, pressure and acceleration sensing [26], [27],[28]. FPW devices have also been used for both chemical and bio-sensing [13], [29], [30] as well as liquid density and viscosity determination [31], [32].

For applications in chemical vapor sensing, the most widely employed platforms are QCMs, SAWs and FPWs. Generally, FPW devices demonstrate the highest achievable sensitivities, up to an order of magnitude higher than that of SAW devices. Due to their thin membranes, however, FPW devices suffer from poor temperature stability. For these reasons, and because of their ease of manufacturing and wide use as filters in the electronics industry, SAW sensors are more widely used for gas sensing applications. SAW devices are generally poorly suited to liquid sensing applications because of their high wave velocity, which leads to acoustic radiation into liquids. FPW, as well as other wave types, such as acoustic plate mode and Love waves do not radiate energy into liquids, making them more widely used for applications in liquid-phase bio-sensing and viscosity sensing.
1.4 Flexural Plate Wave Sensors

Elastic waves in a plate (Lamb waves) were first described by Lamb in 1917 [33] and later by Viktorov [34]. Wenzel first studied Lamb waves for their applications in sensing in 1992 [2]. FPWs are a first-order Lamb wave. FPW devices have several advantages over other acoustic wave sensors. Since waves propagate on both surfaces of the substrate, the underside of an FPW device can be exposed to the environment of interest, while the electrodes on the top surface can be accessed and protected as needed. The wave velocity of the lowest-order antisymmetric mode, $A_0$, is much less than that of SAWs of the same wavelength, and it decreases with decreasing substrate thickness, making it well suited to liquid phase sensing. The sensitivity of FPW devices is also independent of their fundamental frequency, unlike SAW devices, meaning that lower frequency operation is possible. This section will give an overview of the general models used to describe the properties of Lamb waves, as well as the equations derived by Wenzel relating to gravimetric sensing [2].

1.4.1 Properties of Lamb Waves

Lamb waves occur in plates whose thicknesses, $d$, are small compared to the acoustic wavelength, $\lambda$. In FPW devices, the wavelength is defined by twice the center-to-center distance between adjacent IDT fingers. The fundamental frequency is

$$f_0 = \frac{v_p}{\lambda},$$  \hspace{1cm} (1.8)

and

$$\omega_0 = \frac{2\pi v_p}{\lambda},$$  \hspace{1cm} (1.9)

where $v_p$ is the phase velocity. Lamb waves exhibit plane strain which refers to particle motion in the longitudinal direction and in the direction normal to the plate (the x and z directions, respectively, as defined in Figure 1.2). Surface acoustic waves also exhibit plane strain and are the limiting case of Lamb waves where $d$ approaches infinity.
Figure 1.2: Coordinate system used for Lamb waves in a plate where \( x \) is the direction of wave propagation

The dispersion relation for Lamb waves can be derived from the linear equations of elastodynamics as \([34]\) symmetric modes

\[
\frac{\tanh qh}{\tanh sh} = \frac{4k^2qs}{(s^2+k^2)^2}, \tag{1.10}
\]

and anti-symmetric modes

\[
\frac{\tanh qh}{\tanh sh} = \frac{(s^2+k^2)^2}{4k^2qs}, \tag{1.11}
\]

with

\[
q = \sqrt{k^2 - k_l^2}, \quad s = \sqrt{k^2 - k_t^2}, \tag{1.12}
\]

\[
k_l = \frac{\omega}{c_l}, \quad k_t = \frac{\omega}{c_t}, \tag{1.13}
\]

where \( h = d/2 \), \( k = \beta - j\alpha \), \( \beta = 2\pi / \lambda \), and \( \alpha \) is the attenuation and \( c_l \) and \( c_t \) are the bulk longitudinal and transverse wave velocities, respectively. Symmetric and anti-symmetric refer to the particle motions in the \( z \)-direction about \( z = 0 \). Figure 1.3 schematically shows the substrate deformations of the first order symmetric and anti-symmetric modes. Solving Equation 1.10 and Equation 1.11 numerically, the phase velocity, \( v_p = \omega / \beta \), is plotted as a function of the ratio of substrate thickness to acoustic wavelength, \( d/\lambda \), for the first symmetric and antisymmetric modes in Figure 1.4. This plot is for the specific case of a silicon nitride substrate, however,
other materials exhibit the same general form. The first order anti-symmetric mode, \( A_0 \), is the mode of interest in flexural plate devices. For large values of \( d \), the phase velocity approaches that of a surface acoustic wave.

For small values of \( d/\lambda \), a linear approximation can be used which yields simplified analytical expressions that conveniently describe the response of \( A_0 \) waves to changes in mass and tension. This approximation can be derived by balancing the force components acting on a plate,

\[
T \frac{\partial^2 u_x}{\partial y^2} - D \frac{\partial^4 u_x}{\partial y^4} + H \frac{\partial^4 u_x}{\partial y^2 \partial t^2} - M \frac{\partial^2 u_x}{\partial y^2} = 0.
\] (1.14)

This equation accounts for in-plane tension, \( T \), stiffness, \( D \), rotary inertia, \( H \), and mass per unit area, \( M \). By substituting appropriate expressions for each term, the equation simplifies to [2]

\[
\omega = \beta \left( \frac{T + \beta^2 D}{M + \beta^2 H} \right)^{1/2}.
\] (1.15)

It is useful to write this relation in terms of \( \beta \), which is inversely proportional to \( \lambda \), since \( \lambda \) is usually defined by the placement of electrode fingers on a device.
For acoustically thin plates, the rotary inertia ($H$) is often considered negligible, simplifying the expression to

$$\omega = \beta \left( \frac{T + \beta^2 D}{M} \right)^{1/2}. \quad (1.16)$$

From Equation 1.16 the phase velocity, $v_p = \omega / \beta$, is

$$v_p = \left( \frac{T + \beta^2 D}{M} \right)^{1/2}. \quad (1.17)$$

The stiffness and mass terms can be solved from the geometry and material constants,

$$D = \frac{E'd^3}{12}, \quad (1.18)$$

$$M = \rho d. \quad (1.19)$$

$E' = E(1 - \sigma^2)$, where $E$ is Young’s modulus and $\sigma$ is Poisson’s ratio.
The tension term depends on the in-plane stress, $\tau$,

$$T = \tau d.$$  \hspace{1cm} (1.20)

If a constant tension and stiffness in the membrane is assumed, the phase velocity is simply proportional to $M^{-1/2}$. This convenient expression provides a direct relationship between the mass loading and the resulting change in phase velocity, and hence, change in frequency. Assuming mass loading has no effect on tension or stiffness, the mass sensitivity is

$$S_M = \frac{1}{v_{p0}} \frac{dv_p}{dM} = -\frac{1}{2M} = -\frac{1}{2\rho d},$$  \hspace{1cm} (1.21) (1.22) (1.23)

where $\rho$ is the density and $d$ the thickness of the membrane. Wenzel showed this approximation to be valid for silicon/ZNO FPW devices with long wavelengths ($d \ll \lambda$) [2]. Since smaller thicknesses result in increased sensitivity, and low velocity operation is desirable, the condition $d \ll \lambda$ applies to most cases of FPW sensors.

### 1.4.2 Transduction Mechanisms

The purpose of the transducers in acoustic wave devices is to couple energy from an input source into the desired acoustic mode(s) and then couple that acoustic energy back into a measurable signal at the output. In this work, surface and Lamb waves are of most interest. Energy is most commonly coupled into these modes via piezoelectric transduction using IDTs.

The acoustic modes generated by IDTs depend on the IDT geometry and the associated electric fields as well as the electromechanical properties of the material. Figure 1.5 shows the electric field generated by a pair of IDT fingers. There are components to the electric field in both the normal (3) and the transverse (1)
Figure 1.5: Electric field lines generated by two IDT fingers

directions. The piezoelectric effect in both ZNO and PVDF is dominated by the $d_{31}$ and $d_{33}$ terms (see Section 1.5.1). This means strain is generated in the transverse (1) and normal (3) directions in response to the normal (3) component of the electric field. A ground plane, located on the underside of the piezoelectric film, is sometimes used for FPW devices to enhance the normal component of the electric field, increasing the strains in both 1 and 3 directions.

In the case of a FPW device, it is possible to generate both $S_0$ and $A_0$ modes using IDTs. The $S_0$ mode is generated mostly as a result of compression and extension in the normal direction resulting from the field in the normal direction ($d_{33}$), but also from transverse strain from the $d_{31}$. The $A_0$ mode is generated exclusively by compression and extension in the transverse direction resulting from field in the normal direction ($d_{31}$). This generates a bending motion in the plate similar to that of a waving flag.

1.5 Polymer-Based Acoustic Wave Sensors

Of all the polymers, only PVDF and its copolymers demonstrate an appreciable piezoelectric effect. As a result, these materials have been the primary choice for polymer acoustic wave applications. Section 1.5.1 describes the piezoelectric and other properties of interest of PVDF. Polymers generally exhibit high acoustic damping, making attenuation a significant factor in PVDF acoustic wave devices. As a result, the study of PVDF as a material for acoustic wave sensors has been somewhat limited. Some of the most relevant work as it relates to PVDF FPW
Table 1.1: Typical material properties for uniaxially stretched PVDF films

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ</td>
<td>Density</td>
<td>1.78</td>
<td>g/cm³</td>
</tr>
<tr>
<td>E</td>
<td>Young’s modulus</td>
<td>2-4</td>
<td>GPa</td>
</tr>
<tr>
<td>σ</td>
<td>Poisson’s ratio</td>
<td>0.35</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Tensile strength</td>
<td>45-55</td>
<td>MPa</td>
</tr>
<tr>
<td>ε</td>
<td>Relative Permittivity</td>
<td>12-13</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Dielectric strength</td>
<td>80</td>
<td>MV/m</td>
</tr>
<tr>
<td></td>
<td>Melting point</td>
<td>175-180</td>
<td>°C</td>
</tr>
<tr>
<td>c₁</td>
<td>Longitudinal velocity</td>
<td>2250</td>
<td>m/s</td>
</tr>
<tr>
<td>c t</td>
<td>Shear velocity</td>
<td>1410</td>
<td>m/s</td>
</tr>
<tr>
<td>Z</td>
<td>Acoustic impedance</td>
<td>3.81x10⁶</td>
<td>kg/m²s</td>
</tr>
<tr>
<td>α</td>
<td>Acoustic attenuation</td>
<td>13.4</td>
<td>(dB/cm)/MHz</td>
</tr>
<tr>
<td>d₃₃</td>
<td>Piezoelectric strain</td>
<td>-20 to</td>
<td>pm/V</td>
</tr>
<tr>
<td></td>
<td>coefficients</td>
<td>-33</td>
<td></td>
</tr>
<tr>
<td>d₃₁</td>
<td></td>
<td>18-23</td>
<td></td>
</tr>
<tr>
<td>d₃₂</td>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>k₃₁</td>
<td>Electromechanical</td>
<td>12%</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>coupling factors</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k t</td>
<td></td>
<td>14%</td>
<td>-</td>
</tr>
</tbody>
</table>

PVDF is an inert fluorocarbon similar to Teflon. Typical material properties of PVDF films are listed in Table 1.1. PVDF is commercially available in the form of powder, pellets or films of thickness ranging from 76 µm to several millimeters. The cost of the films is as low as $3 per square foot in small volumes. PVDF is semi-crystalline with a unit cell of CH₂ = CF₂ monomer and PVDF polymers have alternating CH₂ and CF₂ groups. Four polymorphs are known to exist: the α, β, γ and δ phases. The α-phase has a trans-gauche-trans-gauche’ conformation as shown in Figure 1.6; and is the lowest energy and most common phase; however, it is also non-polar. The β-phase has an all-trans conformation, making it polar. The β phase is the phase of interest for piezoelectric PVDF due to this polarity.

Piezoelectricity can be described by four sets of piezoelectric coefficients $d_{ij}, e_{ij}, g_{ij}$ and $h_{ij}$. Each set of coefficients relates an electrical characteristic to a mechanical
Figure 1.6: Schematic of the $\beta$ (A) and $\alpha$ (B) phases of PVDF. Image courtesy of Dr. John Madden [3].

characteristic. The $d_{ij}$ coefficients relate the electric induction in the $i$ direction, $D_i$, to the mechanical stress in the $j$ direction, $X_j$, (direct effect) and the mechanical strain in the $i$ direction, $x_i$, to the electric field in the $j$ direction, $E_j$, (converse effect) as follows:

$$d_{ij} = \left( \frac{\partial D_i}{\partial X_j} \right)_E = \left( \frac{\partial x_i}{\partial E_j} \right)_X. \quad (1.24)$$

The subscripts $E$ and $X$ indicate the experimental conditions under which $d_{ij}$ is measured (constant electric field and stress respectively). In the case of PVDF films, the electromechanical interactions can be summarized with the following matrix [40]:

$$\begin{bmatrix}
0 & 0 & 0 & 0 & d_{15} & 0 \\
0 & 0 & 0 & d_{24} & 0 & 0 \\
d_{31} & d_{32} & d_{33} & 0 & 0 & 0
\end{bmatrix}. \quad (1.25)$$

The coefficients of most interest are $d_{33}, d_{32}$ and $d_{31}$. For the case of a thin PVDF
film, the coordinate system is defined as in Figure 1.2. The negative $d_{33}$ indicates that, under an applied electric field in the 3 direction, a film compresses in the 3 direction but stretches in the 2 and 1 directions. For an undrawn film, there is no orientation in the 1 and 2 directions, meaning the $d_{31}$ and $d_{32}$ are equivalent. For this work, however, the films will be stretched in the 1 direction, resulting in an anisotropic film with a high $d_{31}$ and a low $d_{32}$.

The acoustic properties of interest for PVDF transducers and sensors are acoustic velocity and attenuation. The acoustic velocity will determine the fundamental frequency and acoustic coupling into liquids. Attenuation affects the quality factor of transducers as well as the maximum distance a wave can propagate before being significantly damped. Even among similar polymers, PVDF has a very high attenuation (13.4 dB/cm/MHz) [38]. This high attenuation leads to dispersion which widens the bandwidth of a transducer. This makes PVDF particularly well-suited to broadband applications such as speakers and microphones, but poorly suited to narrowband applications such as SAW and FPW devices. The large bandwidth ultimately results in greater noise levels in resonant frequency measurements, which will increase the limits of detection for gravimetric sensing applications. This represents one of the greatest challenges in developing a PVDF FPW sensor with a useful detection limit (10-100 PPM gas concentrations).

1.5.2 Lamb Waves in PVDF

Several early studies were conducted to measure various characteristics of Lamb waves in PVDF. The attenuation and phase velocity, for the first order symmetric Lamb mode, as a function of frequency for several PVDF thicknesses was measured [41], [42]. In one study, the Lamb waves were generated using a PZT transducer and attenuation was found to be 9.76 dB/cm at 300 kHz and increased with frequency [42]. Similar results were presented when Lamb waves were generated using IDTs [41]. In this case, the attenuation, $\alpha$, was seen to increase as

$$\alpha = 4.53 f^{1.335} \times 10^{-3} \text{dB/cm}. \quad (1.26)$$

PVDF transducers have also been studied widely for the excitation of Lamb waves in structural materials for non-destructive testing applications [43], [44],
In this work the generation of Lamb waves through the use of IDTs was of primary interest. The propagation of Lamb waves in PVDF was not considered. The main challenge reported in the generation of Lamb waves using PVDF was due to its large bandwidth. The PVDF transducers tend to excite many Lamb modes simultaneously, causing dispersion in the propagating signal which can make the data difficult to interpret [45]. In order to overcome this problem, the IDTs were specially designed to excite as few modes as possible.

1.5.3 Prior Art in PVDF Sensors

Polymers, especially PVDF, have been used widely for various ultrasonic transducer applications. Some examples include range sensors [46], hydrophone probes [47], microphones [48], [49], transducers for non-destructive testing (NDT) [50], [51], [43], [44], biosensors [52], [53] and bending curvature radius sensors [54]. The related modes of sensor operation can be classified into four groups: time-of-flight sensors, broadband receivers, longitudinal acoustic wave oscillators and Rayleigh-Lamb wave oscillators. PVDF is well suited to broadband receivers, such as microphones, due to its high damping and low Q. It is especially well suited to hydrophone applications due to its good mechanical impedance match with water. PVDF is also applicable to time-of-flight sensors, including range sensors, due to its low acoustic velocity which results in higher spatial resolution.

PVDF has also been used to fabricate various transducers for NDT. Most notably, PVDF IDTs were used to generate Lamb waves in structures of interest [43]. The Lamb waves can propagate significant distances in metallic or ceramic media and are easily detected using another PVDF transducer located elsewhere on the structure. In this way, reflections from fractures within the structure can be detected and since there is high damping in the PVDF itself, there is little chance of reflections within the PVDF transducers interfering with the measurements. Further motivation for the use of PVDF in these applications comes from its large bandwidth, flexibility and low cost.

PVDF has some disadvantages as a substrate for delay-line oscillator devices such as biosensors and bending curvature radius sensors. Due to its low Q, the frequency noise can be substantial, leading to poor detection limits. The length
of a delay line over which waves can propagate without significant damping is also restricted in PVDF due its high attenuation. Nevertheless, both longitudinal and surface wave sensors of PVDF have been successfully demonstrated [52], [53], [54]. These two applications are most relevant to this work and will, therefore, be discussed in more detail.

The longitudinal bulk wave biosensors described by Walton et al. are fabricated from a 9 \( \mu m \) thick film of PVDF which is stretched across a machined perspex block [52]. A metal transmitting electrode generates longitudinal bulk waves that propagate across the film and are detected by a receiving electrode. The output signal is fed back through an amplifying circuit to the transmitter, causing the system to oscillate at a frequency proportional to the wave velocity and inversely proportional to the length between the transmitter and receiver. The PVDF is then functionalized to bind specific proteins, which will decrease the wave velocity and hence the resonant frequency. This device had a resonant frequency around 100 kHz and responded with a change of -40 Hz to the adsorption of a monolayer of bovine serum albumin (BSA). They reported an improvement by a factor of 30 over existing QCM devices. This improvement was attributed to the increase in mass sensitivity due to the lower density and thickness of the PVDF film as compared to quartz wafers.

Preethichandra et al. reported on PVDF SAW sensors for measuring bending curvature radius [55], [54]. Gold IDTs were deposited on a PVDF film. The exact geometry of the sensors tested was not specified. The input was excited with a 4kHz sinusoidal input and a lock-in amplifier was used to measure the output. The lock-in amplifier measured the amplitude of the 4kHz component of the output signal as well as its phase referenced to the input signal. These two signals were measured as the sensor was bent around cylinders of various radii and the signals varied non-linearly with radius of curvature. For this application, PVDF was chosen primarily due to its flexibility.

To this author’s knowledge, aside from the examples presented above, there are no other examples of PVDF being used as the substrate material for acoustic wave delay line sensors. Though not without challenges, there is much potential in a PVDF-based low cost FPW chemical vapour sensor. This platform also holds potential for applications in liquid-phase sensing such as bio-sensing and viscosity measurement.
Chapter 2

Sensor Design and Fabrication

In order to meet the objective of developing a low-cost chemical vapour sensing platform, polymer materials were chosen for use as the substrate, transducer electrodes and sensing layers of a FPW sensor. The piezoelectric polymer, PVDF was chosen as the substrate material. PVDF is well suited to FPW sensing since low density, thin films are possible. The electrically-conductive polymer, PEDOT:PSS, was chosen as the transducer electrode material. Aqueous solutions of PEDOT:PSS are commercially available and can be deposited using simple methods such as inkjet or screen printing. Polymer sensing layers have been widely used for applications in chemical vapour sensing and can be easily applied to any substrate using air brushing or spin coating.

The following sections will describe the target performance parameters for the PVDF FPW sensor platform and the practical limitations of the materials and technology. The design parameters will be specified and the fabrication processes will be described.

2.1 Flexural Plate Wave Sensor Design

2.1.1 Performance and Design Parameters
The use of polymer materials and low-frequency operation immediately decreases the cost of these sensors and their supporting electronics, but they will still have to
Parameter | Typical Value | Unit  
---|---|---  
Mass sensitivity | 10 - 1000 | cm²/g  
Vapour sensitivity | 0.001 - 0.05 | (Hz/MHz)/PPM  
Detection limit | 1 - 100 | PPM  
Operating frequency | 100 k - 1 G | Hz  
Temperature sensitivity | 10 - 1000 | Hz/°C  

Table 2.1: Typical performance parameters for gravimetric acoustic wave sensors.

compare in performance to commercially available sensors if they are to be worthwhile. The performance of acoustic wave chemical vapour sensors is measured by several parameters. These are the mass sensitivity, vapour sensitivity, limit of detection, operating frequency and temperature stability. Typical values for these parameters of commercially available gravimetric sensors are given in Table 2.1. This section will describe the effect of different design parameters on the performance parameters and will specify the optimal design parameters within the constraints of the materials and processes.

**Mass Sensitivity**

The mass sensitivity, $S_M$, is one of the most important aspects of a gravimetric sensor. In the case of a FPW sensor, it is approximated by $S_{FPW} = -1/2 \rho d$. Since $\rho$ is a material property, the theoretical sensitivity for a PVDF film is simply optimized by decreasing the thickness of the substrate. Extremely thin membranes may be very fragile, providing a practical lower limit to the substrate thickness. Since PVDF is a very tough material, membranes thinner than 10 µm are easily achievable. PVDF films ranging from 76 µm to several mm are commercially available at low cost. After the stretching process described in Section 2.3.1, the 508 and 76 µm thick films are reduced in thickness to 125 and 18 µm. These are the substrate thicknesses used in this work. The corresponding theoretical mass sensitivities are -22.47 and -156.1 cm²/g. These values are on the same order as typical gravimetric sensors and can be further improved by using even thinner membranes.

The approximate equation for mass sensitivity assumes that the phase velocity of the FPWs in the substrate depends only on the mass term, $M$, in Equation 1.17
Figure 2.1: FPW phase velocity as a function of mass layer thickness for varying mass layer stiffness, where the substrate is an 18 µm thick film of PVDF.

and not the $T$ or $D$ terms. The $D$ term, from Equation 1.18, however, can be modified to include a term that captures the fact that stiffness increases for an increasing thickness of the added mass layer,

$$D = \frac{E_M d^3 + E_M^' d_M^3}{12} = D_S + D_M,$$  \hspace{1cm} (2.1)

where $E_M^'$ is the modified Young’s modulus of the layer of added mass and $d_M$ is its thickness. If the substrate material is much stiffer than the layer of applied mass (i.e. $D_S > D_M$), the effect of the added stiffness, $D_M$ will be negligible. This is the case for highly crystalline substrates with polymer mass layers. For the case with a PVDF substrate and a polymer mass layer, such as the poly-vinyl alcohol (PVA) to be used in this work, the additional stiffness term cannot be neglected. This is illustrated in Figure 2.1, which shows the phase velocity as a function of mass layer thickness for the cases of $D_M$ equal to zero, and equal to $D_S$, one tenth $D_S$ and one hundredth $D_S$. For $D_M << D_S$, the phase velocity as a function of mass layer thickness is well approximated by the the case of $D_M = 0$. However, when the stiffness of the mass layer is comparable to that of the substrate, the approximation does not hold.
Vapour Sensitivity

The vapour sensitivity, $S_V$, is dependent on the density and thickness of the sensing layer and the partition coefficient between the sensing layer and analyte of interest as defined in Equation 1.5. The vapour sensitivity increases with increasing sensing layer thickness. There is a tradeoff here between vapour sensitivity and response time, as response time is faster for thin films due to shorter diffusion lengths. The HSP are used to calculate RED scores for various sensing layer/analyte pairs. Lower RED scores indicate a stronger ability of the pair to dissolve. The sensing layer/analyte pairs used in this work were chosen because they have low RED scores, they are convenient, and they do not interact with PVDF. The pairs used are poly-vinyl acetate (PVAC) with acetone and with toluene. The RED scores between acetone/PVAC and toluene/PVAC are 2.41 and 0.6, respectively. The partition coefficient between toluene and PVAC was measured previously by Kelly He and was found to be 2881 [18]. The thickness of the PVAC layer used is 7 µm, as discussed in Section 2.3.3. The corresponding frequency shift is given as

$$\Delta f_s = S_m f_0 t_s \rho_s,$$

(2.2)

where $t_s$ and $\rho_s$ are the thickness and density of the polymer layer, respectively. Using $\rho_s = 1.19 \text{ g/cm}^3$, this corresponds to a $\Delta f_s = 96.8$ Hz. The theoretical vapour sensitivity from Equation 1.5 is then equal to 0.390 (Hz/MHz)/PPM.

Quality Factor and Detection Limit

The limit of detection describes the minimum detectable concentration of a particular analyte and is limited mainly by the noise level of the sensor and measurement system. While the theoretical mass and vapour sensitivities have no direct dependence on attenuation, the limit of detection is greatly affected by it. As a result, the success of polymer based acoustic sensors may hinge on their achievable detection limits.

PVDF is typically considered a damped rather than a resonant material, having high attenuation and low quality factor, $Q$. This means that PVDF transducers will not resonate strongly at one frequency. Instead, the acoustic energy is spread
out over a broad range of frequencies. This increases the minimum detectable frequency shift, posing a challenge in developing PVDF sensors with useful detection limits. Due to their low $Q$, PVDF transducers are actually more suited to a time-of-flight measurement scheme. In a time-of-flight sensor, a broadband impulse is launched from one transducer and detected at another. Using time-of-flight measurements, the detection limit depends on the length of the delay line. For a measurement system with a given temporal resolution, the corresponding spatial resolution, and hence the phase velocity resolution, will be higher for a higher delay length between input and output IDTs. This makes it advantageous to use long delay lines. However, in materials with high attenuation, the acoustic signal may be significantly damped at the output if a long delay line is used. For PVDF, the attenuation can be so significant that it is necessary to use a short delay length. With the configurations used in this work, the acoustic waves could only propagate several wavelengths before being damped out below detectable levels. Longer wave propagation may be possible with different configurations. As a result of the high damping and short delay lengths, the ultimate sensitivity and detection limit using a time-of-flight measurement scheme are also limited.

The frequency noise level of a sensor depends on its quality factor, $Q$. The overall $Q$ depends on the IDT geometry as well as the attenuation of the acoustic medium. The electrical input signal will have a $Q$ associated with it. The transduction of the electrical signal into an acoustic signal by the input IDT will broaden the signal, decreasing the $Q$ of the acoustic signal. $Q$ will be further decreased due to acoustic attenuation as the wave propagates to the output IDT, and again through transduction back to an electrical output signal. The amount of broadening due to the IDTs can be minimized by increasing the number of finger pairs, $N$. The broadening due to the acoustic propagation through a medium depends on the attenuation in the medium and the length of acoustic propagation. In this work, PVDF, with high acoustic attenuation, is used as the acoustic medium and $N$ is limited by available poled area of PVDF. Both these factors are expected to contribute to a very low overall $Q$, though one effect may be dominant over the other.

Due to the limited available area of poled PVDF, values of $N = 4$ and 8 will be used, with acoustic wavelengths of $\lambda = 800$ and 400 $\mu$m. In both cases, the acoustic delay line is one wavelength long. These parameters, combined with the
two film thicknesses, result in 4 different sensor geometries to be studied. The 4 sensor geometries are summarized in Table 2.2. Also included are the theoretical mass sensitivities (Equation 1.21) and the phase velocities (Equation 1.17) and fundamental frequencies for the cases of 0 and 100 MPa of in-plane stress, \( \tau \). As will be shown in Chapter 4, both fundamental frequency measurements and time-of-flight measurements will be explored.

### Temperature Sensitivity

Temperature affects FPW sensor response in several ways. With the use of a polymer for the FPW substrate, the temperature effects are likely to be enhanced. Temperature affects the phase velocity of FPWs through all three terms in Equation 1.17.

The density and stiffness of the PVDF will change with temperature. If the sensor is composed of different materials with different coefficients of thermal expansion, the tension in the membrane will also be a function of temperature. Temperature also affects interactions between the polymer sensing layer and the analyte. All these effects contribute to variations in the sensor measurements due to temperature change. In order to compensate for temperature effects, a reference sensor is often used.

#### 2.1.2 Differential Sensor Design

FPW sensors generally have poor temperature stability. It is well known that temperature sensitivity is typically more extreme in polymer materials. Because of these factors, PVDF FPW sensors are expected to have very high temperature sensitivity. In order to overcome this, a reference sensor can be used. The reference...
device will be identical to the sensing device except that it will be lacking a sensing layer. It should be placed as close as possible to the sensing device so environmental factors, such as temperature, affect the two in an identical fashion. The difference of the two signals is taken as the output signal. If both sensors are identical, the signals should perfectly cancel out, resulting in zero amplitude. A frequency shift in one of the sensors will affect the phase, frequency and amplitude of the output signal. Since the overall amplitude of the signal should be close to zero, the relative amplitude changes in response to mass loading should be very large.

In order to maintain the reference and sensing device at the same environmental conditions, both sensors will be printed on the same PVDF substrate. Due to the limited poled area available on the PVDF film prepared with the method described in Section 2.3.1 the sensors will share an input IDT, but have separate output IDTs. This is shown schematically in Figure 2.2. The input IDT has twice as many finger pairs as the outputs in order to increase the quality factor. The input IDT will be driven with an input signal which will generate acoustic waves propagating towards

Figure 2.2: Schematic of a differential FPW sensor with reference IDT. $\lambda = 800\mu m$, $N = 4$ at the outputs and $N = 8$ at the input IDT.
both outputs. The output signals can then be measured independently and used to digitally compensate for environmental factors, or they can be multiplexed or subtracted at the output. Both output IDTs will be coated with the sensing layer, but on opposite sides of the film, so that one can be exposed to sample gas, while the other is not.

2.2 Aspects of PVDF Substrate Preparation

2.2.1 PVDF Film Poling
Films of PVDF are readily available in the $\alpha$-phase. In order to transform films into the piezoelectric $\beta$-phase, they are typically stretched to around 4.5 times their original length \cite{56,57}. The transformation occurs because the molecular chains are more extended in the $\beta$-phase than in the $\alpha$. Once in the $\beta$-phase, the dipoles must be aligned to polarize the film. This process is called poling and is done by applying a high electric field across the thickness of the film at a temperature above the Curie temperature, which is around 100$^\circ$C for PVDF. The poling can be achieved by either static or corona poling.

Static poling is accomplished by applying a DC field across the film while it is heated above the Curie temperature. The field is applied using electrodes on either side of the film. The electrodes can be deposited by evaporation or externally contacting the film. Electric fields up to 160 MV/m have been used with an optimal stretch ratio of 4.5x \cite{58}. At fields higher than 160 MV/m, dielectric breakdown of the PVDF is likely to occur.

Corona poling uses a corona needle to produce ions which are accelerated towards the PVDF film, depositing them on the surface and creating a field across the film. This method allows for more uniform charge across the surface of the film \cite{59}. It also makes dielectric breakdown of the PVDF less likely, permitting the use of higher poling fields. In both static and corona poling, it has been shown that simultaneous stretching and poling results in films with higher piezoelectricity \cite{57,58}.
2.2.2 Pre-tensioning

The propagation of acoustic waves from the input transducer to the output transducer is substantially increased by pre-tensioning the PVDF films into a supporting frame. Preliminary measurements of the acoustic vibration of the substrate in response to excitation from the input transducer indicated that tensioning of the film is necessary to reduce acoustic damping and enhance the amplitude of acoustic waves at the output transducer.

2.3 FPW Sensor Fabrication

2.3.1 Substrate Preparation

In this work, stretching and subsequent static poling is performed to produce piezoelectric PVDF films as follows. PVDF films of thicknesses 508 and 76 µm are purchased from McMaster-Carr. They are first cut into 7.5 mm x 10 mm rectangles and rinsed with isopropanol. Two holes are drilled or punched into each end of a film and the film is placed into the clamps of the stretching apparatus (Figure 2.3). The stretcher is placed inside a temperature control chamber with its handle protruding from the access port of the oven. The chamber is heated to 120°C and the film is stretched manually by 4.5 times its original length at an average rate of 6.7 mm/min. Once stretched, the film is returned to room temperature and is then sandwiched between round electrodes with 25.4 mm diameters, heated to 120°C and poled under an electric field of 125 MV/m for 30 minutes using a Gamma ES30P-10W high voltage power supply. With the field still applied, the temperature is ramped back down to room temperature over a 20 minute duration to hold the molecular chains in their poled orientation.

There are several disadvantages of this process that will be addressed with a new poling system currently under development. The stretching is currently performed manually, which is time-consuming and limits the repeatability of the process. The static poling method uses small electrodes to minimize leakage current around the PVDF films. This limits the useful area of the poled PVDF films to approximately 5 cm². There is also risk of dielectric breakdown of the PVDF, which destroys the films, resulting in low yield. A new stretching and poling apparatus
was designed by Tristan Miller [60]. This system uses simultaneous stretching and corona poling and will address the issues described above.

XRD is used to measure the proportions of $\alpha$- and $\beta$-phases present in the film through the stretching and poling process. X-ray diffractograms of PVDF films as purchased, after stretching, and after stretching and poling are shown in Figure 2.4. Films are initially in the $\alpha$-phase. Upon stretching, the $\beta$-phase is predominant, however, the dipoles are likely to be randomly oriented. After subsequent poling, the dipoles should now be aligned with the electric field, however, some of the molecular chains have relaxed back into the $\alpha$-phase. This is likely due to the high poling temperature used. To prevent relaxation to the $\alpha$-phase and to maintain a sufficient poling temperature, simultaneous stretching and poling should be used. This will be accomplished with the automated stretching system described above.

Once stretched and poled, the films must be pre-tensioned to reduce the damp-
Figure 2.4: XRD of PVDF film (a) as purchased, (b) after stretching and (c) after stretching and poling. Red peaks correspond to $\alpha$-phase and green peaks correspond to $\beta$-phase.
Several attempts were made to maintain uniform tension on the films throughout the lifetime of the sensors. Bonding the PVDF films under tension to glass slides using Bondit B45TH resulted in delamination of the films within a period of 24 hours. Acrylonitrile butadiene styrene (ABS) frames were then designed and fabricated using a MakerBot Thing-O-Matic 3D printer. The frames were bonded on either side of the tensioned PVDF film using dimethylformamide (Figure 2.5a). This configuration was able to hold the frames under tension for longer than a week, but eventually delaminated. Another potential problem with the ABS frames is their ability to absorb and emit VOCs, which would directly affect the sensor response to vapours.

The final design incorporates two stainless steel frames which are bolted together, sandwiching the tensioned PVDF film (Figure 2.5b). Using the stretcher, the films are tensioned to 100 ± 17 MPa using a torque wrench. Stainless steel frames are then clamped to the films using the custom clamp in Figure 2.6. This is necessary to prevent the films from tearing while holes are drilled. Once clamped, holes are drilled through the PVDF and bolts are inserted and tightened. The clamp is then removed and the PVDF is cut around the frame. Applying tension using these frames results in more repeatable and durable films than with the plastic frames. The stainless steel frames have been able to maintain tension in the PVDF films for more than four months; however, detailed analysis of the creep in the films has yet to be completed.

### 2.3.2 Transducer Patterning

IDTs of PEDOT:PSS are patterned on the prepared PVDF films using an inkjet printer. PEDOT:PSS is a conductive polymer available in aqueous dispersions. Once dried, the conductivity of a PEDOT:PSS film can be as high as 900 S/cm. It has also been found that the conductivity can be increased an order of magnitude with the addition of organic solvent dimethylsulfoxide (DMSO) [61]. The surface wetting properties of PEDOT:PSS inks, as printed with inkjet nozzles, on PVDF have been studied previously by Gabriel Man [1]. It was found that the minimum achievable track width of PEDOT:PSS on PVDF was 55 µm using a 20 µm nozzle and a multilayer printing process. This limits λ to greater than 220 µm which is sufficient for
Figure 2.5: PVDF films pre-tensioned and clamped in (a) ABS plastic and (b) stainless steel frames

Figure 2.6: Clamp system for clamping PVDF films
Figure 2.7: Schematic of multi-layer printing process

Figure 2.8: Interdigital transducer (a) macro pattern and (b) printed result with $\lambda = 800 \mu m$ and $N = 5$

A custom inkjet printer based on nozzles from MicroFab Technologies with orifice diameters of 40 $\mu m$ is used to pattern the IDTs. An aqueous dispersion of PEDOT:PSS (Clevios™HP 1000) with 5 wt% DMSO and 0.2 wt% Triton®X-100 is used as the ink. The DMSO is added to enhance the conductivity and Triton®X-100, a surfactant, is added to increase the wettability of the ink on the PVDF. When printing the IDT fingers, agglomeration of consecutive droplets causes non-uniform tracks with minimum widths much greater than 100 $\mu m$. In order to prevent agglomeration to achieve track widths smaller than 100 $\mu m$, the IDT fingers are printed with a three-layer printing process. Drops are printed 200 $\mu m$ apart for the first layer and 100 $\mu m$ for the second and third layers, as in Figure 2.7. Us-
ing this method, drops in one layer are far enough apart to prevent agglomeration and are given sufficient time in the printing process to dry before the next layer is deposited. The effect of this process on conductivity has not been fully studied.

The overall sensor pattern is defined by a macro. The use of a macro allows precise control over the order in which different parts of the pattern are printed. This is important to ensure one layer of PEDOT:PSS ink is dried before another layer is applied. A Matlab program was developed, in part by Derek Tsan and Christoph Sielmann, that generates a macro for IDTs with geometry specified by user input. The program also creates a plot of the resulting pattern. For a single sensor with $\lambda = 800 \, \mu m$ and $N = 5$, the Matlab plot and a photograph of a printed PEDOT:PSS IDT are shown in Figure 2.8. Additional macros and plots, as well as the Matlab program, are given in Appendix B.

In order to make electrical contact to the IDTs, several approaches were explored. Micropositioners were used to bring metallic probes into contact with the IDT pads. This method did not provide stable contact, easily damaged the PEDOT:PSS layers and introduced electromagnetic coupling into the system. Instead, a carbon-based wire glue was purchased from Think Geek. This was used to bond 20 gauge wire to the IDT contact pads. Although this solution provided good contact, it still caused damaged to the IDT pads. To protect the pads, copper tape with conductive adhesive was first applied. Wires could then be bonded to the copper without risk of damaging the pads. This is shown schematically in Figure 2.9. The electrical characteristics of this contact were sufficient and the details were not studied.

### 2.3.3 Application of Polymer Sensing Layers

In order to use the FPW device for chemical sensing, a polymer sensing layer must first be applied. The polymer layer should be uniform and of a thickness less than one acoustic wavelength. Airbrushing was used to achieve this. The sensing layers were applied to the back side of the PVDF (the side without the PEDOT:PSS IDTs). For the case of a single sensor, the sensing layer was deposited over the entire area covered by the input IDT, delay line, and output IDT. For the case of a differential sensor, sensing layers were deposited on the bottom side of the PVDF film over the
area of the sensing IDT and on the top side of the PVDF film over the area of the reference IDT.

Airbrushing was accomplished by first dissolving the sensing layer polymer, polyvinyl acetate (PVAC), in toluene with a concentration of 3.5 wt%. This solution was spray-deposited on the bottom side of the FPW sensors using a Badger 250 airbrush and a cardboard mask. The airbrush stream was started away from the sensor and swept across it in order to deposit a layer with consistent thickness. 20 of these layers were deposited and the total thickness after drying was measured to be 7 µm using a Wyko NT1100 optical profilometer.
Chapter 3

Experimental Procedures

In order to characterize the PVDF FPW sensors, several techniques are used. A scanning LDV is used to measure the vibrations of the substrate. The LDV provides a qualitative means of observing the vibrations induced by the IDTs as well as precise measurements of the out-of-plane displacements. Characteristics of the FP waves are also measured through the electrical signal at the output IDT. Temperature, mass and vapour sensitivities of the devices are also characterized. This chapter describes the experimental methods and measurement systems used to characterize the FPW sensors.

3.1 Optical Vibration Measurements

In order to characterize the electromechanical coupling and acoustic wave propagation of the sensors, a Polytec MSA-500 LDV is used to optically measure out-of-plane vibrations. The LDV uses a scanning laser to create a 2D map of out-of-plane vibrations on a target. Laser light is back-scattered from the target with a Doppler frequency shift caused by the out-of-plane motion of the target. Displacements on the order of pm and velocities on the order of µm/s can be measured this way. The system uses a fast Fourier transform method to determine the velocity and displacement of the different frequency components of the signal. The MSA-500 also has an internal function generator that can be used to actuate devices synchronously with measurements. Using this feature, it is possible to measure the instantaneous
velocity or displacement of a frequency component with a given phase shift from the input signal. The internal function generator can produce sinusoidal, triangle, square or periodic chirp signals with amplitudes up to 10 V<sub>pp</sub>. By feeding the output of the function generator into a Trek 2100HF high frequency amplifier, the input signal, V<sub>in</sub>, can be amplified 50x with a 3 MHz bandwidth. A schematic of the overall measurement system is shown in Figure 3.1.

The MSA-500 has a maximum scanning area of 4.4 mm x 4.4 mm. For a sensor with λ = 800 µm, this corresponds to 5.5 wavelengths. For an IDT with 4 finger pairs, the vibrations of all 4 finger pairs can be scanned in one measurement. The same is true for sensors with λ = 400 µm and N = 8. When taking measurements with the LDV, the area scanned is either the input IDT, the output IDT or centered exactly midway between the input and output, over the delay line region. The scanning region for a midway measurement is shown in Figure 3.2.

In order to measure the vibration velocity as a function of frequency, the input IDT is excited with a 10 kHz - 2 MHz periodic chirp signal of 100 V<sub>pp</sub> amplitude. The laser is scanned across one of the regions mentioned above and the out-of-plane velocity is measured at each point. The instantaneous velocity of each point at different phases from the input trigger can be viewed for each frequency component. An example of such an instantaneous velocity profile of a sensor is shown in
Figure 3.2: LDV scanning area for measurements made midway between input and output IDTs

Figure 3.3: Instantaneous velocity profile of a given phase for the fundamental frequency component of a 125 µm thick sensor with $\lambda = 800 \mu$m
Figure 3.4: The velocity magnitude spectrum of a sensor with $\lambda = 800 \, \mu m$ and $d = 125 \, \mu m$

3.2 Electrical Characterization

3.2.1 Measurement Schemes

There are four quantities of interest when measuring the electrical output signal of the FPW sensor. These are amplitude, fundamental frequency, phase and time delay. The output amplitude is related to the input amplitude, attenuation and frequency of the system. The fundamental frequency is related to the wave speed in the medium and the wavelength, which is determined by the IDTs. The phase represents the phase velocity in the delay line. The time delay is measured from the rising edge of the input signal to the point of maximum amplitude of the output signal. This quantity represents the group velocity both in the IDT regions and through
the delay line separating the two IDTs. In order to measure these quantities, two measurement schemes were explored: feedback oscillator and time-domain.

Typically, fundamental frequency measurements are done by feeding back the output of the FPW sensor through an amplifier to the input of the sensor. This will cause the system to oscillate at the fundamental frequency of the FPW sensor, as defined by the wave speed in the medium and the IDT geometry. With these PVDF sensors, however, this type of measurement scheme was difficult to implement. Due to the high acoustic attenuation, the electromagnetic (EM) coupling of the signal, through stray capacitances and RF crosstalk was much stronger than the electromechanical coupling, through the delay line. As a result, any oscillations of the system would be dominated by EM effects, making a delay line oscillator impossible. Many efforts were made to shield the input and output signals to reduce crosstalk, but in all cases, the electromechanical coupling was overwhelmed by EM coupling. As a result, time-domain measurements were instead investigated.

Time-delay measurements were performed by exciting the input IDT with a broadband impulse signal. The output signal was a combination of an EM signal, which occurred almost instantaneously, followed by an electromechanical signal, delayed by several microseconds due to the slower acoustic wave speed. It was then possible to isolate the acoustic signal, as described in Section 3.2.2, and its frequency, phase, amplitude and time delay were measured.

3.2.2 Measurement System

The overall electrical measurement system is shown schematically in Figure 3.5. An Agilent 33220A arbitrary waveform generator was used to generate the input signal, which was amplified by a Trek 2100HF high frequency amplifier and connected to the input of the FPW sensor. A high-input-impedance instrumentation amplifier was connected at the output of the FPW sensor. For initial testing, the output of this circuit was analyzed using an Agilent DSO6034A oscilloscope. The signal was further processed digitally using LabView to acquire data from the oscilloscope and measure the amplitude, fundamental frequency, phase and time delay. This setup was limited to the resolution constraints imposed by the 8-bit analog to digital converter within the oscilloscope. To replace the oscilloscope, a data acqui-
Figure 3.5: Schematic of FPW measurement system

Figure 3.6: BNC connector used to make input connection to sensor

...sition (DAQ), based on an Analog Devices Blackfin 506F digital signal processing unit (DSP) and an AD9262 16-bit analog to digital converter (ADC), was developed. This system provided higher resolution measurements and afforded more flexibility.

Since the acoustic coupling between the input and output is relatively small, the output signal was amplified 100x and efforts were made to reduce the EM coupling between the input and output IDTs and contacts. Initially, with a periodic impulse signal at the input, the EM coupling sent the amplifier into saturation, causing it to ring and bury the electrical signal from the converted acoustic signal. EM coupling was reduced by minimizing the length of unshielded leads. This was done on the input by using the modified BNC connector shown in Figure 3.6. On the output, short wires were wire-glued to the IDT pads and connected to the amplifying circuit. This configuration reduced the EM coupling, allowing the acoustic signal to
be seen in the output. There was still a significant EM component to the output signal, making it difficult to pick out the acoustic component. This also caused the system to be very unstable, occasionally causing the instrumentation amplifier to go into saturation and ring. In order to further reduce the EM coupling, the input signal was modified to have a smaller bandwidth focused around the acoustic fundamental frequency (Figure 3.7). This allowed more energy to be coupled into the acoustic mode and less energy into the higher frequency EM modes. The resulting output signal with this configuration is shown in Figure 3.8.

The DAQ was configured to wait a specified amount of time ($t_d$) after the input trigger and then sample the output for 10 $\mu$s. The delay was set so that the EM signal was completely outside the acquisition window. The DSP samples the signal at 50 MS/s and sends the average of 5000 cycles to the LabView program. LabView displays the averaged waveform and computes its highest-energy frequency component, its phase, amplitude, and time delay referenced to the trigger. These values are all stored in a data file and plotted in real time. The LabView interface is shown in Figure 3.9 and the real-time plots of frequency, phase, amplitude and time delay are shown in Figure 3.10. Also plotted are the output of a semiconductor metal oxide sensor and test chamber temperature, as described in Section 3.5. The frequency noise floor of the overall measurement system, excluding the sensor, was found to be around 0.6 Hz.
Figure 3.7: (a) Time domain and (b) frequency domain representation of modified input pulse waveform
Figure 3.8: Output signal with reduced EM coupling
Figure 3.9: LabView interface
Figure 3.10: Real-time plotting of sensor parameters
3.3 Temperature Sensitivity Measurements

The temperature sensitivity of the FPW sensors is characterized by monitoring the sensor response to varying temperatures. A Sigma Systems Model C32 temperature chamber is used to vary the temperature. The sensor is placed inside the temperature chamber and electrical contact is made through an access port on the side of the chamber. The frequency, phase and delay of the sensor are measured while temperature is swept in 5 °C increments from 40 to 0 °C over 10 minute intervals.

3.4 Mass Sensitivity Measurements

In order to achieve similar frequency shifts due to mass loading for the 125 and 18 µm sensors, different amounts of mass are required. The change in mass per unit area, $\Delta m$, necessary to achieve a given frequency shift, $\Delta f$, is given by

$$
\Delta m = -2M \frac{\Delta f}{f_0}.
$$

(3.1)

In order to achieve a detectable relative frequency shift of -1000 Hz/MHz, $\Delta m$ should be 0.445 and 0.064 mg/cm$^2$, respectively, for 125 and 18 µm thick sensors. Due to this difference, different methods are used to load different amounts of mass for the different sensors.

Mass is loaded onto the 125 µm films using Kapton tape. The tape is 51 µm thick, with a mass per area of 6.925 mg/cm$^2$. The estimated relative frequency response to one layer of Kapton tape is -15400 Hz/MHz. This neglects any effects the Kapton tape may have on the substrate in addition to the mass loading. In practice, the tape may also cause changes in the stiffness and tension in the film. To determine the mass sensitivity of the sensors using this configuration, a differential sensor is used. Several layers of Kapton tape are applied to the underside of the sensor in the region below one of the output IDTs (Side A). The other output IDT (Side B) acts as a reference sensor to compensate for drift of environmental factors throughout the experiment. The progression of the experiment is as follows:

1. Side A is connected to the DAQ setup and allowed to stabilize for 10 minutes.
2. $f_0$ and phase are then recorded over a period of 5 minutes.

3. Steps 1 and 2 are then repeated for Side B.

4. One layer of Kapton tape is applied to Side A.

5. Steps 1 through 3 are then repeated.

6. The Kapton tape is then removed and steps 1 through 3 are again repeated.

7. This whole process is repeated for 2, 3, and 4 layers of Kapton tape.

The mean frequency value of each 5 minute data segment is used. The shift measured for Side B is used to compensate for environmental effects affecting Side A. The fundamental frequency and phase can then be plotted as a function of the total added mass per area to determine the mass sensitivity.

Mass loading of the 18 µm films is accomplished using an inkjet printer. Solutions of 2 wt % PVA in distilled water are printed using an 80 µm nozzle. The dried weight of PVA per droplet, $m_d$ was measured by printing several hundred thousand droplets onto a PVDF sheet over a period of 4 hours and measuring the total mass change, $\Delta m$. The total mass per area, $m_l$, of a printed layer was then determined from the number of droplets per layer, $N_d$, and the total area of the layer, $A_l$,

$$m_l = \frac{m_d N_d}{A_l}. \quad (3.2)$$

For layers consisting of 1240 droplets, the total mass per area of the layer was found to be 0.03010 mg/cm$^2$. The corresponding theoretical frequency shift for this change in mass is 470 Hz/MHz.

Mass sensitivity experiments are conducted similarly to those described above:

1. Side A is connected to the DAQ setup and allowed to stabilize for 10 minutes.

2. $f_0$ and phase are then recorded over a period of 5 minutes.

3. Steps 1 and 2 are then repeated for Side B.

4. Two layers of PVA are printed onto Side A.
3.5 Vapour Sensitivity Measurements

Vapour sensitivity measurements are accomplished by exposing sensors with selective coatings to known concentrations of an analyte. As described in Section 2.3.3, a 7 µm layer of polyvinyl acetate is used as the selective coating. The analytes used are toluene and acetone. In order to measure the response of a sensor to varying concentrations of analyte, it is necessary to measure the response of a sensor in real time while delivering a known concentration of analyte to the sensor, in a sealed environment, at a constant flow rate and, ideally, a constant temperature. This system monitors the sensor temperature using a thermistor, as well as the analyte concentration using a semiconductor metal oxide sensor. In order to accomplish this, an Owlstone OVG-4 gas calibration system, a sensor test chamber and the data acquisition system described in Section 3.2 are used. A schematic of the overall system is shown in Figure 3.11.

The Owlstone OVG-4 gas calibration system generates precise concentration levels of VOCs ranging from PPB to PPM. To do this, permeation tubes are assembled and used. A VOC is placed inside a poly-tetrafluoroethylene (PTFE) tube, with PTFE caps sealing both ends. The VOC will permeate through the tube at a rate determined by the length of the tube, the properties of the VOC and the temperature.
The permeation rate (in ng/min) at a specified temperature can be calibrated by measuring the change in mass over time while the permeation tube is maintained at a constant temperature. Air flowing past the permeation tube will pick up the VOC that has permeated out of the tube. The concentration, $C$, in units of $ng/ml$, can then be determined from the permeation rate, $r_p$, in units of $ng/min$, and the volumetric flow rate, $r_f$, in units of ml/min,

$$C = \frac{r_p}{r_f}.$$  

Once calibrated, the permeation tube is placed inside an oven in the OVG-4 system. Compressed air, filtered with a carbon VOC scrubber, flows through the oven at a flow rate precisely controlled by a mass flow controller (MFC), resulting in a well defined concentration of the sample gas. This air can then be diluted further by mixing with clean air from another MFC. Owlstone provides an online tool that can be used to calculate the total concentration of gas generated by the system for varying permeation tube temperatures and system flow rates [62]. The sensor is exposed to the sample air using the test chamber shown in Figure 3.12. The sensor is placed, sensing side down, inside the chamber. A PVDF gasket is placed between the sensor frame and the test chamber to provide a tight seal. The lid is then secured to the test chamber using 4 bolts. Since the PEDOT:PSS IDTs are printed on the side of the film opposite the sensing layer, electrical contact can easily be made through the top of the test chamber lid. The test chamber is then connected via Swagelok compression fittings and 1/8 stainless steel tubing to the outlet of the OVG-4. The outlet of the test chamber is directed past a semiconductor metal oxide (SMO) VOC sensor, which acts as a reference, and then into the fume hood. A thermistor is also placed inside the test chamber in order to monitor and compensate for temperature.

A LabView interface for the OVG-4 was developed, as described in Section 3.2. The program allows the user to set the oven temperature and the flow rates. It has the ability to record, in real-time, the actual temperatures and flow rates. It also monitors the temperature inside the test chamber and the voltage level of the SMO sensor. In addition, a test file can be used. The test file specifies the desired temperature and flow rate set points over the period of a test run. This type of test run is used to test the sensor response to different concentrations of analyte, as
Figure 3.12: (a) Perspective view and (b) cross section of the sensor test chamber used for gas calibration tests
described in Section 4.5.

The processes and equipment described in this chapter are useful for characterizing the nature of vibrations generated by the IDTs, the fundamental frequencies of different sensor geometries, and the sensitivities to mass, temperature and vapour concentrations. The results of such experiments will be presented and discussed in the following chapter.
Chapter 4

Results and Discussion

The performance parameters of interest for a FPW sensor are described in Section 2.1. These include the sensitivity to mass loading, to vapour concentration, and to temperature, the operating frequency and the detection limits. The experimental setups used for measuring these various parameters were described in the previous chapter. The objectives of the current chapter are to present the results of these experiments and to compare them to values predicted in Section 2.1. Results are presented for three sensor geometries, which are listed in Table 4.1. As will be shown, the fundamental frequencies of the sensors are well predicted by FPW theory, however, the mass and vapour sensitivities require more complete models to improve the accuracy of the predictions.

4.1 Verification of Flexural Plate Waves

In order to verify that the IDTs are producing acoustic waves in the PVDF membrane, the Polytec MSA-500 scanning LDV was used to measure the vibrations.

<table>
<thead>
<tr>
<th>Name</th>
<th>Substrate thickness</th>
<th>Number of finger pairs</th>
<th>Acoustic wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thick 800</td>
<td>125 µm</td>
<td>4</td>
<td>800 µm</td>
</tr>
<tr>
<td>Thick 400</td>
<td>125 µm</td>
<td>8</td>
<td>400 µm</td>
</tr>
<tr>
<td>Thin 800</td>
<td>18 µm</td>
<td>4</td>
<td>800 µm</td>
</tr>
</tbody>
</table>

**Table 4.1:** Geometries of the three sensors to be tested.
Figure 4.1: The instantaneous displacement of (a) the top and (b) the bottom of the PVDF film. The blue lines indicate the first IDT finger.
The vibrations were confirmed to be Lamb waves, and not Rayleigh (surface acoustic) waves, through measurements on both sides of the PVDF. The MSA-500 was also used to determine which Lamb mode (symmetric or anti-symmetric) was being measured. To do this, the instantaneous displacement on the first input IDT finger was measured on both the top and bottom side. Both measurements were taken with an input 180 V$_{pp}$ periodic chirp signal. The 500 kHz component of the signal was measured in both cases with a phase delay of 90° from the input trigger. These results are shown in Figure 4.1. The blue line indicates the location of the first finger in both cases and the results clearly show that the top displacement is out of phase by 180° relative to the bottom. This indicates that the waves are, in fact, anti-symmetric Lamb waves.

### 4.2 Sensitivity to Temperature

The temperature sensitivity of a Thick 800 sensor was measured using the setup described in Section 3.3. Figure 4.2a shows the change in $f_0$ over time in response to varying temperatures and Figure 4.2b shows $f_0$ as a function of temperature. The relationship is approximated to a second order polynomial fit. Linearizing the curve around room temperature (from 20 to 30 °C), the temperature sensitivity is 1870 Hz/°C or 0.33% per °C. This value is at least twice that of typical ZNO/silicon FPW sensors. As predicted, the sensors show very high sensitivity to temperature. This necessitates precise temperature control and compensation by a reference sensor for reliable measurements.

### 4.3 Fundamental Frequency Measurements

The fundamental frequencies for each of the sensor geometries listed in Table 4.1 was measured using LDV and electrical measurement setups, as detailed in Chapter 3. The average velocity spectra for all three sensors, as measured by the LDV, are shown in Figure 4.3. The spectra, focused on the respective fundamental frequencies, are plotted again in Figure 4.4 with decibel units. The fundamental frequencies, bandwidths and quality factors are found from these plots and listed in Table 4.2.

Electrical measurements were conducted for all three sensor geometries. The
Figure 4.2: Temperature response of a Thick 800 sensor. (a) The fundamental frequency over time with varying temperatures (in °C). The actual response is given by the blue curve and the average response with a 50-point rolling median filter is given by the red curve. (b) The fundamental frequency as a function of temperature.
Figure 4.3: Average velocity spectra for all three sensors measured midway between input and output IDTs with MSA-500 and 100 V_pp periodic chirp excitation signal

Table 4.2: Electrical and MSA-500 measurements for $f_0$ compared with the theoretical values. Frequencies are reported in kHz.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Theoretical $f_0$ (kHz)</th>
<th>Measured $f_0$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thick 800</td>
<td>516.9</td>
<td>575</td>
</tr>
<tr>
<td>Thick 400</td>
<td>1795</td>
<td>1600</td>
</tr>
<tr>
<td>Thin 800</td>
<td>302.5</td>
<td>330</td>
</tr>
</tbody>
</table>

corresponding fundamental frequencies are listed in Table 4.2 alongside the LDV measurements. The theoretical values calculated in Section 2.1, accounting for in-plane tension, are also listed for comparison. The differences between the LDV and electrical measurements range from 2.8 to 4.1%. These differences can be attributed to temperature, since they correspond to a temperature difference of less than 10°C and the two types of measurements were performed in separate labs without temperature control.

The measured values vary from the theoretical values by around 8 to 14%. Possible sources of error in these experiments include temperature sensitivity, error in
Figure 4.4: Velocity spectra, in dB, focusing on the peaks for (a) Thick 800 (b) Thick 400 and (c) Thin 800 with the -3dB bandwidths indicated by the black lines and the fundamental frequencies by the red lines.
the measurements and inaccuracies in the fabrications steps. The good agreement between the MSA-500 and electrical measurements suggests that there is little error in the measurement systems.

There is error associated with most steps of the fabrication process. The application of in-plane tension is accomplished using a torque wrench and the stretching apparatus described in Section 2.3.1. The torque may not accurately describe the tension in the film due to variations in friction throughout the stretching apparatus. There is also expected to be variations in tension over time throughout the film as a result of temperature fluctuations and relaxation/creep of the PVDF. The inkjet printing of PEDOT:PSS IDTs also introduces some error as the printed drop locations can vary with standard deviations of up to 13 µm [1]. This could account for deviations in the wavelength of up to 26 µm and deviations in frequency up to 3.25 %. These errors likely account for most of the difference between theoretical and experimental values. Additional error may come from neglecting the rotary inertia term in calculating the theoretical values (Equation 1.17).

The values of $Q$ measured from Figure 4.4 represent the $Q$ of the acoustic waves midway through the delay line. The measured values are very low due to the high attenuation in the PVDF and the low number of IDT finger pairs. The $Q$ of the electrical signals generated at the output IDTs will be still lower than these values due to further broadening of the signal from acoustic attenuation and electromechanical coupling at the output IDT. From these measurements, the relative effects on $Q$ of the acoustic attenuation and the electromechanical coupling of the IDTs is unclear. In order to characterize the separate effects, the $Q$ of the electrical output signal should be measured and compared to the $Q$ of the propagating acoustic waves. If the broadening of the signal is mainly due to the IDTs, it may be possible to significantly improve $Q$ by increasing the number of IDT finger pairs. The use of different IDT geometries, such as an apodized structure and acoustic reflectors, could also help to improve the overall $Q$.

### 4.4 Sensitivity to Mass Loading

Mass sensitivity measurements were performed for both Thick 800 and Thin 800 sensors. Experiments were carried out as described in Section 3.4. The measured
Table 4.3: Experimental and theoretical values for mass sensitivities.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Theoretical $S_M$(cm²/g)</th>
<th>Measured $S_M$(cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thick 800</td>
<td>-22.47</td>
<td>-0.569</td>
</tr>
<tr>
<td>Thin 800</td>
<td>-156.1</td>
<td>-55.9</td>
</tr>
</tbody>
</table>

mass sensitivities are summarized in Table 4.3 and compared to the theoretical sensitivities.

FPW sensors of 18 $\mu$m thickness were mass-loaded by inkjet printing of PVA. The fundamental frequency was plotted over 5 minute intervals. In between each window, the sensor was removed from the measurement system and additional layers of PVA were applied. Figure 4.5 shows $f_0$ with varying number of PVA layers with and without compensation for environmental factors. The compensated plot shows good linearity for the cases of 0, 2, 4, and 8 layers (Figure 4.5c). The mass sensitivity for mass loading up to 8 layers, calculated as the slope of Figure 4.5c, is -55.9 (cm²/g). With the application of the last 8 layers, for a total of 16 layers, the fundamental frequency is seen to increase. This is consistent with the results predicted in Section 2.1, where the stiffness effects are accounted for. Figure 4.5d shows the fundamental frequency as a function of mass layer thickness, including the 16 layer data, with a 2nd order polynomial fit. This follows the same trend as described in Section 2.1, though the minimum occurs at a lower mass layer thickness, indicating that the PVA has a higher stiffness than that of PVDF.

FPW sensors of 125 $\mu$m thickness were mass-loaded by application of Kapton tape layers. Figure 4.6 shows $f_0$ with varying number of Kapton tape layers with and without compensation for environmental factors. The frequency shift as a function of mass loading is given in Figure 4.6c. These results, again, show a good linear response to mass loading up to 3 layers with a sensitivity of -0.569 (cm²/g). The addition of the fourth mass layer results in almost twice the frequency shift of previous layers, as shown in Figure 4.6d. This data point cannot be described with the model presented in Equation 2.1. The error may have been due to aliasing effects in the electrical measurement system.

The experimental mass sensitivities are much lower than theoretical values. Equation 1.21 used to calculate the theoretical mass sensitivities, assumes mass
loading has no effect on the in-plane tension or stiffness. Due to the competing effect caused by the close stiffness match of the PVDF and PVA, the mass sensitivity of the thin sensor is less than predicted. This is likely the same reason for the low mass sensitivity in the case of the thick sensor, although this is hard to verify since the results do not follow the same trend described by Equation 2.1. In order for these sensors to demonstrate a linear response to mass loading, the applied mass should have a negligible effect on stiffness. This could be accomplished using very low stiffness polymers.

Figure 4.5: (a) Uncompensated and (b) compensated fundamental frequency of a Thin800 sensor over time for varying layers of PVA. (c) compensated as a function of applied mass up to 8 layers with a linear fit and (d) as a function of mass layer thickness up to 16 layers with a polynomial fit.
Figure 4.6: (a) Uncompensated and (b) compensated fundamental frequency of a Thick 800 sensor over time for varying layers of Kapton, (c) compensated as a function of applied mass to 3 layers with a linear fit and (d) as a function of mass layer thickness up to 4 layers with a polynomial fit.

4.5 Chemical Vapour Sensitivity

The response of a Thick 800 sensor to vapour concentrations of toluene and acetone was measured using the setup described in Section 3.5. The theoretical vapour sensitivity of this sensor with a 7 µm PVAC layer was calculated in Section 2.1 as 0.390 (Hz/MHz)/PPM. The frequency noise floor of the sensor and measurement system is typically around 200 Hz, resulting in a theoretical detection limit of around 2980 PPM.

There were many challenges associated with performing vapour sensitivity
measurements. Sensitivity to temperature was the most significant. Variations in sensor temperature occurred both due to environmental temperature change and temperature changes in the sample gas caused by the Owlstone gas calibration system. Rapidly varying gas concentrations with the Owlstone system, by means of changing the split flow rate, caused spikes in temperature of several degrees. This made the sensor response to temperature and concentration difficult to distinguish.

Another challenge was the unrepeatable nature of the sensor’s response to varying gas concentrations.

In order to prevent rapid temperature changes due to internal flow rate changes in the Owlstone system, flow rates were ramped slowly over the course of 20 minutes, rather than 20 seconds. This prevented any systematic temperature changes from occurring simultaneously with changes in concentration. To verify this, the internal flow rates of the Owlstone system were ramped slowly and the temperature of the sample gas was monitored with a thermistor.

In order to compensate for environmental temperature fluctuations, the differential sensor design, described in Section 2.1.2, was used. Due to inconsistency in the inkjet patterning and polymer layer spray-coating, the differential sensor was not perfectly symmetric and was difficult to balance by the addition of polymer mass to one side. The differential signal demonstrated a complicated, unpredictable behaviour in response to mass loading. Because of these issues with the differential sensor, a single sensor was used, with a thermistor placed near the sensor in the sensor chamber for temperature compensation.

Given the high limit of detection, exposure of the sensor to concentrations of toluene less than several thousand PPM did not provide any meaningful results. Exposure to toluene concentrations between 5570 to 36900 PPM resulted in detectable fundamental frequency shifts. These measurements were not very repeatable, in that the temperature-compensated fundamental frequency varied by more than 10 kHz over time with exposure to a constant concentration and did not return to the same levels for different trials of exposure to the same concentrations. Similar tests with acetone concentrations ranging from 1050 to 10500 PPM yielded similar results with higher repeatability. The temperature-compensated fundamental frequency varied by approximately 5 kHz for a constant concentration. The results of one test are shown in Figure 4.7a. The relative frequency change as a
Figure 4.7: Normalized frequency shift of a Thick 800 sensor (a) over time with varying concentrations of acetone and (b) as a function of acetone. The error bars in (b) correspond to the variation over time of the normalized frequency shift for constant concentration.

The vapour sensitivity, measured as the slope of Figure 4.7b, is -0.0337 (Hz/MHz)/PPM.

Although these results may show some correlation between vapour concentrations and fundamental frequency shift, it cannot be said, conclusively, that vapour sensing was accomplished. Due to the viscoelastic nature of the PVDF, and the close impedance match with the polymer sensing layer, the same relationships that hold for crystalline sensors may be unable to predict the behaviour of PVDF sensors. Stiffness, in-plane tension, and attenuation effects due to mass loading may also contribute to the sensor response. Further study of the phenomena affecting this sensor platform is required in order accurately predict its response to mass loading and chemical vapours.
Chapter 5

Conclusions

5.1 Summary of Results
Films of PVDF were made piezoelectric through a stretching and subsequent poling process. The piezoelectricity of the films was verified using laser Doppler vibrometry to measure electric field induced surface vibrations. Interdigital transducer electrodes were patterned on pre-tensioned PVDF films by inkjet printing of the conductive polymer, PEDOT:PSS. The resulting FPW delay line devices were characterized using LDV and electrical measurements. Good agreement was demonstrated between fundamental frequency measurements and theoretically predicted values for three different sensor geometries. Mass sensitivity was demonstrated, though the measurements were inconsistent with theoretical predictions. The highest mass sensitivity demonstrated was -55.9 cm²/g for a device with an 18 µm thick membrane. Temperature sensitivity was measured and was found to be extremely high. Chemical vapour sensitivity experiments were conducted, using a PVAC sensing layer and toluene and acetone vapours, but the measurements were neither repeatable nor predictable by the theory. They did, however, follow the expected trend of a decrease in fundamental frequency in response to mass loading through vapour concentration.
5.2 Strengths and Limitations

The polymer-based FPW sensors presented here have great potential in offering a low-cost alternative to existing gravimetric sensors. The materials are readily available at low cost and the processes are simple and do not require a clean room environment or expensive equipment. The operating frequencies of the PVDF FPW sensors range from around 300 to 1700 kHz. This is roughly an order of magnitude lower than conventional FPW sensors and two to three orders lower than SAW sensors. Due to the low frequency of operation, less-expensive measurement electronics can be used than with higher frequency devices. The density of PVDF is relatively low and thin membranes are easily produced, resulting in high theoretical mass sensitivity. The theoretical mass sensitivities of the sensors used in this work are as high as -150 cm$^2$/g, though sensors with substrates as thin as 1 µm and theoretical mass sensitivity of -2900 cm$^2$/g may be achievable. This is slightly higher than that of conventional acoustic wave sensors.

The overall detection limits of the PVDF FPW sensors are limited by the low quality factor caused by electromechanical coupling and acoustic attenuation in the PVDF. This low Q results in a high frequency noise floor of around 200 Hz, resulting in a practical detection limit of around 3000 PPM, which is not sufficient for low-PPM detection of VOCs. In practice, chemical vapour sensing was difficult to achieve. This is mainly due the extreme temperature sensitivity of around 2000 Hz/°C, or 0.33%/°C, which is at least an order of magnitude higher than conventional acoustic wave devices.

Overall, the PVDF FPW sensing platform is very promising. The mass sensitivities are potentially very high and the fabrication processes are simple and low-cost. The sensors suffer from instability caused by extreme temperature sensitivity and high frequency noise. These issues should be addressed in order to improve the performance of these sensors.

5.3 Future Work

There is much room for optimization of these types of sensors. Stronger electromechanical coupling in the PVDF may be achievable through optimization of the stretching and poling process. In theory, mass sensitivity is inversely proportional
to membrane thickness. It may be possible to fabricate sensors with membranes on the order of 1 µm or lower, in order to optimize the mass sensitivity. The simplest IDT geometry has been used in this work. Using SAW filter design methods, it may be possible to increase the efficacy of these sensors through the use of different IDT geometries. Different measurement schemes should also be investigated. The resolution of fundamental frequency measurements is restricted by the low quality factor of the sensors. A time-of-flight measurement scheme may be more appropriate for this application.

To improve chemical vapour measurements, further study of the interactions between gases, selective coatings and the PVDF substrate itself should be conducted. The effects of different gases on PVDF should be taken into account, as well as any stiffening and attenuation caused by the application of sensing layers. Much improved temperature stability is also required for consistent characterization of vapour sensitivity. Temperature compensation through the use of a reference sensor may not be enough to produce meaningful results. It may be necessary to precisely control the temperature of the sensor environment as well.

Attenuation is also a source of uncertainty in PVDF sensors. In the current FPW models, attenuation is considered negligible due to the highly-crystalline, low attenuation materials typically used. Attenuation of the acoustic waves in PVDF was apparent throughout this work, greatly complicating electrical measurements. Its effects may also be contributing to the sensors’ response to mass loading and vapour concentrations. Attenuation simply cannot be neglected in PVDF and until it is included in future models, its effects cannot be fully understood.

Further applications of this technology should also be explored. FPW devices have been used for applications in liquid-phase sensing due to the low velocity of the $A_0$ mode. PVDF FPW devices exhibit still lower wave speeds than conventional FPW devices, making them very appealing for liquid-phase sensing. This platform may also find application in bio-sensing, as PVDF is widely used as an affinity membrane in protein blotting applications.
Bibliography


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[37] Precision Acoustics Ltd., “Pvdf properties and uses,” 2010. → pages[16]


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Appendix A: Macros and Macro Code

The Matlab code written to produce macro code for the custom inkjet printer is given in Table 5.3. The code was originally written by Derek Tsan and has since been modified by Christoph Sielmann and myself. The main file for a differential sensor with $\lambda = 800 \, \mu m$, 4 pairs of output fingers, and 8 pairs of input fingers is given, followed by all the associated functions. Several macros and their corresponding patterns are given in Appendix 5.3.

Macros
Table 1: $\lambda = 800 \mu m$ Differential Sensor with 8 input pairs and 4 output pairs
Table 2: $\lambda = 400 \mu m$ Differential Sensor with 16 input pairs and 8 output pairs
Table 3: $\lambda = 800 \, \mu m$ Single Sensor with $N = 5$
Macro Code
FPW_Diff_Macro.m

% Revision 1 FPW Sensor - Differential measurement
% Original code by Derek Tsan. Modified by Robert Busch and Christoph Sielmann

INIT;

print_plot = 1;

% User configurable parameters
parm.resolution = 80; %Initial resolution of dots
parm.in_length = 44; %Input IDT length
parm.spacing = 2; %Input/Output IDT spacing
%parm.in_idt_dist = 40; %Distance between both input transducers
parm.idt_dist = 4; %Distance between input and output IDTs
parm.out_length = 44; %Output IDT length
parm.end_space = 2; %Spacing between finger and side conductor
parm.num_in = 8; %Number of input fingers
parm.num_out = 4; %Number of output fingers

% Start with fingers
%Calculate offsets given different lengths of IDTs
disp = (parm.in_length - parm.out_length) / 2;

%Initial positioning
REZ(parm.resolution);
MX(20);

%First layer

%Output IDT bottom
REZ(parm.resolution);
MX(1);
loops = {'PX(parm.out_length)' 'MY(parm.spacing)' 'PX(-parm.out_length)'
'MY(parm.spacing)'};
LOOP(parm, parm.num_out, loops);
MX(-1);

%Leave space between input and output electrode and align for output
MY(parm.idt_dist);
MX(disp);

%Input IDT
loops = {'PX(parm.in_length)' 'MY(parm.spacing)' 'MX(parm.end_space)'
'PX(-parm.in_length)' 'MY(parm.spacing)' 'MX(-parm.end_space)'};
LOOP(parm, parm.num_in, loops);

%Leave space between output electrodes for contacts
%MY(parm.in_idt_dist);

%Leave space between input and output electrode and align for output
MY(parm.idt_dist);
MX(-disp);

%Output IDT top
```plaintext
REZ(parm.resolution);
loops = {'PX(parm.out_length)' 'MY(parm.spacing)' 'MX(parm.end_space)'
'PX(-parm.out_length)' 'MY(parm.spacing)' 'MX(-parm.end_space)'};
LOOP(parm, parm.num_out, loops);

%Print second layer
%Reset back to start and shift
REZ(parm.resolution);
MY(-((parm.num_in + parm.num_out*2) * parm.spacing * 2 + 2 * parm.idt_dist));
REZ(parm.resolution / 2);
MX(-1);

%Output IDT bottom
REZ(parm.resolution);
MX(1);
loops = {'MX((parm.end_space-1))' 'PX(parm.out_length)'
'MY(parm.spacing)' 'MX(-(parm.end_space-1))' 'PX(-parm.out_length)'
'MY(parm.spacing)'};
LOOP(parm, parm.num_out, loops);
MX(-1);

%Leave space between input and output electrode and align for output
MY(parm.idt_dist);
MX(disp);

%Input IDT
loops = {'PX(parm.in_length)' 'MY(parm.spacing)' 'MX((2*parm.end_space-1))'
'PX(-parm.in_length)' 'MY(parm.spacing)' 'MX(-(2*parm.end_space-1))'};
LOOP(parm, parm.num_in, loops);

%Leave space between input and output electrode and align for output
MY(parm.idt_dist);
MX(-disp);

%Output IDT top
REZ(parm.resolution);
loops = {'PX(parm.out_length)' 'MY(parm.spacing)' 'MX((2*parm.end_space-1))'
'PX(-parm.out_length)' 'MY(parm.spacing)' 'MX(-(2*parm.end_space-1))'};
LOOP(parm, parm.num_out, loops);

%Print third layer
%Reset back to start and shift
REZ(parm.resolution);
MY(-((parm.num_in + parm.num_out*2) * parm.spacing * 2 + 2 * parm.idt_dist));
REZ(parm.resolution / 4);
MX(1);

%Output IDT bottom
REZ(parm.resolution / 4);
MX(1);
loops = {'MX((parm.end_space*4-3))' 'PX(parm.out_length*4)'
'MY(parm.spacing*4)' 'MX(-4*parm.end_space+3)'
'PX(-parm.out_length*4)'
'MY(parm.spacing*4)'};
```
LOOP(parm, parm.num_out, loops);
MX(-1);

%Leave space between input and output electrode and align for output
REZ(parm.resolution);
MY(parm.idt_dist);
MX(disp);

%Input IDT
REZ(parm.resolution / 4);
loops = {'PX(parm.in_length*4)' 'MY(parm.spacing*4)' 'MX(parm.end_space*4-1)' 'PX(-parm.in_length*4)' 'MY(parm.spacing*4)' 'MX(-4*parm.end_space+1)'};
LOOP(parm, parm.num_in, loops);

%Leave space between output electrodes for contacts
REZ(parm.resolution);
MY(parm.idt_dist);

%Output IDT top
REZ(parm.resolution / 4);
loops = {'PX(parm.out_length*4)' 'MY(parm.spacing*4)' 'MX(4*parm.end_space-1)' 'PX(-4*parm.out_length)' 'MY(parm.spacing*4)' 'MX(-4*parm.end_space+1)'};
LOOP(parm, parm.num_out, loops);

%Leave space between input and output electrode and align for output
REZ(parm.resolution);
MY(parm.idt_dist);
%MX(-disp);

%Side bars

%Left input
REZ(parm.resolution/2);
MX(-parm.spacing*2);
loops = {'PY(-parm.num_out*parm.spacing*4+parm.spacing*2)' 'PX(-1)' 'PY(parm.num_out*parm.spacing*4-parm.spacing*2)' 'PX(-1)'};
LOOP(parm, 9 , loops);
MX(18);
MY(-2*(parm.idt_dist+parm.num_out*parm.spacing*2));
loops = {'PY(-parm.num_in*parm.spacing*4+parm.spacing*2)' 'PX(-1)' 'PY(parm.num_in*parm.spacing*4-parm.spacing*2)' 'PX(-1)'};
LOOP(parm, 1 , loops);
MY(-parm.num_in*parm.spacing-parm.spacing + (parm.num_out*parm.spacing)/2);
loops = {'PY(-parm.num_out*parm.spacing*4+parm.spacing*2)' 'PX(-1)' 'PY(parm.num_out*parm.spacing*4-parm.spacing*2)' 'PX(-1)'};
LOOP(parm, 8 , loops);
MX(18);
REZ(parm.resolution/4);
MY(-1);
REZ(parm.resolution/2);
MY(-2*(parm.idt_dist+parm.num_out*parm.spacing+parm.num_in*parm.spacing));
loops = {'PY(-parm.num_out*parm.spacing*4+parm.spacing*2)' 'PX(-1)'
'PY(parm.num_out*parm.spacing*4-parm.spacing*2)' 'PX(-1)'};
LOOP(parm, 9, loops);

%Right input
REZ(parm.resolution);
MX(parm.in_length + parm.end_space+8);

REZ(parm.resolution/4);
MX(4);
REZ(parm.resolution/2);
MY(-parm.num_out*parm.spacing*4+1);
loops = {'PY(parm.num_out*parm.spacing*4-parm.spacing*2+1)' 'PX(1)'
'PY(-parm.num_out*parm.spacing*4+parm.spacing*2+1)' 'PX(1)'};
LOOP(parm, 9, loops);
MX(-18);
MY(2*(parm.idt_dist+parm.num_out*parm.spacing+parm.num_in*parm.spacing+1));
loops = {'PY(parm.num_out*parm.spacing*4-parm.spacing*2)' 'PX(1)'
'PY(-parm.num_out*parm.spacing*4+parm.spacing*2)' 'PX(1)'};
LOOP(parm, 9, loops);
endmacro;

INIT.m
clear all; close all; clc;

global XY;
global code;
global res;
global isloop;
global print_plot;

XY = [0 0];
isloop = 0;
code = [];
res = 0;

numstring.m
function input = numstring(var)
input = '00000';
if var>0
input(1) = '+';
else
    input(1) = '-';
end
var = abs(var);
digits = int2digits(var);
[m,n] = size(digits);
for i = 1:n
    input(6-i) = num2str(digits(n+1-i));
end

storeplot.m
function [outx,outy] = storeplot(x, y, add)
persistent xdata;
persistent ydata;

if isempty( xdata )
    xdata = [];
    ydata = [];
end

xdata = [xdata x];
ydata = [ydata y];

outx = xdata;
outy = ydata;

end

printplot.m
function printplot(i)
global XY;
global xplot;
global yplot;
global res;
global numpoints;
global print_plot;
doplot = 0;

if print_plot == 1
    figure(1);
    if i==1
        if doplot
            plot(xplot+XY(1), (yplot+XY(2)), 'o');
        end
        storeplot( xplot+XY(1), yplot+XY(2), 1 );
        XY = XY+[res*2.5*numpoints 0];
    elseif i==2
        if doplot
            plot(xplot+XY(1), (yplot+XY(2)), 'o');
        end
storeplot( xplot+XY(1), yplot+XY(2), 1 );
XY = XY+[0 res*2.5*numpoints];
end
if doplot
    plottitle = sprintf('X: %d Y: %d',XY(1),XY(2));
    xlabel('X ('mum)'); ylabel('Y ('mum)');
    title(plottitle);
    hold on;
end
else
end

LOOP.m
function LOOP(parm, times, arg)

    global XY;
    global code;
    global res;
    global isloop;
    global print_plot;

    digits = int2digits(times);
    [m,n] = size(digits);
    looptimes = '00';

    for i = 1:n
        looptimes(3-i) = num2str(digits(n+1-i));
    end

    code = [code '{' looptimes];

    N = size(arg);
    for m = 1:times
        if m==1
            isloop = 0;
        else
            isloop = 1;
        end
        for n=1:N(2)
            command = char(arg(n));
            eval(command);
        end
    end

    code = [code '}'];
    isloop = 0;
end

REZ.m
function REZ(var)
    global code;
    global res;
    global isloop;
res = var;
var = numstring(var);
var = var(2:5);
output = strcat('REZ',var);
if isloop ==0
    code = [code output];
end
end

MX.m
function MX(var)
global XY;
global code;
global res;
global isloop;
if var~=0
    XY = XY+[2.5*res*var 0];
    var = numstring(var);
    output = strcat('MX',var);
    printplot(0);
    if isloop ==0
        code = [code output];
    end
end
end

MY.m
function MY(var)
global XY;
global code;
global res;
global isloop;
if var ~=0
    XY = XY+[0 2.5*res*var];
    var = numstring(var);
    output = strcat('MY',var);
    printplot(0);
    if isloop ==0
        code = [code output];
    end
end
end

PX.m
function PX(var)
global XY;
global code;
global res;
global isloop;
global xplot;
global yplot;
global numpoints;
res_act = res*2.5;
if var ~=0
    if var <0
        res_act = -res_act;
        xplot = res_act:res_act:var*-res_act;
        res_act = -res_act;
    else
        xplot = res_act:res_act:var*res_act;
    end
end
yplot = zeros(size(xplot));
numpoints = var;
printplot(1);
var = numstring(var);
output = strcat('PY',var);

if isloop ==0
    code = [code output];
end
end
end

PY.m
function PY(var)
global XY;
global code;
global res;
global isloop;
global xplot;
global yplot;
global numpoints;

res_act = res*2.5;
if var~=0;
    if var <0
        res_act = -res_act;
        yplot = res_act:res_act:var*-res_act;
        res_act = -res_act;
    else
        yplot = res_act:res_act:var*res_act;
    end
end
xplot = zeros(size(yplot));
numpoints = var;
printplot(2);
var = numstring(var);
output = strcat('PY',var);

if isloop ==0
    code = [code output];
end
end
end
PXH.m

function PXH(var)
    global code;
    global XY;
    global isloop;
    if var ~=0
        figure(1); plot(XY(1),XY(2),'o');
        hold on;
        printplot(0);
        var = numstring(var);
        var = var(2:5);
        output = strcat('PXH',var);
        if isloop ==0
            code = [code output];
        end
    end
end

endmacro.m

function endmacro
    global code;
    code = [code 'S'];
    fid=fopen('output.txt','w');
    fprintf(fid, code);
    fclose(fid);

    [x,y] = storeplot(0,0,0);
    plot(x,y,'o');
end