Development of Flexible Sensing Systems and Energy Harvesters Using Printing Techniques

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Development of Flexible Sensing Systems and Energy Harvesters Using Printing Techniques

by

Sepehr Emamian

A dissertation submitted to the Graduate College in partial fulfillment of the requirements for the degree of Doctor of Philosophy Electrical and Computer Engineering Western Michigan University December 2017

Doctoral Committee:
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Printed electronics (PE) has been gaining a significant level of interest and is being used for developing a wide range of electronic systems for various applications, specifically in the sensor fields. This dissertation focuses on the development of flexible sensors and energy harvesters for application in sensing systems by employing additive manufacturing processes.

Initially, an efficient surface enhanced Raman spectroscopy (SERS) substrate was fabricated by gravure printing a thin film of silver nanoparticle ink on a flexible polyethylene terephthalate (PET) sheet. The feasibility of the printed substrate to be used as a SERS substrate for the detection of explosive materials, such as DNT in the vapor phase, was demonstrated. An enhancement factor of three and four for the peaks at 1350.13 cm\(^{-1}\) was obtained for the SERS-based response of the printed SERS substrate toward DNT solution and vapor, respectively, when compared to target molecules adsorbed on bare PET. The effect of temperature on the intensity of Raman spectrum was also examined. The effect of bending on the SERS response was also investigated. The fabricated SERS substrate has the promising potential to be used as a cost-effective substitution in commercialized SERS detection applications.

Then, piezoelectric-based touch sensors were successfully fabricated on flexible PET and paper substrates by using the screen printing technique. The capacitive devices were fabricated using silver and polyvinylidene fluoride (PVDF) inks as the
metallization and piezoelectric layers, respectively. Characterization of the substrates and various printed layers of the touch sensor were performed. Piezoelectric-voltage analysis demonstrated that the printed sensor can be used as both touch and force sensors. The advantage of fabricating touch sensors on flexible substrates is the ability to fold and place the sensor on nearly any platform or to conform to any irregular surface, whereas the additive properties of printing processes allow for a faster fabrication process, while simultaneously producing less material waste in comparison to the traditional subtractive processes.

Finally, three generations of novel piezoelectric-based vibration energy harvester (PVEH) were fabricated and tested. For the first generation, the screen printing technique was used to deposit all piezoelectric and conductive layers of the device. In this device, a PVDF layer was sandwiched between two printed silver electrodes, all fabricated on a PET substrate. PVEHs in different dimensions were fabricated and tested. Test results showed that this fabrication process along with the polarization setup used in this project was not able to provide large enough piezoelectric coefficient so that the vibrated PVEH generates large enough voltage output to pass the rectifying circuit and power the resistive load. For the second generation, PVDF ink was screen printed onto a glass substrate and was peeled-off from the glass substrate after being cured. Then, conductive Metglas was tapped on both sides of the peeled-off PVDF film. The fabricated device was then characterized and tested. However, there were some opportunity to improve the performance of the second generation PVEH. Therefore, the third generation of PVEHs was fabricated by direct printing of silver ink onto PVDF film. In this approach, an aluminum mold was used to form a PVDF film. Then, screen printing technique was used to deposit silver ink onto both sides of the PVDF film as the bottom and top electrodes. The obtained results demonstrated the potential of using additive print manufacturing processes for the fabrication of cost-efficient, lightweight and flexible vibration energy harvesters.
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Sepehr Emamian
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CHAPTER I

INTRODUCTION

1.1 Motivation

Detection of explosive compounds such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) have been continuously researched throughout the history of the manmade wars [25, 26]. Physical probing based methods, typically used to clear landmines, are often labor intensive and time consuming. Moreover, these methods often confront problems due to other metal debris in the minefield, thereby resulting in false positives. The detection of the vapors of the explosive compounds is thus a better solution to overcome the drawbacks associated with physical probing methods. DNT is known to be more concentrated in the vapor phase, when compared to TNT. Therefore, the development of new methods that can be employed for the detection of explosive organic compounds in vapor phase is important. Chemical sensors, based on different techniques, such as electrochemical sensors, cantilever sensors, surface acoustic wave (SAW) sensors, luminescence based sensors, quartz crystal microbalance (QCM) sensors and spectroscopy sensors have been employed for explosive detection [27, 28, 29, 30, 31, 32]. However, these methods have some disadvantages such as low sensitivity, low detection specificity and need for elevated working temperatures. Raman spectroscopy (RS), which is a rapid, sensitive and low temperature method of detection, has also been used for the detection of explosive compounds. RS has been proven to be a reliable technique for the detection of various compounds due to its non-destructive nature and ability to provide signature vibrational fingerprints of target molecules. It has been demonstrated that nano-scale metallic surfaces, such as nano-pillars and nano-domes, can enhance the
Raman scattering and this phenomenon is known as surface enhancement Raman spectroscopy (SERS). Several methods, such as chemical bath deposition [33], anodic alumina oxide membrane decorated [34], wet chemical fabrication [35], physical vapor deposition [36], and combination of top-down photolithography and hydrothermal growth [37], have been used for the fabrication of SERS substrates. The drawbacks associated with these deposition methods are their complexity, excessive time consumption and expensive procedures. The use of traditional printing methods, such as ink-jet and gravure printing, which are typically cost efficient and do not require high working temperatures, has shown to overcome these drawbacks for the fabrication of SERS substrates. However, there are no reports on the use of gravure printing for development of flexible SERS substrates for the detection of explosive organic compounds such as DNT in the vapor phase. Therefore, the development of cost effective, and rapid detection techniques for the detection of explosive compounds in vapor form becomes very important.

User interfaces of electronic devices have been transitioning from old-fashioned button-type controls to embedded touch pads during the last few decades. This trend of employing touch pads as part of the as built environment has resulted in an inevitable demand for the fabrication of flexible touch sensitive devices. Researchers have utilized different transduction mechanisms, such as piezoelectric [38, 39, 40], capacitive [41, 42], resistive [43], and optical [44, 45], for fabrication of touch sensing devices. Among these, the piezoelectric technology has generated significant interest due to its accuracy and capability to measure dynamic events regardless of the material of the object that becomes in contact with the sensor. Touch sensors are typically manufactured using conventional CMOS processes, which are often expensive and fabricated on rigid substrates [13, 46, 47, 48, 49]. Moreover, most of the configurations used do not provide the high flexibility and conformability, required for various touch sensing applications, thereby limiting their application areas. Therefore, developing
a promising approach to overcome the drawbacks associated with conventional touch sensors becomes very important.

During the last few decades, electronic devices, such as wireless sensors, implantable medical devices, and handheld electronic devices, have become more energy efficient due to the advances in integrated circuit (IC) manufacturing and micro electromechanical systems (MEMS) technology. The power consumption of these devices has dropped down to tens to hundreds of microwatts (µW) of power [3]. The main power sources for these miniaturized electronic devices are rechargeable and disposable batteries. The main drawbacks of battery-powered systems are the limited life-times of batteries, which causes the inevitable need for maintenance involving battery replacements. Battery replacement can be inconvenient in some applications, such as infrastructure monitoring or implanted medical devices. In addition, batteries have adverse environmental effects due to their non-recyclable and non-biodegradable nature. An effective approach for eliminating batteries or extending their life-time is to harvest energy form low-level vibrations available in various environments, such as machinery, buildings, bridges, human body motion, etc. which is sufficient to power up low-power electronic devices. There are three conversion mechanisms for converting mechanical vibrations into electrical energy i.e., electromagnetic [50], electrostatic [51], and piezoelectric [52]. Among these mechanisms, piezoelectric power conversion has generated significant interest due to its capability of generating high voltage levels without requiring additional electrical power sources.

Traditionally, piezoelectric energy harvesters are fabricated by using conventional silicon-based technologies [53, 54, 55, 56, 57], which involves high-vacuum and high-temperature deposition processes along with sophisticated photolithographic patterning techniques. These drawbacks can be overcome by using printing techniques. The advantages of printing include improved cost efficiency, reduction of material wastage during fabrication, flexibility in the substrate and low manufacturing temperatures.
Even though a steady and considerable effort has been directed towards the development of flexible electronics, there have been no reports on a fully printed flexible vibration energy harvester. This has led to the research of traditional printing techniques for the manufacture of flexible vibration energy harvester.

Printed electronic (PE) technologies have demonstrated the ability to produce flexible and mechanically stable circuits and sensors. The main advantage of PE technology is that it is an additive process. All the layers, having different designs, are selectively deposited, which excludes the need for masking and etching. The additive nature of this process results in less usage of material and a faster fabrication process. These techniques offer other advantages such as low manufacturing temperatures, mechanical flexibility (roll-to-roll), and light weight products, which all ultimately lead to cost efficiency in the fabrication process. The use of printing technologies thus overcomes some of the drawbacks associated with conventional silicon based technology. PE is a rapidly expanding technology to fabricate electronic devices on flexible substrates, such as plastic, paper, and textiles using electrically functional ink materials, such as metallic, dielectric, and semiconductors in combination with printing processes, such as offset lithography, gravure, ink-jet, and screen printing [58, 59, 60, 61, 62]. Recent advances of PE technology has received substantial interest as a technique for developing 2D and 3D printed devices, such as flexible storage devices, organic thin film transistors (OTFT), organic light emitting diodes (OLED), flexible solar cells, disposable diagnostic devices, radio frequency identification tags (RFID), and biochemical sensors [63, 64, 65]. Moreover, PE enables the possibility of printing large area electronic systems when compared to conventional electronic devices which are fabricated at silicon wafer sizes [66].
1.2 Author’s Contribution

The author’s research work has resulted in 31 conference publications, 2 intellectual property (IP) disclosures, and 8 high-quality peer-reviewed journal publications as given in the list of publications in Appendix A. The publications directly related to the research performed for this dissertation have been marked with “∗”, in the Appendix A. The results of the projects have been published in prestigious journals such as Sensors and Actuators: B Chemical and Sensors and Actuators: A Physical. The author has also presented the research work at several international conferences which have been published in the proceedings of the IEEE Sensors Conference (2014, 2015, 2016); 15th International Meeting for Chemical Sensors (IMCS); and Eurosensors Conference (2016). The author was also awarded the All-University Graduate Research and Creative Scholar Award for 2015-16, the Graduate College Research Award for 2015, the Graduate Student Research Grant (2015), and the Graduate Student Travel Grant to attend FlexTech 2016 Conference in Monterey, California by Western Michigan University.

1.3 Organization of the Dissertation

This dissertation presents the details of the three research projects that the author performed during his doctoral studies. In all three projects, conventional printing techniques have been used to develop sensing or energy harvesting systems. This includes developing an efficient optical based detection sensing system to be used for the detection of explosive compounds in the vapor phase. In the second project, fabrication of a fully printed and flexible piezoelectric-based touch sensor will be presented. In the third project, details of fabrication and testing of a novel fully printed piezoelectric-based vibration energy harvester (PVEH) will be provided.

In Chapter II, the author presents a comprehensive literature review. This review
provides the principle science and background about surface enhanced Raman spectroscopy (SERS) based explosive detection systems, flexible touch sensors, and energy harvesters. This is followed by an introductory discussion about PE, a relatively new method of fabricating electronic devices, as well as the need for implementing this manufacturing technique, some of the challenges associates with PE and the different types of printing.

In Chapter III, a project on the development of an efficient optical based detection system to be used for the detection of explosive compounds in the vapor phase is presented. A SERS substrate was designed and fabricated using the gravure printing technique. This includes the design, fabrication, and characterization of a SERS substrate, which incorporates silver nanoparticles, for optical detection of 2,4-dinitrotoluene (DNT) in vapor form. The experiment setup, testing and results obtained are also presented. The optical based response demonstrates the capability of the developed system to detect explosive compounds in the vapor form.

In Chapter IV, a project on using the conventional screen printing technique for the fabrication of a fully printed and flexible piezoelectric-based touch sensor on paper and plastic is presented. This includes the design, simulation, fabrication and characterization of the printed touch sensor. The measurement setup for testing and the response of the printed sensor are described. The capability of the fabricated device to be used as a force sensor has been demonstrated by investigating the piezoelectric response of the sensor based on applying different forces. Piezoelectric-voltage analysis demonstrates the capability of the device to be used as a touch sensor in flexible electronics, which need light weight sensing devices attached conformably onto their surface to improve user-device interactions.

In Chapter V, a project on the development of a flexible piezoelectric-based vibration energy harvester using the screen printing technique is presented. This includes the modeling, design, simulation, fabrication, and characterization of three gener-
ations of vibration energy harvesters. The measurement setup, testing and results obtained are also presented. The capability of the printed energy harvester to be used in powering of sensor nodes in a wireless sensor network has been demonstrated by measuring the DC output voltage and maximum power delivered to varying load resistances.

Finally, in Chapter VI, the author concludes with a summary of the dissertation along with suggestions for future work.
CHAPTER II

LITERATURE REVIEW

2.1 Introduction

This chapter is divided into four sections followed by a summary. Section 2.2 provides a review on the structure of the Trinitrotoluene (TNT) molecule, currently used explosive detection techniques, the fundamentals of Raman scattering, and surface enhanced Raman spectroscopy (SERS). Also, previous works on using the SERS technique for detection of explosive compounds will be reviewed. Section 2.3 provides a review on touch sensing technologies and currently used touch sensors. Also, an overview of previous works on development of flexible touch sensors will be provided. Section 2.4 provides a review of ambient energy harvesting technologies followed by a comprehensive literature review on vibration-based energy harvesters. Finally, an introductory discussion about printed electronic (PE), a relatively new method of fabricating electronic devices, as well as the need for implementing this manufacturing technique, some of the challenges associates with PE and the different types of printing will be provided in Section 2.5. It is the author’s hope that those who are just developing an interest in sensing systems and printed electronics, will gain a practical understanding of the interdisciplinary field of study, from this chapter.

2.2 Explosive Detection Using SERS Based Systems

This section provides a review on the structure of TNT molecule and currently used explosive detection techniques. It also presents the background on fundamentals of Raman scattering (RS) and SERS. Advantages of SERS over other techniques and an account of previous works on SERS for detection of explosive compounds are also
2.2.1 Trinitrotoluene (TNT)

Explosives are reactive compounds with a large amount of potential energy. These compounds rearrange their molecular structure when exposed to mechanical shock or heat, resulting in their spontaneous expansion. This sudden explosion forms high speed shock waves and releases high energy. This detonation can be used in both peaceful and non-peaceful applications. Some examples of their peaceful applications are rocket launching, quarrying, mining, and avalanche control. Bombs and explosive weapons are the main non-peaceful applications of these materials.

Explosives can be categorized based on their chemical structure. Explosives that contain nitro groups are the most threatening compounds. Based on their nitro groups, these compounds are classified as nitro aromatics (Ar-NO$_2$), aliphatic nitrate esters (R-O-NO$_2$), and cycloaliphatic nitramines (>N-NO$_2$) [67]. Nitro-containing and non-nitro-containing compounds can be identified based on the symmetric and asymmetric NO$_2$ bands in their vibrational spectra.

One of the most famous explosives from nitro-aromatic group is TNT. This compound is a secondary explosive that can be used by itself or mixed with other explosives. TNT is a yellow-colored crystalline solid which was first synthesized using toluene, sulfuric acid, and nitric acid by a German chemist, Joseph Wilbrand, in 1863. A three-step nitration of toluene using batch or continues process that produces TNT is shown in Figure 2.1 [4, 68, 69]. In the first stage of this process, the mixed acid stream counterflows to the toluene stream. 2-Nitrotoluene (2-NT) and 4-Nitrotoluene (4-NT) formed after the first step are subjected to further nitration. In the second stage of nitration, 2,4-Dinitrotoluene (2,4-DNT) and 2,6-Dinitrotoluene (2,6-DNT) are produced. DNTs are treated with HNO$_3$ and oleum (sulfur trioxide in anhydrous sulfuric acid) to produce 2,4,6-TNT and other isomers of TNT. Crude
TNT produced from nitration is washed with water to remove traces of acid, and is neutralized with soda ash. An aqueous sodium sulfite solution (Stellite) is used to remove the contaminating isomers [4, 68, 69].

Figure 2.1: Production of TNT using three-step nitration process [4].

Before its explosive potential was realized, TNT was used as a dye for thirty years. Even though it dissolves in most organic solvents, TNT has low solubility in water, varying from 100-200 mg/L at room temperature [70, 71]. TNT has a density of 1.58 g/cm$^3$, a melting point of 80.4 °C, a detonation velocity of 6700 ms$^{-1}$, and a vapor pressure of $\sim$3 ppb at room temperature [72, 73]. Due to its high stability and less sensitivity to shock and friction, TNT has convenient handling, which reduces the risk of accidental detonation.

X-ray studies of TNT have shown two crystallographic forms; monoclinic and orthorhombic in its structure [74, 75, 76, 77]. Figure 2.2 shows the Skeletal structure of TNT molecule. Theoretical calculations of the TNT structure reveal two minimum energy structures [77]. The geometry of the low energy structure, closest to the crystal structure of TNT, shows that one of the methyl hydrogen atoms is perpendicular to the phenyl ring. Also, the 4-nitro group is planar with the phenyl ring and the 2, 6-nitro groups are non-planar with the phenyl ring due to the steric hindrance between the methyl and nitro groups [77, 78].

TNT is considered as a Class C potential human carcinogen, which can cause hepatitis, enlarged spleen, gastritis, anemia, cataracts, cyanosis, and jaundice. Also,
incomplete burning of TNT and improper disposal of large concentrations of its waste would lead to significant contamination of soil and water [79, 80]. Hence, in order to reduce the environmental risks and fight against the increasing terrorist attacks caused by explosives, effective detection techniques of explosive compounds have to be investigated.

Currently, different techniques such as Ion-mobility Spectroscopy (IS), Gas Chromatography (GC), Raman Scattering (RS), UV/Visible method, and electronic nose are used in commercial detection sensors. However, low vapor pressure of explosive compounds make their vapor phase detection very difficult. Therefore, either large volume of the sample or detection methods with exceedingly high sensitivity are required for detection of explosive compounds in the vapor phase. Also, explosive vapors are usually blocked using other materials that complicates the detection process. Even though the vapor pressure of explosives can be increased by increasing the temperature, thermal degradation of the material makes the detection process more challenging [81]. Hence, the development of cost effective and rapid techniques for the detection of explosive compounds in the vapor form becomes very important.
2.2.2 Current Explosive Detection Techniques

In general, explosive detection techniques can be classified into trace-level detection and imaging detection techniques. In trace-level detection techniques, sampled air or residue obtained from body or clothes of an individual is chemically analyzed. The main advantage of these techniques is the capability of detecting low amounts of explosives, while avoiding the risk of false alarms. In imaging techniques, X-rays or millimeter waves are used to capture images of an object (human or luggage) followed by analyzing the radiation back-scattered from the body. These techniques work based on the fact that hidden objects on the human body reflect different radiations thus producing distinct images for metallic and non-metallic objects on the body [82]. Following subsections provide a review of some of the imaging and trace-level detection techniques.

2.2.3 X-Ray Systems

X-ray based detection systems are commonly used in airports for scanning of human body and luggage. In this method, the front and rear sides of the object are scanned to produce an electronic image using the intensity of the X-ray back-scattered from each location on the object. This intensity is a function of atomic number and density of the material [82]. For the systems with high energy X-rays, the absorbed energy is primarily a function of the material density. Hair and clothing on human bodies absorb less X-ray and appear transparent while metals with high density absorb more X-ray and appear as dark areas on the image. These dark areas on the image make tracing of the objects covered by metal accessories on the body very difficult [82]. This problem has been solved by employing a dual-energy X-ray system that has an additional low-energy X-ray [83]. At low energy levels, the absorption primarily depends on the atomic number and thickness of the material. Low atomic number materials such as explosives scatter more X-ray and appear as bright areas on
an image. Hence, explosives and other harmful objects can be traced by comparing the high and low energy views. The main disadvantage of this technique is that the system uses an approximation of atomic number for the material thus potentially mistaking a lethal item for a non-hazardous one.

2.2.4 Millimeter Wave Technology

Millimeter wave technologies utilize high-frequency (30-300 GHz) electromagnetic waves called millimeter waves. Since they are non-ionizing, millimeter wave systems do not cause any health hazards at low-power levels. These systems have high resolution and provide good discrimination between objects due to a short wavelength range (1-10 mm) [84, 85]. These waves penetrate into clothing materials and reflect from the human body and weapons. Hence, hidden items can be detected by illuminating a person by millimeter-wave transceiver at low power. A millimeter-wave transmitter receiver, a high-speed digital signal processor, a cylindrical scanner along with a holographic system are used in this technique. In this system, the amplitude and the phase of the reflected signal are recorded and reconstructed as a holographic image [85]. Figure 2.3 shows an example of a holographic image generated by a millimeter wave system. This technique provides high resolution, real-time operation, and a full body field view [84, 85]. However, this technique also displays the human physical features, making it not implementable in airports due to privacy concerns.

2.2.5 Gas Chromatography

The gas chromatographic (GC) technique is used to measure the content of components in a gaseous sample. In this technique, a mobile phase (carrier gas) such as helium or nitrogen is used to transport an injected sample solution into a separation tube known as the “column”. The mobile phase carrying the injected sample will then percolate through a stationary phase with a large surface area. Inside the col-
umn, various components of the sample interact differently with the stationary phase, emerging from the column at different retention times [86]. Standard samples with known concentration are then used to measure separated components of the sample with unknown concentrations. High Performance Liquid Chromatography (HPLC) is used for direct separation of liquid samples [81]. As an application, HPLC is utilized in Environmental Protection Agency (EPA) Method 8330, which is the standard method for trace explosive residue detection of Nitroaromatics and Nitramines [87]. The main advantages of GC are their high resolution, cost-efficiency, simplicity, and reliability. However, the sensitivity of GC is limited to low ppm levels, i.e., GC cannot detect ppb levels. Moreover, this technique is limited to volatile samples and is not suitable for thermally stable samples.

2.2.6 Ion-Mobility Spectroscopy

Ion-mobility spectroscopy (IMS) is an analytical technique used to separate and identify ionized molecules in the gas phase. An IMS system consists of a drift tube, sample inlet, an atmospheric pressure ion source, an ion gate, and a detector at the
end of the drift tube. In this technique, ions from the source are electronically injected into the drift region through the ion gate [88]. Inside the isolated drift tube, a uniform electric field is used to accelerate the ions. As the ions move along the tube, they are separated based on their mobility, which is a function of their mass, charge, size, and shape. The difference in migration time of the ions along the tube provides the ability for distinguishing various analyte species. While migrating along the drift tube, ion collisions hinder their movement. Depending on the ion impact, a current is generated which is measured over the time of migration. The cross-section of these collisions depends on the size and shape of the ions. The greater the cross-section of the collisions, the longer time it takes for an ion to travel along the drift tube. The output of this system is a spectrum of ion current versus time of ion drift [81, 88, 89].

There are some disadvantages related to the IMS technique. First, this technique does not allow quantification. Also, there is a possibility of false alarms due to masking by non-explosive materials in the environment. Therefore, other analytical methods are required to be used along with IMS system. Another problem happens when two components form ions of similar size and mass, resulting in a single broad peak in the IMS spectrum. Spectrometric techniques along with the IMS system are required to produce a spectrum unique for each molecule.

2.2.7 Raman Spectroscopy

Raman spectroscopy (RS) is an optical based detection method that can be used as an analytical tool for studying the real-time vibrational information of chemical structures and physical forms. In this method, characteristic spectral patterns are used as fingerprints for identifying bio/chemical substances. Due to its bulky, expensive and complicated equipment, RS has been mainly used in academic or industrial research labs. However, with recent advancements in instrument technology, manufacturers have developed smaller and portable RS equipment, making it more
accessible to the non-specialist researchers. The main advantage of RS is that it can be used for examination of bulk or microscopic particles in different states such as solid, liquid and vapor. Moreover, this technique does not require complicated sample preparation and uses simple data interpretation.

RS was first introduced by Smekal in 1923 [90] and was then observed experimentally by Raman and Krishnan in 1928 [91]. RS can be described based on inelastic scattering of light due to the interaction between the laser source and the vibration modes or states of the test molecules [92]. This interaction causes a frequency shift between the incident and scattered photons, known as molecular vibration energy, which can be detected. Typically, when light is shone on a material, the photons from the light source are either absorbed or scattered. The absorption of the photons can be employed in absorption spectroscopy. The scattering of the photons, which is dependent on the molecule of the materials, can be collected and used for molecular identification in RS. In this method, a single wavelength radiation excites the sample and the radiations from the sample are detected. When excited, the incident light interacts with the molecules and alters the electrons around the nuclei. This creates a virtual-state of the electrons that is not stable and the incident photons are rapidly reradiated.

The photons are radiated in two different ways depending on how the energy changes during vibrational spectroscopy. The photons will be scattered with very small frequencies if only electron cloud alteration occur [93]. This process is regarded as elastic scattering and is known as Rayleigh scattering. In some cases, energy will be transferred either from the incident photon to the molecule or from the molecule to the scattered photon. This process is considered to be inelastic, because the energy of the scattered photon will be different from that of the incident photon by one vibrational state and is called Raman scattering. The basic processes that occur for one vibration are depicted in Figure 2.4. At room temperature, most molecules exist
in the lowest vibrational energy states. The virtual states are created only when a sample is excited by a light source. Since the energy level does not change in the Rayleigh process, the light returns to the same state.

Two different types of scattering have been observed for RS. The first one is known as Stokes scattering, where a molecule is promoted to a higher energy state (n) from the ground vibrational state (m). The second type is called anti-Stokes scattering, in which a molecule that exists in the higher energy state (n) is transferred to the ground vibrational state (m) (Figure 2.4). In the case of Stokes scattering, both the energy level and the frequency of emitted photon are shifted. The incident photon has an interaction with the molecule at the ground mode and the molecule moves to a higher vibrational excited state. In this case, the scattered photon has less energy compared to the incident photon [93, 94]. In anti-Stokes scattering, the emitted photon is shifted in frequency and energy level, but the incident photon interacts with the molecule at
the excited state, which causes the molecule to move to a lower vibrational state [93]. In the anti-stokes case, the scattered photon has a higher energy rather than the incident photon.

The Raman shift unit is cm\(^{-1}\) and the intensity of Raman shift is dependent on the incident wavelength. In most of the studies, a Raman shift is shown as a function of Raman intensity. The peaks in this demonstration correspond to the vibrational modes of the molecule, which are based on the group theory and vibrational motion of the molecules. This vibrational energy of each mode determines the Raman shift of a peak corresponding to that mode. It should be noted that these peaks are unique for each material. The Raman intensity varies from each mode to another due to different amounts of energy released by different vibrational modes.

2.2.8 Surface Enhancement Raman Spectroscopy (SERS)

In 1974, Fleischmann, Hendra and McQuillan reported the observation of a huge amplification in the Raman spectrum of pyridine in the presence of silver electrodes, which were roughened electrochemically [93, 95]. Initially, they thought that this large enhancement is due to larger amount of target molecule which covered bigger surface area. However, in a later report by Jean Maire, Van Duyne, Albrecht and Creighton, this high enhancement in intensity of the Raman signal was identified as being the result of the formation of “hot spots” on the boundaries of metallic particles leading to the observed enhancement of the electromagnetic field [93, 94].

The important issue associated with Raman scattering is the weakness of the Raman spectrum. Basically, SERS is an enhancement of the Raman signal up to several orders of magnitude. This enhancement is mainly due to the interaction between light and the metal surface, which is related to the effect of plasmonic resonance. Plasmonic resonance will be explained in section 2.2.8.1 [93]. A SERS effect happens when the molecule is very close to or on a metallic surface. Only in this situation,
plasmonic resonance enhances the Raman spectrum [93, 94]. Due to the dependence of enhancement in Raman to plasmonic resonance and the optical properties of a metallic surface, this feature requires an in depth understanding of multiple fields of study, particularly chemistry, physics and electrical engineering.

2.2.8.1 Plasmonic

Plasmonic is the study of the properties of metals and their interaction with light result in an electromagnetic field from this interaction [93, 94]. Recently, due to progresses in nano-science, it has been possible to design and fabricate metallic structures in the scale of nanometers. This development has opened another window to the study of the characterization of metallic nanoparticles, which is also sometimes referred to nano-plasmonics. There is a strong overlap between plasmonic and SERS.

Metals have the ability to reflect light very well. This ability along with the conductive properties of metal come from the existence of free electrons in the conduction layers. These unique properties enable the optical characterization of metals to be analyzed by their dielectric function [93, 94]. The plasmonic resonance of metal cannot be explained before analyzing the electromagnetic mode that can be identified by the dielectric function. The dielectric function describes the electromagnetic modes of molecules, which resonate with the incident light. This makes it possible to use SERS as a tool for plasmonic studies of different materials and in fact, the plasmonic effect is the main reason behind enhancement in SERS.

2.2.8.2 Enhancement Mechanisms in SERS

The fundamental theory of enhancement in SERS is still a topic of debate. However, two major enhancement factors have been proposed in the literature; i.e., optical (also referred to as electromagnetic enhancement) and electronic (also referred to as chemical enhancement). There are two proposed models for chemical enhancement in
the literature. The first model implies that the metal surface increases the polarizability of the target molecules, which in turn increases the Raman cross-section area [96]. The second model implies that the metal surface either broadens or shifts the electronic states of the target molecules, which in turn results in the resonant Raman effect [97]. However, chemical enhancement is not as much as the electromagnetic enhancement.

The basic working principle of the electromagnetic effect lies in the fact that a tiny fraction of the incident photons undergoes inelastic scattering that causes a change in frequency of the electromagnetic field [98]. The intensity of the Raman signal is proportional to the square of the electromagnetic field of an analyte, which is mathematically given as

$$I \propto E_{a}^{2},$$

(2.1)

where $I$ is the intensity of the Raman field and $E_{a}$ is electromagnetic field of the analyte [99].

An enhancement in the Raman signal can be achieved by electromagnetic interactions between light and metal, which is due to the plasmonic resonances. The closeness of the molecules to the metallic surface is a very important requirement to obtain this enhancement. Plasmonic resonances of these metallic particles build the optical frequency field, which in turn creates electromagnetic field, resulting in enhancement of Raman spectrum. The deposited metal particles on the substrate in the molecular scale are not uniform which causes a different electromagnetic field on the surface based on the location of metallic particles. A very high enhancement can be achieved at some points known as “hot spots” (Figure 2.5) [100, 101, 102].

When an analyte is loaded onto the SERS substrate, the molecules settle in the hotspots. This causes spatially localized surface plasmon resonances where the electric
field of the laser enables an enhancement in the intensity of the Raman field, which is given mathematically as

\[ I \propto (E_a + E_p)^2, \]  

where \( E_p \) is the electromagnetic field because of the added metallic particles [103].

### 2.2.8.3 SERS Substrates

In a simple definition, an efficient SERS substrate provides high plasmonic resonance and enhances a weak Raman spectrum. This substrate provides a high amplification of Raman spectra. It has to be mentioned that the enhancement from this substrate can be uniform or there might be a variation in the enhancement. This enhancement usually comes from a metallic surface such as gold or silver, which are both very commonly used in fabrication of SERS substrates due to their optical properties, making them able to provide a good plasmonic resonance in the visible or near infrared range [104]. SERS measurements have been reported on different metallic surfaces such as copper and platinum, although with lower enhancement than gold and silver.

SERS substrates can be classified into three types based on the following forms
of materials:

1. Metallic particles in solution such as a colloidal solution

2. A planar metallic structure which is array of nanoparticles that are supported by a planar structure such as glass and silicon

3. Metallic electrodes.

Metallic electrodes had an important role in the SERS process and even its discovery. However, because of their low enhancement factor, they are not being used as much as before. One of the good examples of metallic particles in solution can be the tracing of the molecule in water, where gold and silver colloids can exist and amplify the Raman spectra. The same colloids can be attached or dried on an appropriate substrate to develop the planar metallic structure [93, 94].

Several methods have been used for the fabrication of SERS substrates [34, 35, 36, 100, 105]. One of the most popular approaches for fabricating SERS substrates is the deposition of metallic nanoparticles, such as silver and gold, close enough to form hot spots [37, 106]. Different techniques such as mechanical deformation, photolithography, chemical vapor deposition (CVD), electroplating and oblique angle deposition have been used to deposit silver and gold nanoparticles on various types of substrate [107, 108, 109, 110, 111]. The drawbacks associated with these deposition methods are their complexity, excessive time consumption and expensive procedures. The use of traditional printing methods such as inkjet and gravure printing, which are typically cost-efficient and perform under low working temperatures, has shown to overcome these drawbacks for the fabrication of SERS substrates [112, 113].

To the knowledge of author, there are no reports on the fabrication of SERS substrates for detection of explosive compounds in the vapor phase using printing methods. In this study, gravure printing has been used to fabricate a flexible SERS
substrate for detection of explosive organic compounds such as DNT in the vapor phase.

2.2.9 Why SERS?

When compared to other detection techniques, SERS offers several advantages that are described below:

1. Unlike most of the imagery based detection techniques that do not provide any chemical analysis, SERS is a fingerprint spectroscopic method that provides detailed information about the molecular structure of the target analyte.

2. SERS is not only useful for detection of explosives but also can be used to distinguish between molecules, which in turn eliminates the possibility of interferences.

3. SERS peaks are direct properties of the energies of the vibrational modes of a molecule. Therefore, even a small change in molecular structure causes a significant change in the spectrum that can be detected.

2.2.10 Application of SERS in Detection of Explosive Compounds

The first study of employing colloidal gold and silver as SERS substrate for detection of explosives was performed by K. Kneipp et al. [114]. In their study, they showed that near-IR excitation provides strong electromagnetic enhancement factors if the excitation laser and the Raman scattered light are in resonance with the longitudinal surface plasmon resonances of aggregated colloidal silver and gold. It was also shown that the signal amplification factor in gold ($10^5$) was better than that of silver ($10^2$).

In another work, Hainer et al. developed a SERS based explosive detection device, which was able to differentiate between an explosive and perfume [5]. In their study,
a stream of airborne compounds was focused and resublimated on a cooled (5 °C) nano-structured gold surface on which the SERS spectra were recorded. Their reason for cooling of the nanostructured gold surface was to adsorb the airborne explosive from the stream at the surface. Figure 2.6 shows the schematic of their portable and robust detection system. Using this technique, different explosives were detected based on the Nitro modes. However, the proposed technique was limited by the substrate temperature.

![Schematic of the principle for the detection of explosives](image)

Figure 2.6: Schematic of the principle for the detection of explosives [5].

Vapor phase detection of 2,4-DNT at concentration levels of 5 ppb was investigated by Sylvia [6]. For development of SERS substrates, pieces of gold foil of 0.1 mm thickness were initially polished to a smooth finish. The polished foils were then electrochemically roughened in 0.1 M KCl. The roughened substrates were then soaked in distilled water to remove excess chloride ions. Finally, the substrates were cleaned in a plasma cleaner. Figure 2.7 shows the schematic of the SERS adapter sleeve designed for detection of vapor signals. In this design, a stainless-steel sleeve slides over the fiber-optic Raman probe. A fan draws the vapor through the sleeve at a rate of 1.2 L/s. The gold SERS substrate is positioned at the focal point of the Raman probe and partially blocks the air flow, creating turbulent flow at the substrate face. The SERS spectrum toward various concentrations of aqueous 2, 4-
DNT solutions were collected. The main disadvantage of the proposed technique is the complicated preparation procedure of the SERS substrate.

Figure 2.7: Illustration of the SERS adapter sleeve designed for detection of vapor signals [6].

In another work, metal nanoparticles, with particle size of 35-80 nm, were synthesized using chemical reduction methods to be used for detection of TNT in an aqueous solution [115]. In this study, TNT detection was conducted using an indirect method that involved the alkaline hydrolysis of TNT. Among their different synthesized nanoparticles, silver colloids prepared using citrate as a reducing agent provided the most enhancement. However, their work is limited to aqueous solutions of TNT.

M. Schmidt et al. used the reactive ion etch (RIE) process to form an aperiodic array of free standing nano-pillars on a silicon wafer followed by using electron beam physical vapor deposition (EBPVD) for metal coating of the pillars [7]. Figure 2.8 shows the schematic of their fabrication process. Their proposed fabrication process requires a cleanroom, RIE, and EBPVD processes, making it expensive and time consuming.

S. Tamane et al. developed a SERS substrate by employing metal nanoparticles
on semiconductor film for the detection of various explosives in the vapor phase [116]. In this study, a plasma-enhanced chemical vapor deposition (PECVD) technique was used for the deposition of silicon film on a glass substrate. The SERS substrate was prepared by reducing a monolayer of surfactant-free silver nanoparticles on the deposited silicon film. The SERS spectrum of several nitro-explosive compounds in the vapor phase were obtained.

R. Kodiyath et al. developed a robust and tunable SERS substrate by aggregating silver nanocubes within cylindrical pores to be used for trace level organic vapor detection [117]. By switching the absorption behavior of silver nanocubes between highly aggregated and more disperse though varying the number of adsorption-mediating polyelectrolyte bilayers on the pore walls of the membrane they were able to tune both the detection limit and the onset of signal saturation of the SERS substrate. They also showed that their proposed SERS substrate can be reusable while demonstrating consistent SERS activity after multiple exposure-wash cycles. However, the fabrication process used in this study is expensive, complicated and time consuming.

The main drawback of the above-mentioned works is the expensive and complicated processes used for development of SERS substrates. Moreover, most of these works use rigid substrates for development of SERS substrates, thereby limiting their
application areas. In this work, SERS has been used for the detection of explosive compounds in a vapor phase. Gravure printing will be employed to deposit a thin film of silver nanoparticle ink on flexible polyethylene terephthalate (PET) sheet to be used as a SERS substrate. The capability of the printed substrate for detecting explosive organic compounds, such as DNT, in vapor phase, has been investigated. The effect of varying temperatures and substrate bending on the intensity of Raman spectra obtained for DNT vapor was also studied.

2.3 Touch Sensors

Touch sensing can be described as the technology of converting physical interactions into electrical signals or other types of energy. A mechanical switch with ON/OFF states can be considered as a primitive example of a touch sensor. During the last few decades, various touch sensing mechanisms have been investigated by researchers and different manufacturers have produced various touch sensing technologies [118]. Nowadays, touch sensitive devices are used in many of today’s electrical devices such as mobile phones, tablet, PCs, automobiles, home appliances, medical tools, robotics, etc. In general, touch sensitive devices can be classified into two groups. One group is developed to convert physical touch into a binary output signal such as a touchscreen. This binary signal indicates whether a contact has been made or not with an object. Another group outputs the associated physical quantities in a continuous form, such as force and torque sensors in a robotic manipulation task. In the following sections, the mainstream touch sensing technology and its emerging opportunities are introduced.

2.3.1 Touchscreens - A Multi-Billion Dollar Industry

Among different applications of touch sensors, the touchscreen industry has the greatest amount of investment. Touchscreens are employed in most of today’s com-
puting devices as well as home and auto-appliances. A touchscreen is a transparent array of touch sensitive spots laying on an LCD screens capable of capturing the location of one or multiple finger touch interactions. Most of the commercialized touchscreens consist of three layers: the top glass cover, the touch sensing structure, which contains multiple layers based on its sensing mechanism, and an LCD display. The key technology in the touchscreen industry is the touch sensing element, which can be based on various sensing mechanisms such as surface capacitive, projected capacitive (pro-cap), 5-wire resistive, optical, or acoustic [119, 120].

2.3.2 Touch Sensor Technologies

During the last few decades, touch sensors have been greatly investigated by both researchers and manufacturers. Touch sensors have been used in variety of applications such as Human-Machine Interface (HMI), robotics [121, 122, 123], and medicine [124, 125, 126, 127, 128, 129].

Various transduction mechanisms, such as resistive [130, 131, 132, 133, 134, 135], capacitive [136, 137, 138, 139], and piezoelectric [140, 141], have been used in development of touch sensors. The following subsections provide a review of these currently used techniques.

2.3.2.1 Capacitive

A pro-cap touchscreen consists of two layers of indium tin oxide (ITO) electrodes used to sense the presence and position of a touch made by any conductive object like a finger through capacitance measurements. Figure 2.9 shows the common interlocking diamond design of pro-cap based sensors. In this design, two types of capacitance exist: (1) self-capacitive and (2) mutual capacitive. The self-capacitive scheme measures the capacitance between each row or column electrode with respect to the ground while the mutual capacitive scheme measures capacitances at the inter-
sections of the row and column electrodes, as shown in Figure 2.9(b). Even though change in either of these capacitances can be used for sensing purposes, different driver designs are required based on the capacitance measurement scheme. The advantages of self-capacitive sensor are high speed, low noise, and simplicity of driver design.

![Figure 2.9: (a) Schematic of an interlocking diamond design for pro-cap electrode layout [8]. (b) The driver scans through rows and columns for the intensity of capacitance change.](image)

The computational load of the self-capacitive scheme does not scale up as the number of sensors become larger, which makes it a proper choice of technology when a large array of sensors is required. The main drawback of this scheme is that it is only capable of sensing the accurate position of one finger and some well-defined gestures. Most of the touchscreen manufacturers use pro-cap sensing technology due to its simple mechanical structure, reliable sensing performance and multi-touch sensing capability [142]. On the other hand, the mutual capacitive scheme allows multiple finger sensing, while it is more noise sensitive and it requires more complex driver design and consuming power. In recent years, the demand for mutual capacitive sensors is exceeding self-capacitive sensors with the development of integrated circuits.
2.3.2.2 Resistive

Resistive based touch sensors are the second most popular type of sensors used in touchscreen technologies. This type of sensor was dominantly used in earlier generations of touchscreens. The main advantage of resistive based touchscreens is that they operate irrespective of the material of the object that comes in contact with them, making them ideal for stylus interactions such as signature pad and drawing panels. A common configuration for resistive based touch sensors consists of two transparent conductive layers separated by a spacer array. In this technology, a constant excitation voltage is applied to one of the conductive layers while the voltage at the other conductive layer is used as the sensing signal. When the top conductive layer is pressed by a finger, an electrical conduction path will be created between the top and bottom conductive layers which in turn results in a voltage change at the sensing layer. This voltage change is then used to register a touch. The main drawback of resistive based touchscreens is the significant amount of pressure that they require to register a touch, making then non-responsive when compared to their capacitive counterparts. Also, due to the high-pressure threshold, resistive based touchscreens suffer from poor durability and performance deterioration over time.

2.3.2.3 Piezoelectric

Piezoelectricity is the ability of certain types of materials to generate a temporary charge in response to an applied mechanical stress and vice versa. In other words, when a voltage is applied to a piezoelectric material, it undergoes a dimensional change. This electromechanical behavior enables the use of one single component for both sensor and actuator configurations and can be described using following
constitutive equations,

\[ \delta = \frac{\sigma}{Y} + dE, \quad (2.3) \]
\[ D = \epsilon E + d\sigma \quad (2.4) \]

where \( \delta \) is the strain, \( \sigma \) is the stress, \( Y \) is the modulus of elasticity (Young’s modulus), \( d \) is the piezoelectric strain coefficient, \( D \) is the electrical displacement (charge density), \( \epsilon \) is the dielectric constant of the piezoelectric material, and \( E \) is the electrical field.

Piezoelectricity has been largely used to maximize the energy efficiency for low energy user interface technologies. Depending on the design of the sensor, different modes of the piezoelectric element can be used: longitudinal, transversal and shear. As shown in Eq. 4.2, the voltage generated across a piezoelectric element is proportional to the applied pressure. However, it should be noted that the generated charge on these materials is temporary. In other words, if the applied force is maintained, the sensor output decays to zero. Therefore, the piezoelectric-based sensors are not suited for sensing static forces.

2.3.2.4 Comparison of Touch Sensing Technologies

Even though the capacitive, resistive, and piezoelectric-based sensors are the most common technologies used in touch sensor industry, optical and surface acoustic wave based touch sensors are other types of touch sensor technologies in which a change in wave propagation through emitters/receivers can be used for touch detection.

The main disadvantage of capacitive based touch sensors is that their accuracy depends on the capacitance of the person who touches them. Resistive based touch sensors suffer from poor durability when compared to other technologies. Optical based sensors have lower resolutions than other technologies and surface obstruction...
can cause false positives. Among these, the piezoelectric-based transduction mechanism has generated significant interest due to its accuracy and capability to measure dynamic events, irrespective of the material of the object that comes in contact with the sensor. This mechanism has also been widely used especially for applications in sensors, actuators and energy harvesters.

Most of the commercialized touch sensors are fabricated using MEMS technology. The advantages of this technology are its capability to develop sensing devices with small device footprint, high spatial resolution, and excellent sensitivity. However, these sensors are often expensive and fabricated on rigid substrates. Also, none of these configurations offer the high flexibility, stability and conformability, required for various touch sensing applications. An alternative approach to overcome the drawbacks associated with this technology is to use continuous layer-on-layer deposition of electrically functional inks onto flexible substrate materials. Therefore, the development of piezoelectric-based touch sensors using printing processes, on flexible substrates, is important.

2.3.3 Flexible Touch Sensors

Recently, there has been a growing interest in the development of touch sensors on flexible substrates. These sensors have applications such as curved touchscreens, robotics, prosthesis, and wearable electronics. Polymer substrates are the most common substrates used for fabrication of these sensors. J. Engel et al. developed a polyimide-based two-dimensional tactile sensing array using the standard image reversal photolithography technique on a silicon wafer followed by lift-off process (Figure 2.10(a)) [9]. Later in 2005, the same group developed a multimodal tactile sensor by patterning a thin metal layer on a Kapton polyimide substrate, using reactive ion etching (RIE) and spin coating processes (Figure 2.10(b)) [10].

J. Kim et al. fabricated a flexible tri-axis capacitive force sensor using a polymer
Figure 2.10: (a) completed polyimide-based two-dimensional tactile sensor on Si wafer prior to release [9] and (b) photograph of completed multimodal tactile sensor in flexed state [10].

micromachining process (Figure 2.11(a)) [11]. K. Kim et al. used polymer MEMS technology and electroplating to fabricate a flexible tactile sensor array on a polyimide substrate (Figure 2.11(b)) [12].

Figure 2.11: (a) view of the flexible tactile sensor developed using a micromachining fabrication process on polyimide [11] and (b) photograph of the flexible sensor array developed using polymer MEMS technology and an electroplating process [12].

H. Kim et al. developed a flexible and fully transparent capacitive-based tactile
sensor for touchscreen application (Figure 2.12(a)) [13]. C. Hu et al. implemented a carbon nanotube (CNT)-based flexible piezoresistive tactile sensor using micromachining and chemical vapor deposition (CVD) processes [14]. Figure 2.12(b) shows their fabricated tactile sensor. PDMS and Parylene have been used as substrate and encapsulation layer, respectively.

![Image of sensor](image1)

Figure 2.12: (a) fabricated transparent capacitive-based tactile sensor [13] and (b) the integration results of the flexible tactile sensor with the FPC after molding and de-molding processes [14].

X. Li et al. reported a flexible paper-based piezoelectric touch pad [15]. Figure 2.13(a) shows their developed touch pad consisting of an array of touch buttons. In this work, zinc oxide nanowires (ZnO NWs) were hydrothermally grown onto a paper-based substrate. A flexible piezoelectric tactile sensor array based on polyvinylidene (PVDF) film was developed by P. Yu et al. for measuring tri-axis dynamic contact force distribution [16]. In this work, MEMS-based technology was used for fabrication of different layers of the device. Figure 2.13(b) shows the photograph of their fabricated PVDF film with patterned upper and lower electrodes.

As mentioned above, most of these touch sensitive devices are typically manufactured using conventional silicon based processes, which are often expensive and
Figure 2.13: (a) The photograph of the paper-based piezoelectric touch pads consisting of an array of touch buttons showing the blue LED lighting when the number key is pressed [15] and (b) photograph of the PVDF based tri-axis dynamic contact force sensor mounted on a curved surface [16].

Fabricated on rigid substrates [13, 46, 47, 48, 49]. Moreover, most of the configurations used do not provide the high flexibility and conformability required for various touch sensing applications, thereby limiting their application areas. A promising approach to overcome the drawbacks associated with conventional touch sensors is to use continuous layer-on-layer deposition of electrically functional inks onto flexible substrate materials. The development of fully flexible and conformal touch sensors, due to the availability of diverse manufacturing materials and the rapid development of modern fabrication techniques, is thus poised to have a significant impact on the modern society.

Of all the available printing processes, even though screen printing has been used to fabricate piezoelectric-based touch sensors, the top electrodes are often printed on a separate substrate and are bonded to the final device. This is done to avoid short-circuit between the electrodes due to pinholes caused by the porous nature of the piezoelectric layer [143]. It is envisioned that the problem of pinholes can
be overcome by reducing the roughness of the printed bottom electrode and PVDF layers, by optimizing the screen printing process. Moreover, this enables the direct printing of top electrodes onto the piezoelectric layer. In this project, screen printing technology has been used to fabricate a piezoelectric-based touch and force sensor on PET and paper substrates.

2.4 Ambient Energy Harvesters

2.4.1 Motivation: Powering Wireless Sensors Networks

During the last two decades, wireless sensor and actuator networks have generated an increasing interest between researchers and manufacturers. These networks can be employed in a wide variety of applications such as monitoring acceleration and pressure in automobile tires, smart parking systems, distributed heating, ventilating, and air conditioning (HVAC), sensing harmful chemical agents in high traffic areas, monitoring fatigue crack formation on aircraft, etc. It is expected that very low power embedded electronic devices will be inserted in different parts of our environment ranging from factory automation to entertainment applications [144, 145, 146, 147].

Due to the advancements in integrated circuit (IC) manufacturing and low power circuit design, as well as creative networking techniques, the power consumption of a wireless sensor node can be reduced to less than 1 mW. These sensor nodes could form ad-hoc networks transmitting data from 1 to 10 meters. As a matter of fact, when the communication distance is greater than 10 meters, the energy required for transmitting data dominates the overall energy budget [148]. The issue of large transmission distances can be addressed by employing a multi-hop ad-hoc network protocols such as Zigbee and PicoRadio with transmission power of 1 mW and 100 µW, respectively [149].

Table 2.1 shows the power consumption for various sensor devices used in a build-
ing management system, providing a general idea of the order of the energy requirements for sensing and computing.

Table 2.1: Sensor specification for wireless module used in building management system [1].

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Voltage (V)</th>
<th>Current (mA)</th>
<th>Power (mW)</th>
<th>Sampling Time (s)</th>
<th>Energy/Sample (µJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>3.3</td>
<td>0.008</td>
<td>0.026</td>
<td>0.00002</td>
<td>0.00528</td>
</tr>
<tr>
<td>Light</td>
<td>3.3</td>
<td>0.03</td>
<td>0.099</td>
<td>0.0002</td>
<td>0.0198</td>
</tr>
<tr>
<td>Humidity</td>
<td>3.3</td>
<td>0.3</td>
<td>0.99</td>
<td>0.8</td>
<td>792</td>
</tr>
<tr>
<td>Vibration</td>
<td>3.3</td>
<td>0.6</td>
<td>1.98</td>
<td>0.02</td>
<td>39.6</td>
</tr>
<tr>
<td>Barometric Pressure</td>
<td>5.0</td>
<td>7.0</td>
<td>35.0</td>
<td>0.02</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Therefore, for a wireless sensor node with peak power consumption of 2-5 mW (1 mW for the radio transmitter and 2-4 mW for sensing and computing) and standby power consumption of 50 µW, and assuming that the node spends 1% of its time at peak power consumption and the rest in idle, the average power consumption of the node is roughly 100 µW. In case of powering this node using a 1 cm³ lithium battery containing 2,880 J of energy, the device could last almost a year [55]. Clearly, a lifetime of one year is far from sufficient when considering annual maintenance of thousands or hundreds of thousands of sensors operating in a wireless sensor network. As it is shown in Figure 2.14, even though battery technology has been steadily improving, it has not been able to keep up with the rapid growth of other technologies, such as disk capacity, CPU speed, or wireless transfer speed. The aforementioned example along with the severe limits of the battery technology illustrate why developing alternative methods for improvement of powering wireless technologies has been studied in recent years.

2.4.2 Ambient Energy Harvesting

The problem of powering the emerging wireless technologies can be addressed by (a) improving the energy density of storage systems, (b) developing novel methods for distributing power to nodes, or (c) developing technologies that enable a node to
generate its own power. Among these possible approaches, the third one, in which a wireless node generates its own power, has been generated so much interest in recent years. Since in this method, a node converts energy from its immediate environment into electricity to be used by the electronics, it has been called “ambient energy harvesting”. The main advantage of this method is that the lifetime of the node would solely be limited by failure of its own components. Also, there are some applications such as industrial automation, environmental monitoring, infrastructure monitoring and implanted medical devices in which battery replacement and disposal is either hard or impossible. Figure 2.15 illustrates the cost of battery maintenance in wireless sensor networks from 2006 to 2015, showing that a projected total amount of $1.1 billion dollars has been spent by wireless sensor users for maintenance during the course of 10 years. Combining this number with the battery and its disposal provides an approximation of the market size for energy harvesting from ambient sources.
Harvesting ambient energy surrounding the wireless microsystems can thus become an enabling technology, facilitating various applications in which lifetime and battery maintenance would inhibit their development.

Figure 2.15: Projected annual battery replacement labor cost for wireless sensor networks from 2006 to 2015, $1.1 billion in total [18].

2.4.3 Survey of Ambient Energy Sources

This section provides a brief discussion of different ambient energy sources, outlining the advantages and disadvantages of each energy source. Table 2.2 shows some of the potential ambient energy sources and their corresponding energy densities for powering wireless electronic devices.

2.4.3.1 Solar Energy

The increase of the Earth’s population along with rapid technology development and economic growth, is projected to produce demand for a continuous power consumption of 46 terawatts (TW) by the end of the century, even in the most aggres-
Table 2.2: Comparison of typical ambient energy sources.

<table>
<thead>
<tr>
<th>Energy Source</th>
<th>Characteristics</th>
<th>Efficiency</th>
<th>Power Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar</td>
<td>Outdoor</td>
<td>10-25%</td>
<td>100 mW/cm²</td>
</tr>
<tr>
<td></td>
<td>Indoor</td>
<td></td>
<td>100 µW/cm²</td>
</tr>
<tr>
<td>Thermal</td>
<td>Human</td>
<td>0.1-3%</td>
<td>60 µW/cm²</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td></td>
<td>10 mW/cm²</td>
</tr>
<tr>
<td>Ambient RF</td>
<td>GSM 900 MHz</td>
<td>50%</td>
<td>0.1 µW/cm²</td>
</tr>
<tr>
<td></td>
<td>WiFi 2.4 GHz</td>
<td></td>
<td>0.001 µW/cm²</td>
</tr>
<tr>
<td>Radioactive</td>
<td>(^63Ni)</td>
<td>0.5-5%</td>
<td>0.52 µW/cm³</td>
</tr>
<tr>
<td>Vibration</td>
<td>Hz-human</td>
<td>25-50%</td>
<td>4 µW/cm²</td>
</tr>
<tr>
<td></td>
<td>kHz-machines</td>
<td></td>
<td>800 µW/cm²</td>
</tr>
</tbody>
</table>

sive energy demand scenarios [150]. Considering 120,000 TW of solar radiation on the surface of the Earth, one might think no other energy source would be necessary. However, capturing and converting this energy into cheap electrical power is challenging.

Solar cells use incident light to generate current through the photoelectric effect. The first solar cell was developed by Charles Fritts in 1885, pre-dating modern electronics and the transistor. The efficiency of this device was 1% [151]. In 1946, Russell Shoemaker Ohl from Bell Laboratories was awarded the first patent for the modern solar cell. Ohl’s solar cell had about 1% efficiency [152]. Due to the advancements in silicon based technologies, researchers have been able to achieve more efficient solar cells and the highest reported efficiency so far is around 46%. By assuming a solar irradiance of 1000 W/m² on a clear sunny day, current advanced solar cells can generate up to 46 mW/cm² [153].

During the last two decades, climate change has become an ongoing concern threatening human life around the world. Photovoltaic is one of the main technologies investigated to address the issue of climate change by replacing the fossil fuels with a clean and cheap energy. So far, low-cost solar cells with low efficiency have been developed using amorphous materials. One of the main approaches for maximizing the efficiency of the solar cells is to use multiple junctions, (Figure 2.16), in which
different bandgap semiconductors are used to capture more of the solar spectrum. Multiple junctions can be coupled with parallel or lateral optical concentrating system to concentrate the sun’s light by factors of 100-10,000 x. More research is going on to develop solar cells with efficiency of higher than 50% in the near future [154].

![Cross sectional schematic of an epitaxial triple junction solar cell. The top cell absorbs the most energetic photons, while the semiconductor at the bottom absorbs the least energetic photons.](image)

Replacement of fixed-capacity power sources with solar cells, in long-lifetime applications, faces two main challenges. First, the available solar energy indoors is 1000-2000 x lower when compared to the direct sunlight outdoors, which means solar cells may not be efficient indoors. Second, harvesting outdoor photovoltaic power has its own challenges when considering cloudy days and the chance of debris, snow, dust, etc. obstructing the line of sight of the solar panels.

2.4.3.2 Thermal Energy

Thermal energy is another ambient source of energy. Thermoelectric generators work based on the Seebeck effect, where a temperature gradient between two different metals or semiconductors creates a voltage between them. The operation principle of a thermoelectric generator is shown in Figure 2.17. The behavior of the thermoelectric
generator can be described by Eq. 2.5 and Eq. 2.6,

\[ V_{\text{out}} = \alpha N(T_H - T_C), \]  

\[ \text{Power} = \frac{V_{\text{out}}^2}{R_g} = \frac{\alpha^2 N^2(T_H - T_C)^2}{R_g}, \] 

where \( \alpha \) is the Seebeck coefficient of the material, \( N \) is the number of thermopiles, \( T_H \) and \( T_C \) are the hot and cold side temperatures, respectively, and \( R_g \) is the internal resistance of the generator. Based on Carnot cycle theory, the maximum efficiency of the thermoelectric conversion is equal to \( \Delta T/T_H \), which means a lower temperature gradient results in lower efficiency.

Figure 2.17: Illustration of the operation principle of thermoelectric generators based on the Seebeck effect. A temperature gradient between two semiconductors of p-type and n-type creates a voltage (\( V_{\text{out}} \)).

Despite its low efficiency and high cost, a thermoelectric generators are an interesting energy source due to their reliability and lack of moving parts. A thermoelectric generator was one of the first commercial energy harvesters used in a Seiko watch in 1999 [155].

One of the key factor in the design of thermoelectric generators is the choice of materials with a high figure of merit in order to optimize the number of thermopiles and
the internal resistance of the device [156]. Another factor in developing thermoelectric generators is creating thermal isolation to increase the thermal gradient between the cold and the hot sides. Due to the advancements in silicon based technologies, researchers have been able to develop more efficient thermoelectric generators and the best performing device reported to date has been developed by Thermo Life Energy Corporation which can generate up to 40 µW/cm² and 2.7 V at $\Delta T = 5$ kelvin [157].

The main drawback of this technology is that not many practical applications can be found where a large enough temperature gradient can be formed to generate an appreciable amount of power.

2.4.3.3 Ambient RF and Coupled Energy

Radio signals transmitted from various sources such as microwave, cell phone, wireless LAN, TV, etc. are ubiquitous in our daily lives specifically in urbanized areas. Therefore, considering this otherwise wasted energy as an alternative source of energy for powering wireless devices would seem logical. However, tapping into this source of energy is challenging [158]. The efficiency of this technology is very small and a large collection area as well as the proximity to the radiation source are critical requirements for harvesting this energy. A rough analysis of this technology shows that the power density for a receiving antenna is approximately $E^2/Z_0$, where $E$ is the local electric field strength in V/m and $Z_0$ is the radiation resistance of free space (377 $\Omega$) [159]. Based on this analysis, an electric field of 1 V/m can produce 0.26 µW/cm². However, it is difficult to find an electric field of 1 V/m unless in proximity to a powerful transmitter.

Another similar approach to harvesting ambient RF energy is the idea of using coupled wirelessly transmitted energy for powering electrical devices. The idea of long distance power transfer was first developed and patented by Nicola Tesla in 1900 [160]. The basic principle of this method is the same as a transformer where a magnetic field
in one of the two coils placed in proximity of each other, induces current in another coil. In 1960, this technology was successfully used by surgically implanting a coil in a dog to power an implanted artificial heart [20]. Figure 2.18 shows the power transfer model of the implanted system and its electrical representation, respectively. Radio frequency identification device (RFID) is another common application of this scheme.

Figure 2.18: Inductively coupled power transfer model for implanted systems: (left) illustration of the system, where one coil outside of the body is used to broadcast energy to another one implanted inside and (right) the electrical representation of the system [20].

2.4.3.4 Radioactive Energy

Another source for harvesting energy is the emitted energy of different radioisotopes that emit low-energy $\beta$ particles. Radioisotopes have much higher energy density when compared to chemical fuels. Also, there are some certain isotopes with hundreds of years half-life, which means that they can supply energy for a long time. For example, a speck of nickel-63 or tritium contains enough energy for powering a MEMS device. Also, different materials such as plastics, metals, or semiconductors can be used to block the radiation of 1 to 10 millicuries of tritium or nickel-36 to avoid any health issue associated with radiation. Hence, this type of energy is a promising potential source for energy harvesting if one can overcome the cost, efficiency and safety related challenges.

Radioactive energy can be converted into electrical energy using both direct or indirect mechanisms. In the case of indirect conversion, radioactive decay is first
converted into another form of energy such as thermal or mechanical. This energy is then used to generate electrical current. One approach for direct conversion is to use emitted beta particles of nickel-63 to ionize the atoms of a p-n junction sitting in its proximity. The ionized atoms of the p-n junction produce electron-hole pairs in the vicinity of the junction, which in turn produce electrical current [21]. However, this approach suffers from low efficiency (< 0.5%) due to long term impact damage of semiconductor material. In another approach, researchers have utilized an electric field developed between a cantilever and a decaying isotope to deflect the cantilever beam. This conversion mechanism is summarized in Figure 2.19 [21, 161]. As shown in this figure, emitted electrons from the isotope are collected at the tip of the cantilever beam, pulling it towards the radiation source. Whenever the bent cantilever touches the isotope, collected electrons from the copper sheet flow back to the radiation source, releasing the beam to resonate at its natural frequency. The resulting vibration along with a piezoelectric material attached to the beam can be used to generate an electrical current. Depending upon the stiffness of the beam and the gap between the cantilever and isotope, the reciprocation period can be as large as several hundred seconds, resulting in a small average power. However, these devices have efficiencies not greater than 5%. R. Duggirala et al. have developed a radioisotope-powered piezoelectric µ-power generator with a maximum efficiency of 3.7%. In this study, a peak output power of 1.13 µW was generated using a microfabricated 1 cm long silicon device with a sol-gel PZT layer [162].

2.4.3.5 Ambient Air/Fluid Flow

Kinetic energy of airflow and other fluids is the first of a series of examples of energy harvesting from ambient motion. The first windmill was invented in Persia in the 9th century. This clean and cheap source of energy along with the advancements in wind turbine technology have generated a growing interest in developing of wind-
farms. However, this technology has received the least attention for the applications where miniaturization is concerned.

The kinetic energy density of a flowing fluid can be calculated by

$$E_k = \frac{1}{2} \rho V^2,$$  \hspace{1cm} (2.7)

where $V$ and $\rho$ are speed and density of the fluid, respectively. Using the kinetic energy given in Eq. 2.7, the power flow per unit area normal to the fluid motion is [163]

$$P_{\text{unit area}} = \frac{1}{2} \rho V^3.$$  \hspace{1cm} (2.8)

Considering that the fluid speed would drop to zero if all of this power is extracted, the power output of a device with area $A$ can be described as

$$P_{\text{out}} = \frac{1}{2} C_p \rho A V^3$$  \hspace{1cm} (2.9)

where $C_p$ is a power coefficient known as Betz limit. The ideal maximum value of
this coefficient is 0.593 [164]. Even though modern wind turbines have yielded $C_p$ values as high as 0.5, miniaturized airflow generators can achieve a maximum $C_p$ of $\sim$0.1 [165, 166].

To the knowledge of author, there has not been many reports on utilizing micromachining in development of miniaturized wind turbine. In one of the few reports, A. Holmes et al. used laser ablation to develop a 12 mm diameter rotor out of SU8 [22]. Figure 2.20 shows their developed micro-turbine generator. This device was able to generate output power of 1 mW using 351/min volume flow in a ducted test chamber. However, this device requires free stream flow rates (40 m/s) that are much larger than practical airflow speed ranges (1-5 m/s). In the best-case scenario, currently developed micro-turbines can generate output power of 750 $\mu$W/cm$^2$ at flow speed of 5 (1) m/s and 6 $\mu$W/cm$^2$ at flow speed of 1 m/s.

![Figure 2.20: Photograph of a micro-turbine generator developed for converting ambient air flow to electrical power [22].](image)

2.4.3.6 Energy Harvesting from Direct Force

Generating electrical energy from direct force is an old example of harvesting energy from mechanical motions. Self-powered flashlights which can be powered by repeatedly squeezing and releasing their handle, or AM/FM radios, which can be pow-
ered by turning a crank, are two old examples in which direct force energy harvesting is utilized.

Direct force energy harvester can be either design to work passively or actively. An example of passive direct force energy harvesters is the shoe sole with an embedded mechanism to harvest energy from human walking. An example of active direct force energy harvesters is a push-button designed to perform certain tasks while being pushed.

Figure 2.21 shows the first example of passive direct force energy harvester developed at MIT in the late 90's [23, 167]. As shown in this figure, two different piezoelectric elements, lead zirconate titanate (PZT) and polyvinylidene fluoride (PVDF), are embedded into the sole of a shoe to harvest energy from human walking. The compression/tension of two pre-bent PZT unimorphs, placed against a back-metal plate, causes strain when the heel comes in contact with the ground. The PVDF element is placed in the front of the shoe, such that its outside corners are pulled in when the center bends, thus causing strain in the piezoelectric element. The average powers of the embedded PZT and PVDF elements are 2 mW and 1 mW, respectively.

![Figure 2.21: The first example of passive direct force energy harvesters developed at MIT [23].](image-url)
A compact piezoelectric push-button device with an embedded RF transmitter was developed by the same group at MIT. This device is able to wirelessly transmit a digital ID code over 50 feet [168]. The 3.5 mm deflection of the piezoelectric element used in this device at a force of 15 N, generates enough energy to power an off-the-shelf RF transmitter which consumes 7.5 mW.

In another work, researchers at the University of Michigan attached piezoelectric beams to the wings of a beetle in order to generate power while the beetle flaps its wings (Figure 2.22). The developed devices with volume of 11 mm\(^3\) and 5.6 mm\(^3\) were able to generate 11.5 µW and 7.5 µW, respectively [24]. They have predicted that utilizing a coiled beam would enable this device to generate 101.6 µW of power.

![Figure 2.22: Photograph of the piezoelectric energy harvester attached to the wings of a live insect [24].](image)

<table>
<thead>
<tr>
<th></th>
<th>Prototype - I</th>
<th>Prototype - II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resonance Frequency</td>
<td>680 Hz</td>
<td>5 kHz</td>
</tr>
<tr>
<td>(V_{pp}) (Open Circuit)</td>
<td>6.56 V</td>
<td>6.60 – 8.28 V</td>
</tr>
<tr>
<td>(V_{RMS}) (on Resistive Load)</td>
<td>875 mV</td>
<td>772 – 945 mV</td>
</tr>
<tr>
<td>Optimum (R_{load})</td>
<td>66.6 kΩ</td>
<td>200 kΩ</td>
</tr>
<tr>
<td>Total Power Output</td>
<td>11.5 µW</td>
<td>7.5 µW</td>
</tr>
<tr>
<td>Device Volume</td>
<td>11.0 mm(^3)</td>
<td>5.6 mm(^3)</td>
</tr>
</tbody>
</table>

In another work, researchers utilized rain drops as a source of energy [169]. Using a 7.5 mm\(^3\) piezoelectric element, they were able to generate 73 µW (8 µW) from a 3 mm (1.6 mm) diameter rain drop traveling at 4.5 m/s (3.2 m/s).
2.5 Printed Electronics

During the last few decades, printed electronic (PE) has become one of the main technologies for fabrication of electronic devices and other kinds of electrically controlled machines and equipment. PE can be defined as a technology that combines electronics manufacturing and text/graphic printing. Using this technology, one can produce electronic products which are thin, lightweight, flexible, wearable, cost-efficient, and environmentally friendly. All these features have generated significant interest among researchers and manufacturers in utilizing printing techniques along with flexible substrate materials and electrically functional inks in fabrication of electronic devices.

The main advantage of PE is its additive process nature where electrically functional materials are deposited selectively without need for masking and etching processes. On the other hand, PE technology does not require high temperature fabrication process and a clean-room environment. All these features result in lower production costs when compared to traditional silicon based fabrication processes. PE also offers usage of flexible substrates for fabrication of flexible electronics where electrical devices are attached onto the surface to improve user-device interactions. These advantages of PE can revolutionize the fabrication and performance of electronic devices.

Sensors and energy harvesters are typically manufactured using traditional silicon based electronics which are often expensive and time consuming with the requirement of high temperature processes [170, 170, 171, 172, 173, 174, 175]. Also, none of these technologies offer high enough conformability and flexibility needed for various sensing and energy harvesting applications. A promising approach to overcome the drawbacks associated with the conventional silicon based technologies is using of continuous layer-on-layer fabrication process associated with PE.
2.5.1 Why Printed Electronics?

The advancements in the field of microelectromechanical systems (MEMS) has radically affected the way in which we interact with the world. This industry has furnished human life with various electronic products such as smartphones and computers. The idea of “large-area electronics”, which aimed at decreasing the cost per unit area for consumer products was introduced in the second half of the 1970s [176]. This new realm of electronics was followed by the introduction of PE, in the 1990s, which uses low-temperature manufacturing with high throughput patterning techniques [177].

The fabrication of electronic devices using printing methods is a relatively new process for electronic manufacturing companies. Integration of printing techniques with conventional fabrication methods has shown the potential for achieving cost efficient and high volume electronic manufacturing. The use of printing methods for deposition of functional materials provides the advantage of additive manufacturing of inexpensive, large-area electronics that paves a path for the design and development of novel electronic devices that have been unimaginable before. The additive nature of this technology, which uses functional materials only in required design areas, is promising for decreasing the usage of materials when compared to the traditional photolithography based subtractive approach.

This trend of transitioning from high vacuum and high temperature manufacturing processes to employing PE has resulted in fabrication of structures and devices that are similar to conventional electronics, with much less complexity, greater speed and lower cost [178]. The availability of functional inks, along with the technical expertise available in printing, facilitates the integration of this technology with current electronic manufacturing. This integration has opened up new markets for development of novel products which go beyond the current paradigm of human imagination. The using of printing techniques for the development of electronic devices is thus very
interesting.

### 2.5.2 Types of Printing

Printing processes can be classified into two main categories: (a) impact printing and (b) non-impact printing [179]. Impact printing uses an image carrier (screen, plate or cylinder) to transfer the image or design onto a substrate. However, non-impact printing works based on digital control of the image, which eliminates the need for a physical image carrier. Figure 2.23 summarizes the classification of different printing technologies.

![Figure 2.23: Classification of printing technologies [2].](image)

Printing techniques used in printed electronics are divided into four main printing methods; flexography, gravure, screen and inkjet printing. Table 2.3 summarizes the image carrier, resolution, ink film thickness, ink viscosity and printing speeds of all the traditional printing techniques.
Table 2.3: Comparison of conventional printing techniques [2].

<table>
<thead>
<tr>
<th>Printer</th>
<th>Image Carrier</th>
<th>Resolution (µm)</th>
<th>Ink Film Thickness (µm)</th>
<th>Printing Speed (ft/min)</th>
<th>Ink Viscosity (Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexography</td>
<td>Plate</td>
<td>20</td>
<td>0.5-2</td>
<td>300-1000</td>
<td>0.05-0.5</td>
</tr>
<tr>
<td>Gravure</td>
<td>Engraved cylinder</td>
<td>15</td>
<td>0.5-8</td>
<td>1500-3000</td>
<td>0.05-0.2</td>
</tr>
<tr>
<td>Screen</td>
<td>Stencil and mesh</td>
<td>50</td>
<td>3-60</td>
<td>300-500</td>
<td>0.5-50</td>
</tr>
<tr>
<td>Inkjet</td>
<td>Digital</td>
<td>20</td>
<td>0.05-0.5</td>
<td>NA</td>
<td>0.001-0.04</td>
</tr>
</tbody>
</table>

2.5.2.1 Flexographic Printing

Flexographic printing can be defined as a modern version of letterpress printing. Figure 2.24 shows the schematic of flexographic printing consisting of a plate cylinder, anilox roller, ink container, doctor blade and impression cylinder. In this process, the required image areas are raised on a plate cylinder, typically made of rubber or other polymers. The ink is transferred from the ink container onto the image areas of the plate cylinder by the anilox roller. The doctor blade removes the excess ink so that the ink is not transferred to the non-raised portions of the image carrier. Finally, the ink from the image areas of the plate cylinder is transferred to the substrate under the impression cylinder [179].

![Figure 2.24: Schematic of flexography printing process.](image-url)
2.5.2.2 Gravure Printing

The basic schematic of a gravure printing process is shown in Figure 2.25. A typical gravure printer consists of an engraved cylinder as image carrier, impression roller, doctor blade and ink pan. The desired image is engraved onto the gravure cylinder. As the gravure cylinder rotates, the ink is transferred from the ink pan onto the surface of the cylinder filling the engraved cells. The excessive ink on the non-engraved portions of the gravure cylinder is then wiped off using the doctor blade. Finally, the impression roller transfers the ink from the cells onto the substrate. The “roll-to-roll” gravure printing is known as a robust, high speed and high quality printing process that uses low viscosity inks [179].

![Figure 2.25: Schematic of gravure printing process.](image)

2.5.2.3 Screen Printing

Screen printing is a process in which the image carrier is not in direct contact with the substrate. Figure 2.26 shows a schematic of the screen printing process. The printer consists of a screen printing plate or mesh and squeegee. Typically, the squeegee is made of rubber or polymeric raw materials. The screen printing
plate consists of a frame that holds the screen mesh and stencil which is the image carrier. A common frame material used is aluminum which is known for its light weight, hardiness, and ease of cleaning. The screen or mesh is composed of screen fabric which is a veil like material composed of metal, fabric, plastic, or other type of material depending on the ink and screen’s functionality. The stencil can be made using different processes, electronically, or photographically, depending on its purpose. The screen mesh and stencil materials are highly dependent on the type of solvents and cleaning agents to be used during printing. The ink is deposited on top of the screen mesh and it is swept from one side of the screen to the other side using a squeegee with a defined force and pressure. The ink passes through the screen mesh and is transferred onto the substrate as the squeegee is stroked across the mesh. This process is very fast and can be performed at room temperature. Screen printable inks have a high viscosity (0.5-50 Pa s); therefore, only the ink under pressure passes through the screen minimizing the amount of ink required. When compared with other methods of printing such as inkjet and gravure, there is relatively less ink spreading in this process that plays an important role in the prevention of electrical short circuits in printed lines. This type of printing also provides thicker film thickness when compared with other methods of printing [180].

Figure 2.26: Schematic of screen printing process.
2.5.2.4 Inkjet Printing

In contrast to flexography and gravure printing techniques, inkjet printing is a non-impact printing technology. This printing process does not require any physical image carrier or mask. Inkjet printers are subdivided into two main categories: continuous inkjet and drop-on-demand inkjet. Figure 2.27(a) shows the schematic of a continuous inkjet printer which is working based on an electronically controlled continuous stream of ink. In this type of inkjet printer, the stream of ink is deflected using a voltage source in the non-image areas consequently recycling the deflected ink back to the printing system. The drop-on-demand inkjet printing system, however, generates ink only in image areas. This type of inkjet printers usually employs two approaches to generate drop-on-demand ink drops: piezoelectric (Figure 2.27(b)) or thermal (Figure 2.27(c)). In the piezoelectric inkjet printer, electric potentials are used to bend in and out a piezoelectric material causing the ink drops to be pushed in and out of the nozzles. In the thermal inkjet printer, a vapor bubble, created due to the vaporization of the ink, is used to push the ink out of the nozzles [179].

2.5.3 Challenges in Printed Electronics

The potential strengths of PE to generate flexible, low cost, and environmentally friendly products can revolutionize the electronics industry. However, like any other technology, PE faces several challenges, which are needed to be addressed for future PE applications. The main challenge of this industry, when compared to the current silicon based manufacturing technology, is to achieve nanoscale production capabilities along with proper device functionality. Printing is known as a microscale manufacturing process, whereas the electronic industry requires nanoscale feature sizes. Some of the other patterning issues that are crucial to include: (a) proper registration for multi-layered devices, (b) adaptation of design rules, (c) standard processing of printed electronic materials with optimum functional properties and (d) attaining
admissible yield.

2.6 Summary

This chapter provided a brief background and introduction to SERS based detection systems, touch sensors, energy harvesters. This was followed by an introductory
discussion about PE, a relatively new method of fabricating electronic devices, as well as the need for implementing this manufacturing technique, some of the challenges associates with PE and the different types of printing.
CHAPTER III

VAPOR-PHASE DETECTION OF EXPLOSIVE USING SERS

3.1 Introduction

Detection of explosive compounds such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) have been continuously researched throughout the history of the manmade wars [25, 26]. Physical probing based methods, typically used to clear landmines, are often labor intensive and time consuming. Moreover, these methods often confront problems due to other metal debris in the minefield, thereby resulting in false positives. The detection of the vapors of the explosive compounds is thus a better solution to overcome the drawbacks associated with physical probing methods. DNT is known to be more concentrated in the vapor phase, when compared to TNT [6]. Therefore, the development of new methods that can be employed for the detection of explosive organic compounds in the vapor phase is important.

Various sensing techniques such as surface acoustic wave (SAW) sensors [29, 181, 182], luminescence based sensors [30, 183, 184], refractive index (RI) based optical sensors [185, 186, 187], cantilever sensors [28, 188], quartz crystal microbalance (QCM) sensors [31, 189], electrochemical sensors [27, 190, 191, 192] and optofluidic ring resonator sensors [193] and have been used for the detection of DNT vapors. However, these methods have some disadvantages such as low sensitivity, low detection specificity and the need for elevated working temperatures. Raman spectroscopy (RS), which is a rapid, sensitive and low temperature method of detection, has also been used for the detection of DNT vapors [194]. RS has been proven to be a reliable technique for the detection of various compounds due to its non-destructive nature and ability to provide signature vibrational fingerprints of target molecules.
The Raman effect, in RS, is based on the principle of excitation and inelastic scattering of photons caused by incident light striking a surface [98]. Typically, the detected signals in RS are weak because the number of photons scattered by these excitations are not sufficient, thereby resulting in lower optical efficiencies. Studies by Jeanmaire and Van Duyne [195] and Fleischmann et al. [196] have focused on enhancing the Raman effect. It was demonstrated that nanoscale metallic surfaces such as nano-pillars [197] and nano-domes [198] can enhance the Raman scattering and this phenomenon is known as surface enhancement Raman spectroscopy (SERS). The effect of incident excitation light, on the surface of a metal, causes free electrons to resonate thereby inducing electromagnetic fields. The absorbed target molecules on the metal surface will therefore be exposed by more intense electromagnetic fields, which increases the number of scattered photons [199]. The use of SERS is thus a promising solution for the rapid, highly sensitive and selective detection of explosive organic compounds.

3.2 Fabrication and Characterization of the SERS Substrate

3.2.1 Design

Figure 3.1 shows the schematic of the designed SERS substrate. This design consists of two layers, PET substrate (blue) and silver nanoparticle layer (yellow). The silver nanoparticle blocks were designed in 1 cm by 2 cm dimensions.

3.2.2 Chemicals, Materials and Sample Preparation

A transparent PET (Melinex ST 506) film from DuPont Teijin Films was used as the substrate. A conductive silver nanoparticle ink, with average particle size of 150 nm, from InkTec Inc. was used for the metallic surface of the SERS substrate. Ethanol and DNT (in powder form) from Sigma Aldrich Chemical Company were
mixed to provide a saturated solution of DNT for testing.

### 3.2.3 SERS Substrate Fabrication

One layer of silver nanoparticle ink was gravure printed on the PET substrate using a laboratory gravure press (K-Printing Proofer) from Testing Machines Inc. The printed substrate consisted of a row of 1 cm by 2 cm blocks. The printed silver nanoparticle was cured in a VWR 1320 temperature controlled oven for 20 minutes at 130 °C. Figure 3.2 shows the gravure printed SERS substrate.

A Bruker vertical scanning interferometer microscope (CounterGT) was used to measure the thickness and roughness of the printed silver nanoparticle layer. Figure 3.3 shows the profilometry image of the printed silver nanoparticle film. Average thickness of ∼900 nm (Figure 3.3(a)) and root mean square (RMS) roughness of ∼150 nm (Figure 3.3(b)) were measured for the printed film.

### 3.3 Experimental Procedure

The experiment setup for transferring the DNT vapor onto the printed SERS substrate is shown in Figure 3.4. Initially, 1 ml of the DNT solution was deposited
onto a wad of steel wool. The steel wool was then inserted into a heated copper pipe (inner diameter of 10 mm). The temperature of the copper pipe was set to 80 °C using a Staco variable autotransformer (3PN 1010) and a wraparound heating
Nitrogen carrier gas was then blown through the heated pipe. The printed substrate was held at the outlet of the copper pipe for 60 seconds.

Figure 3.4: Experiment setup for transfer of DNT vapor onto SERS substrate.

Figure 3.5 shows the experiment setup for the SERS measurement. A laser source in the near infrared region with a wavelength of 785 nm was used to excite the sample using a Raman probe (Inphotonics Inc.) with an integration time of 3 seconds at 300 mW. A spectrometer (QE 65000 Ocean Optics, 7801100 nm) was employed to obtain the Raman spectra through the collection fiber of the Raman probe. The Raman spectra were then analyzed using Spectra Suite software (Ocean Optics) for the Raman signature spectra of the target molecules.

3.4 Results

3.4.1 SERS Response to DNT

Initially, the Raman spectra of DNT solution and vapor on bare PET were measured as reference signals. Then, the Raman spectra of DNT solution and vapor on the printed SERS substrate were obtained. Figure 3.6 shows the comparison of the
Raman spectra of DNT solution (Figure 3.6(a)) and vapor (Figure 3.6(b)) on the printed SERS substrate as well as the spectra on bare PET. The Raman spectrum yielded a strong peak at 1350.13 cm\(^{-1}\), which corresponds to NO\(_2\) stretching modes in the DNT molecule and can be used as a finger-print for the detection of DNT [200].

The enhancement factor (EF), which is defined as a comparison between the intensities of the Raman peaks obtained with and without the use of metallic nanoparticles, under similar test conditions, was calculated. An EF of three and four for the peaks at 1350.13 cm\(^{-1}\) was obtained for the SERS based response of the printed SERS substrate toward DNT solution and vapor, respectively, when compared to target molecules adsorbed on bare PET. The obtained enhanced SERS response can be considered as the result of intense electromagnetic field caused by the “hot-spots” created by the agglomeration of the printed nanoparticles [201]. The distance of the target molecule from the nanoparticles plays an important role in the intensity of Raman spectrum. Placement of the analyte molecules within these regions causes SERS enhancement. In this phenomenon, it is important to obtain accurate control over various parameters such as shape, size, and crystallinity of the nanoparticles, as well as the distance between the nanoparticles. In other words, the intensity of the electromagnetic field
Figure 3.6: Comparison of Raman spectra obtained for DNT (a) solution and (b) vapor on bare PET versus printed SERS substrate using 785 nm excitation.

depends on the size of “nanogaps” between the printed nanoparticles which is directly related to the nanoparticle dimension. Decreasing the size of these nanogaps can be achieved by decreasing the size of nanoparticles which in turn increases the intensity
of the Raman signals [202].

The results obtained show the efficiency of the gravure printed SERS substrate to be used in applications for the detection of DNT, which is known as the most common nitro-aromatic compound in buried landmines and other explosives [6]. The response of the printed SERS substrate also shows that it can be employed for the detection of explosive organic compounds in both aqueous and gaseous states. Therefore, the printed SERS substrate is bound to have substantial effects in medical detection, biological and chemical warfare detection, as well as several security applications.

3.4.2 Effect of Temperature on SERS Response

Temperature is one of the key control variables in vapor phase detection of explosives. Even though high temperature would increase the vapor pressure of explosives, resulting in larger SERS intensity, thermal degradation of the material occurs at high temperatures, which complicates the detection process [81]. In order to investigate the effect of temperature on the intensity of the Raman spectrum, the printed SERS substrate, which was exposed to DNT vapors, was heated from 25 °C to 65 °C, in steps of 10 °C, using a hot plate. Figure 3.7 shows the response of the printed SERS substrate toward varying temperatures. It was observed that the intensity of the Raman spectrum decreased by 85% as the temperature was increased from 25 °C to 65 °C. The effect of temperature on the intensity of the Raman spectra has been studied by Xie et al. [203] in which the decrease in the intensity of the Raman spectrum with increasing temperature is attributed to an increase in the optical absorbance of the target molecule at the frequencies involved in the Raman process. The results obtained show that the vibration of the surface plasmon changes with respect to the temperature, which in turn affects the incident radiation frequency dependence of the SERS response. In another words, the vibrational energy of the molecules will increase as the temperature increases thereby reducing the bonding force between the
molecules; thus decreasing the intensity of the Raman spectrum [204].

![Figure 3.7: Raman spectra of DNT vapor on SERS substrate heated from 25 °C to 65 °C, in steps of 10 °C using a hot plate.](image)

### 3.4.2.1 Effect of Bending on SERS Response

Using flexible substrate for development of SERS substrate enables us to investigate the effect of bending on the intensity of the Raman spectrum. Therefore, the effect of bending, on the intensity of the Raman spectrum, was investigated by bending the SERS substrate to different radii of curvatures (3.4 cm, 2.1 cm and 1.6 cm), while collecting Raman spectra. Figure 3.8 shows the response of the printed SERS substrate toward varying bending angles. It was observed that the intensity of the Raman spectrum increased by around 100%, 200%, and 300% when compared to the Raman intensity of the flat SERS substrate, for the peak at 1350.13 cm\(^{-1}\). While bending, the nanoparticles come closer as a result the number of hot-spots increases. This creates a stronger electromagnetic field which can be attributed to the enhancement
in the intensity of the Raman spectrum. These results demonstrate that bending the substrate can be an advantage in the detection of the target molecules.

![Effect of Bending of the Substrate on SERS Response of 2,4-Dinitrotoluene (DNT)](image)

Figure 3.8: SERS response of DNT vapor on silver nanoparticle film at different bending angles.

### 3.5 Summary

A SERS substrate was successfully designed and fabricated by gravure printing silver nanoparticle ink on flexible PET. The feasibility of the printed substrate to be used as a SERS substrate for the detection of explosive materials such as DNT was demonstrated. An enhancement factor of three and four for the peaks at 1350.13 cm\(^{-1}\) was obtained for the SERS based response of the printed SERS substrate toward DNT solution and vapor, respectively, when compared to target molecules adsorbed on bare PET. The effect of temperature on the intensity of Raman spectra was also examined. An 85% decrease in the Raman intensity was observed at 65 °C when compared with the intensity of Raman spectrum at 25 °C. The effect of bending on the SERS response was also investigated. The intensity of the Raman spectrum was
increased as the SERS substrate was bent to different radius of curvature. Further research is underway for the development of a gravure printed SERS substrate using different substrates such as paper to be used in hand-held SERS based systems for the detection of a wider range of bio/chemicals. Moreover, the fabricated SERS substrates have the promising potential to be used as a cost-effective substitution in commercialized SERS detection applications.
4.1 Introduction

User interfaces of electronic devices have been transitioning from old-fashioned button-type controls to embedded touch pads during the last few decades. This trend of employing touch pads as part of the built environment has resulted in an inevitable demand for the fabrication of flexible touch sensitive devices. Touch sensors are devices which often provide a binary output signal that indicates whether a contact has been made or not with an object, regardless of the magnitude of the contacting force. Touch sensitive devices are typically manufactured using conventional silicon based processes which are often expensive and fabricated on rigid substrates [48, 49, 205, 206, 207]. Moreover, most of the used configurations do not provide the high flexibility and conformability, required for various touch sensing applications, thereby limiting their application areas. A continuous layer-on-layer configuration is envisioned as a promising approach that will overcome the drawbacks associated with conventional touch sensing systems. The development of fully flexible and conformal touch sensors, due to the availability of diverse manufacturing materials and the rapid development of modern fabrication techniques, is thus poised to have a significant impact on the modern society.

Researchers have utilized different transduction mechanisms such as piezoelectric [38, 39, 40, 208, 209], capacitive [41, 42], resistive [43] and optical [44] for fabrication of touch sensing devices. The main disadvantage of capacitive based touch sensors is that their accuracy depends on the capacitance of the person who touches them. Resistive based touch sensors suffer from poor durability when compared to
other technologies. Optical based sensors have lower resolutions than other technologies and surface obstruction can cause a false touch. Among these, the piezoelectric technology has generated significant interest due to its accuracy and capability to measure dynamic events, irrespective of the material of the object which comes in touch with the sensor. This mechanism has been widely used especially for applications in sensors, actuators, and energy harvesters [210, 211, 212].

Over the last decade, a steady and considerable effort has been directed towards the development of printed electronics using conventional printing technologies. To name a few, organic thin film transistors (OTFTs) using inkjet printing [213, 214, 215], flexible displays by means of screen printing [216, 217, 218] and electrochemical sensors by rotogravure printing [219, 220]. The use of printing technologies overcomes some of the drawbacks associated with conventional silicon technology, which involves high-vacuum and high-temperature deposition processes along with sophisticated photolithographic patterning techniques [221]. The advantages of printing include improved cost efficiency, reduction of material wastage during fabrication, flexibility in the substrate and low manufacturing temperatures. Even though the screen printing method has been used to fabricate piezoelectric touch sensors, the top electrodes are often printed on a separate substrate and are bonded to the final device to avoid short-circuit between the electrodes due to pinholes caused by the porous nature of the piezoelectric layer [222]. It is envisioned that the problem of pinholes can be overcome by optimizing the screen printing process and thus reducing the roughness of the printed bottom electrode. Moreover, this enables the direct printing of top electrodes onto the piezoelectric layer.

Both plastic and paper could play an important role in the future of light weight and flexible sensors. Plastic offers the advantages of high smoothness, transparency and low porosity. Even though plastic is not very amenable to the use of different solvents, it has been one of the main materials used in conventional flexible electron-
ics [180, 223]. In comparison to plastic, paper is more temperature resistant and renewable [224]. Currently, paper is the material of choice for many products used on a daily basis, and therefore, the fabrication of sensors on paper may open new market opportunities for PE and the paper industry. The ability to produce flexible touch sensors on PET and paper enables them to be placed conformably on different form factors and surfaces, where spacing or shape would prohibit the placement of a rigid conventional sensor.

In this work, the conventional screen printing technology has been used to fabricate a fully printed and flexible piezoelectric-based touch sensor on PET and paper substrates. Finite element analysis was used to investigate the response of the touch sensor towards various force loads. A laboratory scale screen printer was used to deposit bottom and top electrodes using silver (Ag) flake ink. Polyvinylidene fluoride (PVDF) ink was employed for screen printing of piezoelectric layers. Different layers of the fabricated touch sensor were characterized. Characterization of all different fabricated layers has been performed. Also, the capability of the fabricated devices to be used as a both touch sensor and force sensor has been investigated.

4.2 Piezoelectricity

Piezoelectricity is the ability of certain types of materials to generate a temporary electrical charge displacement due to a mechanical strain input (direct piezoelectric effect), or conversely produce a mechanical strain due to application of an electric field (inverse piezoelectric effect). This electromechanical behavior can be described using constitutive equations,

\[ \delta = \frac{\sigma}{Y} + dE, \quad (4.1) \]
\[ D = \varepsilon E + d\sigma \quad (4.2) \]
where $\delta$ is the strain, $\sigma$ is the stress, $Y$ is the modulus of elasticity (Young’s modulus), $d$ is the piezoelectric strain coefficient, $D$ is the electrical displacement (charge density), $\epsilon$ is the dielectric constant of the piezoelectric material, and $E$ is the electrical field. As shown in Eqs. 4.1 and 4.2, the amount of generated electrical charge displacement (in direct piezoelectric effect) or mechanical strain (in inverse piezoelectric effect) is proportional to the input strain or electric field, respectively. The piezoelectric effect was first experimentally demonstrated in 1880 by Pierre and Jacques Curie who observed electrical charge generation in quartz [225]. Later in 1881, the inverse piezoelectric effect was mathematically predicted by G. Lippman [226].

Since the piezoelectric materials exhibit anisotropic behavior, a set of subscripts $ij$ is used to distinguish between various possible scenarios based on the orientation of the polarization ($i$) and direction of the applied force ($j$). For example, the $d_{31}$ mode means that the electric field direction is perpendicular to the input strain direction while the $d_{33}$ mode means that the electric field direction is parallel to the input strain direction. Although the piezoelectric coefficients of PZT and PVDF are commonly higher in the 33-mode, it is generally more favorable to use this material in the 31-mode, due to the mechanics of bending structures and large lateral/vertical dimension ratios in practical devices. Therefore, 31-mode bending beam and diaphragm sensors and actuators are the most frequently found structures in the literature, and they are shown to provide a very effective electromechanical conversion mechanism providing either high actuation range or high sensitivity [38, 46, 48, 49].

4.3 Design of Touch Sensor

A schematic of the touch sensor is shown in Figure 4.1. The sensor module consists of a $4 \times 4$ sensor array, with each sensor having a piezoelectric layer sandwiched between the top and bottom electrodes. Each sensor has top and bottom electrode with a dimension of $4 \times 4 \text{ mm}^2$ and a piezoelectric layer with dimension of $6 \times 6 \text{ mm}^2$, ...
thereby resulting in a capacitive area of $4 \times 4 \text{ mm}^2$. The sensors were designed with a spacing of 6 mm and 500 µm wide interconnecting lines.

Figure 4.1: Schematic of the $4 \times 4$ sensor array.

4.3.1 COMSOL Simulation of Touch Sensor

COMSOL Multiphysics has been used for simulation of the designed touch sensor shown in Figure 4.1. COMSOL Multiphysics is a simulation software for modeling and solving multiphysics problems based on partial differential equations. The software works based on the finite element method (FEM) in which a variety of numerical solvers are used to run the finite element analysis using adaptive meshing of the model. In COMSOL, the user can define physical quantities such as material properties based on which set of partial differential equations will be complied to represent and analyze the generated model. From various built-in modules in COMSOL, Structural Mechanics and Piezoelectric Devices were used for simulation of the designed touch sensor device.

4.3.1.1 3-D Model

The 3-D model of the touch sensor consisting of substrate, bottom electrodes, piezoelectric layer, and top electrodes was created in COMSOL Multiphysics 5.0 as shown in Figure 4.2. PET was used as the substrate, Ag was used for bottom and
top metallization layers, and PVDF was used as the piezoelectric material.

![3-D model of the touch sensor generated in COMSOL Multiphysics.](image)

**Figure 4.2:** 3-D model of the touch sensor generated in COMSOL Multiphysics.

A Fixed Constrained boundary condition was applied to the bottom face of the substrate, while other faces were free to move. In order to use $d_{31}$ mode of the device, a Floating Potential and Ground were applied to the top and bottom faces of the PVDF layer, respectively, while all other faces of the piezoelectric layer were kept at a Zero Charge constraint. A Boundary Load was applied as an input to the top face of the PVDF layer to induce strain. The created model was then meshed using *Physics-Controlled* mesh feature with fine element size as shown in Figure 4.3.

![Meshed 3-D model.](image)

**Figure 4.3:** Meshed 3-D model.
4.3.1.2 Stationary Analysis

The piezoelectric response of the model was investigated using a Stationary analysis. A Parametric Sweep was employed to apply forces ranging from 0.2 N to 1.4 N, in steps of 0.2 N, to the sensor in the z-direction and its output voltage was monitored. Figure 4.4 shows the voltage response of the sensor for varying applied forces. The simulation result shows a linear relation between the touch sensor response and applied force with sensitivity of 1.05 V/N. This sensitivity depends on the characteristics of the simulated PVDF layer.

![Figure 4.4: Voltage response of piezoelectric-based touch sensor for varying forces obtained from COMSOL Multiphysics® 5.0.](image)

4.4 Fabrication and Characterization of the Touch Sensor

4.4.1 Materials

Flexible PET film (Melinex ST 329) from DuPont Teijin Films and coated paper (NB-RC3GR120) from Mitsubishi were used as two different substrates. Conductive Ag flake ink (Electrodag 479SS) from Henkel was used for the metallization layers. PVDF ink (SOLVENE™), known for its mechanical flexibility along with stable
piezoelectric properties, was used for the piezoelectric layer. Other materials such as two-dimensional transition metal oxides (TMOs) and two-dimensional molybdenum disulfide (MoS$_2$) have been also used in piezoelectronic applications [227, 228]. These materials can be easily formed on a PET substrate.

### 4.4.2 Sensor Fabrication Process

The fabrication of the touch sensor was performed at the Center for the Advancement of Printed Electronics (CAPE) in Western Michigan University using a semi-automatic screen printer (AMI MSP 485) from Affiliated Manufacturers Inc. The design of the touch sensor was created using Adobe Illustrator software (Figure 4.5). The design consists of the top and bottom electrodes (Figure 4.5(a) and Figure 4.5(c)) as well as the piezoelectric layer (Figure 4.5(b)).

![Touch sensor design](image)

**Figure 4.5:** Touch sensor design consisting of (a) bottom electrodes, (b) piezoelectric layer and (c) top electrodes, created in Adobe Illustrator software for screen fabrication.

The fabrication process of the printed sensor is shown in Figure 4.6. A 325 stainless steel mesh count screen (Microscreen®) with 28 µm wire diameter, 22.5° angle
and 12.7 µm thick MS-22 emulsion was used. Initially, the substrate was cleaned using isopropanol alcohol (IPA). Then, a 4×4 array of conductive electrodes (bottom electrodes) was screen printed on PET and paper (Figure 4.6(a)). The printed layer was kept at room temperature for 10 minutes and then cured for 20 minutes in a VWR 1320 temperature controlled oven at 120 °C. Then, two layers of PVDF were screen printed onto the deposited bottom electrode (Figure 4.6(b)). Each deposited PVDF layer was cured in thermal oven at 130 °C for 5 hours to remove the solvents and enhance recrystallization of PVDF. Finally, a 4×4 array of the top electrodes was screen printed using Ag flake ink (Figure 4.6(c)). The printed Ag was then cured for 20 minutes in the oven at 120 °C. The fabricated touch sensors on PET and paper are shown in Figure 4.7.

4.4.3 Polarization of the PVDF Layer

For achieving a piezoelectric response, the randomly ordered and dipole containing nano-crystallites that are embedded in an amorphous constellation must be aligned vertically to the sensor electrodes. PVDF is normally polarized by applying an electric field, typically between 60 to 200 V/µm across its layer [229]. Figure 4.8 shows the polarization setup. The alignment of the dipoles, in the material, can be improved.
by heating the piezoelectric layer during the poling process and cooling it down to room temperature. By heating the piezoelectric material, it loses its polarity and a new poling direction appears along the applied voltage. An air gun was used to heat the printed touch sensor. The heated sensor was poled by applying an electric field of 80 V/µm for 1 hour. The sensor was then cooled down before the external voltage was removed.

4.4.4 Characterization of the Device

The characteristics of the substrates are summarized in Table 4.1. The paper substrate had a higher surface energy, measured using a goniometer (First Ten Angstroms FTA-2000), when compared to the PET substrate. The thickness and roughness of the substrates were measured using a Bruker vertical scanning interferometer microscope (CounterGT). It was observed that PET was relatively thin thus increasing its flexibility. In addition, PET has a smoother surface which reduces the chance of discontinuity in the printed layers and consequently, increases the yield. In comparison with the PET, paper is considerably rougher which provides better ink adhesion.
However, unlike PET, paper is more absorptive which can reduce the amount of ink spreading after printing.

Table 4.1: Summary of characteristics of PET and paper substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Surface energy [dynes/cm]</th>
<th>Thickness [µm]</th>
<th>Roughness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>46.7</td>
<td>54±1</td>
<td>94</td>
</tr>
<tr>
<td>Paper</td>
<td>53.9</td>
<td>177±12</td>
<td>175</td>
</tr>
</tbody>
</table>

A Bruker vertical scanning interferometer microscope (CounterGT) was used to characterize the thickness and roughness of the conductive bottom electrode as well as the piezoelectric layer. Figure 4.9 shows the profilometry images of the printed bottom Ag electrode on PET and paper substrates. The average thickness of the bottom electrode on PET and paper substrates was measured to be 12.1 µm (Figure 4.9(a)) and 9.3 µm (Figure 4.9(b)), respectively. The smaller thickness of the printed Ag layer on paper substrate can be attributed to its absorptive property, when compared to PET. The root mean square (rms) roughness of the calendered Ag layer on PET
and paper substrates was 0.6 µm and 0.9 µm, respectively. The smaller surface roughness of the printed Ag layer on PET substrate is due to its smoother surface, when compared to the paper substrate. The relatively low roughness of the printed bottom electrodes plays an important role in the successful fabrication of the device. Figure 4.10 shows the profilometry images of the printed PVDF layer over the Ag bottom electrode on PET and paper substrates. The average thickness of the PVDF layer on PET and paper substrates was measured to be 10.5 µm (Figure 4.10(a)) and 9.3 µm (Figure 4.10(b)), respectively. The rms roughness of the printed PVDF layer on PET and paper substrates was 0.4 µm and 0.6 µm, respectively.

![Profilometry images](image)

Figure 4.9: Profilometry scan of screen printed Ag electrode on (a) PET and (b) paper substrates illustrating an average thickness (ΔZ) of 12.1 µm and 9.3 µm, respectively.

Four-point probe measurement were used to measure the sheet resistance of the printed bottom electrodes on PET and paper substrates. Sheet resistance of around 48 mΩ/□ and 60 mΩ/□ were measured for printed Ag electrodes on PET and paper substrate, respectively. Lower sheet resistance of the Ag electrodes on PET substrate is due to the thicker printed Ag layer on PET substrate as well as the lower roughness of the PET substrate when compared to paper. Lower surface roughness of the
substrate provides more uniform printed conductive ink which in turn results in lower sheet resistance.

4.4.5 Crystallography of PVDF Film

PVDF is a semi-crystalline polymer with four phases, $\alpha$, $\beta$, $\lambda$, and $\gamma$. Among these phases, the $\beta$-phase has the largest effective dipole moment [230]. Therefore, in order to achieve high piezoelectricity, $\beta$-phase crystallinity should be formed in the material. An X-ray diffraction (XRD) measurement was performed to characterize the crystalline contents of the printed PVDF film, both before and after the curing process. XRD patterns were obtained on a Bruker D8 DaVinci diffractometer equipped with Cu X-ray radiation ($\lambda=1.5406 \text{ Å}$) operating at 40 kV and 40 mA. Peak intensities were obtained by counting with the Lynxeye detector, for every 0.02° at sweep rates of 0.5° $2\theta$/min.

The XRD measurements were performed for four different samples: (1) bare PET, (2) uncured PVDF on PET, (3) PVDF on PET (cured at 90 °C), and (4) PVDF on
PET (cured at 130 °C). Figure 4.11 illustrates the XRD spectra of these samples. The XRD spectra of the bare PET (green), shows that the peaks at \(2\theta = 12.6^\circ\) and \(2\theta = 26^\circ\) are related to the PET substrate. The peak at 19.9° is assigned to the \(\beta\)-phase crystallinity of PVDF. The inset shows the XRD spectra of samples (2), (3), and (4) at \(2\theta = 19.9^\circ\). It was observed that the printed PVDF layer forms the \(\beta\)-phase during the curing process. In addition, the higher curing temperature of 130 °C resulted in a higher intensity \(\beta\)-phase formation, when compared with the 90 °C curing process. The XRD based results thus confirm that the printed PVDF layer have a predominantly \(\beta\)-phase structure.

![XRD spectra](image)

Figure 4.11: XRD spectra of bare PET, uncured PVDF on PET, PVDF (cured at 90°C) on PET, and PVDF (cured at 130°C) on PET (Inset: XRD spectra in the range of 18.5° < \(2\theta < 21.5^\circ\)).

4.5 Results

4.5.1 Capacitance-Voltage Analysis

Capacitance-Voltage (C-V) measurements at varying frequencies were made before and after polarization to check the effect of polarization on the C-V response. For C-V measurements, precision LCR meter (Agilent E4980A) controlled by a program
developed in LabVIEW was used. The block diagram of the experiment setup used for these measurements is shown in Figure 4.12.

![Figure 4.12: Block diagram of the experimental setup used for capacitance-voltage analysis.](image)

Figure 4.12 shows the measured capacitance of the PET based touch sensor for varying frequencies (100 Hz to 900 kHz), before (blue) and after polarization without (black) and with (red) heating the touch sensor. The average capacitance values were measured to be 301 pF, 320 pF, and 329 pF for the unpolarized and polarized devices with and without heating, respectively. The higher average capacitance of the device is due to more dipoles aligned in the piezoelectric material, as a result of polarization while heating the touch sensor, which in turn provides higher piezoelectricity [222]. Even though an average change of 28 pF was obtained for the polarized PVDF, with an applied electric field of 80 V/µm, a larger change can be obtained by applying higher electric fields across the film during the poling process.

### 4.5.2 Touch Sensing Experiment

After polarization of the printed piezoelectric layer, the voltage response of the touch sensor was investigated. Figure 4.14 shows the response of a single sensor in the 4×4 array on the PET and paper substrates while it was repeatedly touched by a human finger. Voltage peaks, as high as 1.84 V and 0.22 V, were observed due to the forces applied on the PET and paper substrates, respectively. Variations in the voltage peak amplitudes were observed due to inconsistency in the forces applied.
by the finger. Smaller voltages in the response of the sensor, printed on the paper substrate, are due to the higher paper thickness, which reduces the effective dipole alignment in the piezoelectric layer, during the poling process. However, it is worth noting that the voltage response of the sensor printed on the paper substrate is comparable to touch sensors fabricated using conventional silicon technology on non-flexible substrates [211, 231].

A block diagram of the experiment setup for testing the capability of the fabricated touch sensor is shown in Figure 4.15. It consists of the printed touch sensor (Figure 4.15(a)), impedance converter (Figure 4.15(b)) and LEDs (Figure 4.15(c)). Touching the individual sensor generates a small amount of energy, which is difficult to measure. Therefore, an impedance converter was used to amplify the sensor signal. The impedance converter forwards the input voltage to the output voltage but amplifies the signal power. In the ideal case the input current should be close to 0 A. Hence, an operational amplifier that supports an ultra-low input current would be preferable. Figure 4.16 demonstrates the capability of the printed touch sensor to turn on LEDs corresponding to the sensor spots that were touched. The results obtained show the
Figure 4.14: Voltage response of the touch sensors on (a) PET and (b) paper upon repeated finger touches.

potential of the printed device to be used as a flexible touch interface.

4.5.3 Force Sensing Experiment

In another investigation, varying forces were applied to the fabricated sensors and their voltage responses towards different force values were studied. The experiment setup used for this testing is shown in Figure 4.17. The touch sensor was placed on the
Figure 4.15: Block diagram of the experimental setup used for touch sensing experiment.

Figure 4.16: Lightening up of LEDs due to force applied to sensing spots.

base compression plate of a motorized test stand (Mark-10 ESM 301). A digital force gauge (Mark-10 M5-200), with a vertically movable rubber-tip attachment, was used to apply varying forces ranging from 0.2 N to 1.4 N, in steps of 0.2 N. The force gauge data were collected using the MESUR™ gauge software. An oscilloscope (Digilent Analog Discovery) along with the WaveForms™ software was used for acquiring and for post-processing of the voltage response of the touch sensor.

Figure 4.18 shows the voltage response of the sensors, printed on PET and paper substrates, for the different applied forces. It was observed that the PET based touch sensor response was linear with a sensitivity and correlation coefficient of 1.2 V/N and 0.9954, respectively. A linear fitting response was also obtained for the paper
based sensor with a sensitivity of 0.3 V/N and correlation coefficient of 0.9859. Even though the responses obtained for both the simulated and practical sensors were linear in nature, the difference in the voltage amplitudes can be attributed to the fact that there are different structural characteristics between the simulated and fabricated devices. The results obtained thus demonstrate that the printed sensors can be used not only as a touch sensors but also as a force sensors.

The stability of the printed sensors was also investigated by applying a constant force load of 1.0 N to one sensor spot for 500 cycles while measuring the generated voltage signal of the sensors during each cycle. It was observed that both PET and paper based sensors showed output voltage stability of less than 18% throughout the 500 cycles of the test. Also, it was observed that the surface morphology of the printed Ag electrodes was degraded due to the repeated applied load. The stability of the printed sensors as well as the durability of the printed Ag layers can be improved by depositing an encapsulation PDMS layer over the sensing area of the sensors. The deposited PDMS layer protects the printed layers from degradation over time, thus improving the stability of the sensor.
4.6 Summary

This chapter provided a brief background and introduction to the need for fully printed and flexible touch sensing systems. A detailed account of the materials and devices to be used, and fabrication of the fully printed touch sensitive device; characterization of the printed sensor; and the experimental procedure was presented. In this work, screen printed piezoelectric-based touch sensors on flexible PET and paper substrates were successfully fabricated. The capacitive devices were fabricated using Ag and PVDF inks as the metallization and piezoelectric layers, respectively. Characterization of the substrates and various printed layers of the touch sensor were performed. The proper formation of the $\beta$-phase crystals in the cured PVDF film was investigated using XRD measurements. The effective polarization of the printed piezoelectric PVDF layer was verified using capacitance-voltage analysis. A sensitivity of 1.2 V/N and 0.3 V/N, with correlation coefficient of 0.9954 and 0.9859, was obtained for the PET and paper based printed touch sensors, respectively. Piezoelectric-voltage analysis demonstrated that the printed sensors can be used as both touch and force sensors.
sensors. The primary advantage of fabricating touch sensors on flexible substrates is the ability to fold and place the sensor on nearly any platform or to conform to any irregular surface, whereas the additive properties of printing processes allow for a faster fabrication process, while simultaneously producing less material waste in comparison to the traditional subtractive processes. It is believed that this technology has a significant potential for use in flexible electronics where light weight sensing devices can be attached conformably onto the surface to improve user-device interactions.
CHAPTER V

DEVELOPMENT OF PIEZOELECTRIC-BASED VIBRATION ENERGY HARVESTER

5.1 Introduction

In the last few decades, there has been a great interest in development of vibration-based energy harvesting devices. Research motivation in this field is due to the rapid development in the field of portable and low-power electronic systems, such as mobile systems and wireless sensors networks used in structural health monitoring applications. The ultimate goal is to use the available vibration energy in the ambient to power small electronic devices. This promising way of powering small electronic components and remote sensors has attracted researchers from different disciplines of engineering, including mechanical, electrical, and civil as well as researchers from the field of material science. If this goal is achieved, then there would be no further requirements for external power sources or periodic battery replacement. Research in this area involves understanding the mechanics of vibrating structures, the constitutive behavior of piezoelectric materials and the electrical circuit theory.

There are three basic mechanisms for converting vibration to electric energy; i) electromagnetic [50, 232, 233], ii) electrostatic [234, 235], and iii) piezoelectric [3, 236, 237] transduction mechanisms. In the last fifteen years, these transduction mechanisms have been investigated by numerous researchers for vibration-based energy harvesting and extensive discussions can be found in the existing review articles [238]. In the last decade, literature shows that piezoelectric transduction has been received more attention than the other two mechanisms for vibration-to-electricity conversion and several review articles with the focus on piezoelectric energy harvesting have been published [175, 239, 240, 241, 242, 243, 244]. Several experimental researches with
different applications of piezoelectric energy harvesting have been introduced in these review articles.

Typically, a piezoelectric vibration energy harvester (PVEH) has a cantilevered beam structure with one or two piezoelectric layers (a unimorph or a bimorph) covered by metallic electrodes. The cantilever beam is placed on a vibrating source structure and the dynamic strain induced in the piezoelectric layer(s) generates an alternating voltage output across the electrodes. In order to better understand energy harvesters, researchers have proposed various mathematical models for describing the working principles of these devices [52, 245, 246, 247, 248, 249]. A reliable mathematical model helps the designer to optimally design the energy harvester device in order to achieve the maximum power output under prescribed base excitation conditions. Although the implementation circuit attached to a piezoelectric energy harvesting for powering a real electronic circuit is more sophisticated [250], researchers usually consider a resistive load in the electrical circuit to develop a simple model for predicting the power output of the harvester for a given base motion input.

Traditionally, cantilever beam structure energy harvesters are fabricated by using conventional silicon-based technologies [53, 54, 55, 56, 57], which involves high-vacuum and high-temperature deposition processes along with sophisticated photolithographic patterning techniques. These drawbacks can be overcome by using printing techniques. The advantages of printing include improved cost efficiency, reduction of material wastage during fabrication, flexibility in the substrate and low manufacturing temperatures. Even though a steady and considerable effort has been directed towards the development of flexible electronics, there have been no reports on fully printed flexible vibration energy harvester. This has led to the research of traditional printing techniques for the manufacture of flexible vibration energy harvesters.

The energy harvesters should be able to sustain operation under harsh vibration
and shock. Fatigue and crack of the energy harvesting devices are destructive for real application. Thus, development of flexible energy harvesting devices is necessary. To the knowledge of the author, there have been no efforts reported on fabrication of fully printed and flexible energy harvesting devices. In this work, a generic model of a vibrational energy harvesting system with focus on piezoelectric transduction mechanism has been introduced. Finite element analysis has been used to analyze various design geometries of a unimorph cantilever-based PVEH, and the author has developed three generations of PVEHs. For all generations, screen printing technique has been used to deposit different layers of the device. PVEHs in different dimensions have been fabricated and tested. Details of the modeling, simulation results, fabrication process and experiment results are provided in the following sections.

5.2 Energy Harvesting from Ambient Vibration

5.2.1 Generic Model of Vibration Energy Harvester

A vibration energy harvesting device can be described as a mass-spring-damper generic model as shown in Figure 5.1 [232]. In this figure, \( z(t) \) represents the displacement of the mass from its rest position; \( y(t) \) is the absolute displacement of the frame; \( Z_0 \) is the amplitude of the mass-to-frame displacement, which is mechanically defined by the structure of the device, and \( Z_l \) is the maximum possible value of the mass displacement. Due to inertia, the mass moves relative to the frame under the input acceleration of the vibration. The generated energy is the result of work done against the damping force. The mass is attached to the frame by a spring that puts a limit on the displacement of the mass and creates a resonant spring-mass-damper system. The damping force used in this model depends on the energy conversion mechanism which may be electrostatic, electromagnetic, or piezoelectric.
The vibration in nature is assumed to be harmonic and is described as follows

\[ y(t) = Y_0 \cos(\omega t), \]  

(5.1)

where \( Y_0 \) is the source motion amplitude.

### 5.2.2 Inertia Generator Model

As mentioned above, the displacement of the mechanical system will be converted to energy through a damper. The damper’s force is proportional to \( \dot{z}(t) \) with a constant \( d \) [232]. The movement of the mass with respect to the frame can be derived from the dynamic forces on the mass as follows

\[ m\ddot{z}(t) + d_e \dot{z}(t) + k z(t) = -m\ddot{y}(t), \]  

(5.2)

where \( m \) is the seismic mass, \( d_e \) is the damping constant, and \( k \) is the equivalent spring constant. The instantaneous power is equal to the rate of change of the kinetic and strain energies plus the power dissipated (or absorbed) by the damper. Hence, in the case of no damper in the system \((d_e=0)\), all the input power will be stored in the mass-
spring system. The resonance frequency, $\omega_n$, and normalized (dimensionless) damping factor, $\zeta_e$, of the mass-spring-damper system, shown in Figure 5.1, are described using Eqs. 5.3 and 5.4, respectively

$$\omega_n = \sqrt{\frac{k}{m}} \quad (5.3)$$

$$\zeta_e = \frac{d_e}{2m\omega_n}. \quad (5.4)$$

By taking the Laplace transform of the Eq. 5.2 and normalizing it by using the resonance frequency (Eq. 5.3) and damping factor (Eq. 5.4), the transfer function from the frame motion, $Y(s)$, to the relative mass to frame motion, $Z(s)$ will be obtained as follows

$$\frac{Z(s)}{Y(s)} = \frac{-s^2}{s^2 + 2\zeta_e\omega_n s + \omega_n^2} \quad (5.5)$$

which is a second order system. By setting $s = j\omega$, the magnitude of this transfer function is given by

$$\frac{Z_0}{Y_0} = \frac{\omega_c^2}{\sqrt{(1 - \omega_c^2)^2 + (2\zeta_e\omega_c)^2}}, \quad (5.6)$$

where $\omega_c = \omega/\omega_n$. The amount of energy, $E$, dissipated in each cycle of the frame motion is equal to the work performed against the damper which can be calculated by integrating the damping force ($f_d = d_e\dot{z}$) over a full cycle as follows

$$E = \oint f_d dz = \oint d_e\dot{z} dz. \quad (5.7)$$
The steady state displacement \( z \) and velocity \( \dot{z} \) are assumed to be

\[
\begin{align*}
  z(t) &= Z_0 \sin(\omega t - \phi) \quad (5.8) \\
  \dot{z}(t) &= \omega Z_0 \cos(\omega t - \phi). \quad (5.9)
\end{align*}
\]

Substituting Eqs. 5.8 and 5.9 into Eq. 5.7, the dissipated energy per cycle \((T = 2\pi/\omega)\) becomes

\[
E = \oint d_e \dot{z} dz = d_e \int_0^{2\pi/\omega} \omega^2 Z_0^2 \cos^2(\omega t - \phi) dt = \pi d_e \omega Z_0^2. \quad (5.10)
\]

Substituting \( Z_0 \) from Eq. 5.6 into Eq. 5.10 and multiplying by the frequency \((f = \omega/2\pi)\), the power dissipated in the damper will be

\[
P = \zeta_e \omega^3 Y_0^2 \omega^3 m \frac{\omega m}{[1 - \omega_n^2]^2 + [2\zeta_e \omega_n]^2}. \quad (5.11)
\]

The power versus angular frequency of vibration \((\omega)\) is plotted in Figure 5.2 using MATLAB software. In this simulation, the dimensionless resonance frequency, \(\omega_n\), is considered to be 1. Figure 5.2 shows that for a given \(\zeta_e\), the maximum power can be generated at the resonance frequency \((\omega_n)\) of the generator (i.e., at \(\omega_c = 1\)) and is equal to

\[
P = \frac{Y_0^2 \omega_n^3 m}{4\zeta_e}. \quad (5.12)
\]

Eq. 5.12 predicts that the power extracted can be increased without limit by decreasing the damping factor at the resonance frequency \((\omega_c = 1)\) which means that as the damping factor approaches zero, the generated power by the system would approach infinity. This conclusion is mathematically correct since no limit is considered on the internal displacement of the model and no parasitic dissipative factor such as
Figure 5.2: Frequency spectrum of power generation around the resonance frequency of the generator for various damping factors \( \omega_n = 1 \).

Air resistance is taken into account. This is physically untenable, since there must always be some positive damping (e.g. friction) to stabilize the system and enforce the second law of thermodynamics.

In order to maximize the generated power, optimal damping factor \( \zeta_{e,\text{opt}} \) can be found by solving the unconstrained optimization problem,

\[
\frac{dP}{d\zeta_e} = 0.
\]  

(5.13)

Solving this optimization problem gives

\[
\zeta_{e,\text{opt}} = \frac{1}{2\omega_c} \left| \omega_c^2 - 1 \right|
\]  

(5.14)
which means that \( \zeta_{e,\text{opt}} \to 0 \) as \( \omega_c \to 1 \). Substituting Eq. 5.14 into Eq. 5.11 results in

\[
P_{\text{max}} = \frac{\omega_c^2 Y_0^2 \omega^3 m}{4 \left| \omega_c^2 - 1 \right|}.
\] (5.15)

However, the unconstrained optimization problem given in 5.13 does not take into account any displacement limit for the mass to frame motion amplitude \( (Z_0) \) which means the maximum power in Eq. 5.15 violates physical constraints imposed on the system. In order to address this problem, the mass to frame motion is considered to be limited by \( Z_l \) which can be varied from several microns to a few millimeters, depending on the size of a typical device. Hence, the maximum generated power will be obtained by solving the constrained optimization problem,

\[
\begin{align*}
\text{maximize} & \quad P \\
\text{subject to} & \quad Z_0 = \frac{\omega_c^2 Y_0}{\sqrt{(1 - \omega_c^2)^2 + (2 \zeta_c \omega_c)^2}} \leq Z_l.
\end{align*}
\] (5.16)

The optimal point, \( \zeta_{e,\text{opt}} \), and value, \( P_{\text{max}} \), of the problem 5.16 are given by

\[
\zeta_{e,\text{opt}} = \frac{1}{2 \omega_c} \left( \frac{Y_0}{Z_l} \right)^2 \frac{1}{\omega_c^4 - (1 - \omega_c^2)}
\] (5.17)

\[
P_{\text{max}} = Y_0^2 \omega^3 m \frac{1}{2 \omega_c} \left( \frac{Z_l}{Y_0} \right)^2 \sqrt{\omega_c^4 \left( \frac{Z_l}{Y_0} \right)^2 - (1 - \omega_c^2)^2}.
\] (5.18)

At resonance frequency, \( \omega_c = 1 \), the maximum power which can be generated is

\[
P_{\text{max}} = \frac{1}{2} Y_0 Z_l m \omega^3.
\] (5.19)

So far, we have assumed that the only present damping in the system is electrical damping, \( d_e \), of the transduction mechanism. However, the more realistic case is when open circuit parasitic mechanical damping, \( d_m \), such as internal strain rate damping and external air damping, is considered in the analysis. This means the total damping...
in the system, \( d_t \), is a combination of electrical and mechanical damping,

\[
d_t = d_e + d_m. \tag{5.20}
\]

Hence, the more realistic model for the vibration energy harvester would be as shown in Figure 5.3. In this case, due to the power loss through the mechanical damping, the maximum power generated by the system would be lower than the case when no mechanical damping is considered in the analysis. By considering this practical limitation, the maximum power generated at resonance will be changed to

\[
P_{\text{max}} = \frac{m\zeta_e Y_0^2 \omega_n^3}{4(\zeta_e + \zeta_m)^2}. \tag{5.21}
\]

Figure 5.3: Schematic of vibration mass-spring-damper system considering parasitic mechanical damping.

Solving optimization problem \( dP_{\text{max}}/d\zeta_e = 0 \) gives the optimal point, \( \zeta_{e,\text{opt}} \), and
the maximum power which can be delivered to the electrical domain, \( P_{e,\text{max}} \), as

\[
\zeta_{e,\text{opt}} = \zeta_m, \quad (5.22)
\]

\[
P_{e,\text{max}} = \frac{mY_0^2 \omega_n^3}{16\zeta_m}. \quad (5.23)
\]

Eq. 5.22 illustrates that the maximum power can be delivered to the electrical domain when the damping related to the transduction mechanism is equal to the mechanical losses, meaning that the damping is balanced or tuned to one another. Eq. 5.21 can be rewritten as Eq. 5.24 where \( A = \omega_n^2 Y_0 \) is the acceleration magnitude of the input vibration. Assuming that \( A \) is constant, Eq. 5.24 shows that the output power is inversely proportional to the vibration frequency. In other words, by maintaining a constant acceleration magnitude of vibration, the output power can be increased by lowering the vibration frequency. Hence, the energy harvesting device has to be optimally designed to have the lowest resonance frequency while satisfying the fabrication process and space constraints [251]. Also, it shows that by having the frequency of the vibration source to match the natural frequency of the device, the power generated is proportional to the square of the source acceleration.

\[
P_{\text{max}} = \frac{m\zeta_e A^2}{4\omega_n(\zeta_e + \zeta_m)^2}. \quad (5.24)
\]

### 5.2.3 Piezoelectric Transduction Mechanism

Piezoelectricity can be coupled into a vibration system as a transduction mechanism to convert the mechanical motion into electricity. As discussed in Section 4.2, the electromechanical behavior of piezoelectric materials is described using constitutive
equations,

\[ \delta = \frac{\sigma}{Y} + dE, \]  
(5.25)

\[ D = \epsilon E + d\sigma \]  
(5.26)

where \( \delta \) is the strain, \( \sigma \) is the stress, \( Y \) is the modulus of elasticity (Young’s modulus), \( d \) is the piezoelectric strain coefficient, \( D \) is the electrical displacement (charge density), \( \epsilon \) is the dielectric constant of the piezoelectric material, and \( E \) is the electrical field. Since the piezoelectric materials exhibit anisotropic behavior, a set of subscripts, \( ij \) where \( i \) represents the direction of the excitation and \( j \) is the direction of the system response, is used to distinguish between various possible scenarios based on the orientation of the polarization and direction of the applied force. For example, the \( d_{31} \) (or transverse) mode means that the electric field direction is perpendicular to the input strain direction while the \( d_{33} \) (or longitudinal) mode means that the electric field direction is parallel to the input strain direction. A cross sectional view of these two modes is shown in Figure 5.4.

![Figure 5.4: Piezoelectric (a) 31 and (b) 33-modes.](image)

These two modes (\( d_{31} \) and \( d_{33} \)) are the most common modes used in piezoelectric energy harvesting devices [3, 56, 167, 252, 253]. Although the electrical/mechanical coupling for 31-mode is lower than for 33-mode, there is a key advantage to operating in the 31-mode. The 31-mode based system is much more compliant, therefore larger
strains can be produced with smaller input forces. Also, the resonance frequency is much lower for this mode. An immense mass would be required in order to design a piezoelectric converter operating in 33-mode with a resonance frequency somewhere around 120 Hz [3]. Therefore, the 31-mode of operation has been used in this project.

Another important constant of piezoelectric materials is the coupling coefficient factor, \( k_{ij} \), which represents the effectiveness with which a piezoelectric film converts mechanical to electrical energy and is a function of the piezoelectric coefficient \( (d_{ij}) \), the Young’s modulus \( (Y_{ij}) \), and the relative dielectric constant \( (\epsilon_{ij}) \),

\[
k_{ij} = \sqrt{\frac{d_{ij}^2 Y_{ij}}{\epsilon_{ij}}}.
\] (5.27)

### 5.2.4 Cantilever Beam Configuration

Typically, a piezoelectric energy harvester has a cantilever beam structure with one (unimorph) or two (bimorph) piezoelectric layers. The harvester beam is located on a vibrating host structure and the dynamic strain induced in the piezoelectric layer(s) generates an alternating voltage output across the electrodes covering the piezoelectric layer(s). The cantilever beam configuration is a relatively compliant structure, which results in the lowest stiffness for a given size and provides a relatively high average strain for a given force input, which in turn results in more power generation [3]. Various configurations such as unimorph, bimorph, and triple layer have been reported for the cantilever-mounted piezoelectric benders [237, 241, 254]. For the purpose of this dissertation, the 31-mode unimorph cantilever was used. In this configuration, one piezoelectric layer is sandwiched between two electrode layers mounted onto a substrate as shown in Figure 5.5.
5.2.4.1 Resonance Frequency of a Unimorph Cantilever

From the Bernoulli-Euler equation, the natural frequencies of vibration for a cantilever beam with one end clamped and the other end free can be written as

\[ f_i = \frac{\nu_i^2}{2\pi} \sqrt{\frac{EI}{m_l}}, \quad (5.28) \]

where \( \nu_i \) is a coefficient related to boundary conditions (and is equal to 1.875104 for the fundamental mode), \( l \) is the length of the beam, \( EI \) is the bending stiffness and \( m_l \) is the mass per unit length of the cantilever beam [255].

Figure 5.6 shows the schematic diagram of unimorph cantilever PVEH consisting of substrate, bottom electrode, piezoelectric layer, and top electrode. \( z_1, z_2, z_3, \) and \( z_4 \) are the coordinates of the lower surfaces of the substrate, the bottom electrode, the piezoelectric layer, and the top electrode, respectively. \( z_5 \) is the coordinate of the upper surface of the top electrode.

In this configuration, 1 and 3 represent the \( x- \) and \( z- \) axes, and the poling direction is considered to be parallel to the \( z- \) axis. The dash line shows the mid-plane position of the substrate, and the neutral plane is located at an unknown distance \( z_0 \) from the central plane of the substrate. Having no axial load, the integral of all stresses across the beam’s cross-section should be zero. Based on this fact and using constitutive
equation for the piezoelectric material, \( z_0 \) can be described as [249]

\[
z_0 = \frac{Y_e h_{e1} (h_{e1} + h_s) + Y_p h_p (h_p + 2h_{e1} + h_s) + Y_s h_{e2} (h_{e2} + 2h_p + 2h_{e1} + h_s)}{2(Y_s h_s + Y_e h_{e1} + Y_p h_p + Y_e h_{e2})}. \tag{5.29}
\]

Hence, \( z_1, z_2, z_3, z_4, \) and \( z_5 \) will be calculated as

\[
\begin{align*}
z_1 &= -z_0 - \frac{h_s}{2} \\
z_2 &= \frac{h_s}{2} - z_0 \\
z_3 &= h_{e1} + \frac{h_s}{2} - z_0 \\
z_4 &= h_p + h_{e1} + \frac{h_s}{2} - z_0 \\
z_5 &= h_{e2} + h_p + h_{e1} + \frac{h_s}{2} - z_0
\end{align*}
\tag{5.30}
\]

For the cantilever beam structure shown in Figure 5.6, \( EI \) and \( m_l \) can be calculated as

\[
EI = w \left[ \frac{Y_s(z_2^3 - z_1^3) + Y_e(z_3^3 - z_2^3) + Y_p(z_4^3 - z_3^3) + Y_e(z_5^3 - z_4^3)}{3} \right], \tag{5.31}
\]

\[
m_l = w(\rho_s h_s + \rho_e h_{e1} + \rho_p h_p + \rho_e h_{e2}) \tag{5.32}
\]

where \( \rho_i \) is the uniform density of each layer in the structure and \( w \) is the width of the beam [249]. Therefore, the first mode natural frequency of the unimorph cantilever
beam can be calculated by substituting 5.31 and 5.32 into 5.28,

\[ f_n = \frac{0.323}{L^2} \left( \sqrt{ \frac{Y_s(z_3^3 - z_1^3) + Y_e(z_3^3 - z_2^3) + Y_p(z_3^3 - z_3^3) + Y_e(z_3^3 - z_4^3)}{\rho_s h_s + \rho_e h_{e1} + \rho_p h_p + \rho_e h_{e2}}} \right) \]  \hspace{1cm} (5.33)

where the \( z_i \)s are given as 5.30.

Ideally, a cantilever beam with a low resonance frequency is desirable for vibration energy harvesting. Based on Eq. 5.33, one approach to decreasing \( f_n \) is to increase the length (\( l \)) of the beam. However, mechanical damping (\( \zeta_m \)) increases as a result of increasing the length. High mechanical damping results in a lower power output. Another approach is to increase the effective mass of the structure by adding a proof mass at the tip of the beam as shown in Figure 5.7.

![Figure 5.7: A unimorph cantilever beam with proof mass.](image)

By adding a proof mass at the tip of the beam, the reduced resonance frequency \( (f'_n) \) will be described as

\[ f'_n = f_n \sqrt{\frac{m_{\text{eff}}}{m_{\text{eff}} + M_m}} \]  \hspace{1cm} (5.34)

where \( M_m \) is the added proof mass and \( m_{\text{eff}} \) is the effective mass at the tip of the beam which is given by [256]

\[ m_{\text{eff}} = 0.236m_b \]  \hspace{1cm} (5.35)
where \( m_b \) is the total mass of the beam that can be calculated by

\[
m_b = wl[\rho_s h_s + \rho_e (h_e + h_{e2}) + \rho_p h_p].
\]  

(5.36)

### 5.2.5 Analytical Model of PVEH

The analytical model of a PVEH can be described based on piezoelectric effect. As mentioned in 5.2.3, piezoelectricity is the combination of electrical displacement \( D = \epsilon E \) and Hooke’s Law \( \delta = \sigma / Y \) in certain types of materials. Considering that strain and stress are 6-element tensors and charge density and electrical field are 3-element vectors, piezoelectric strain coefficient \( d \) is a 3 by 6 matrix described by

\[
d = \begin{pmatrix}
0 & 0 & 0 & 0 & d_{15} & 0 \\
0 & 0 & 0 & d_{24} & 0 & 0 \\
d_{31} & d_{32} & d_{33} & 0 & 0 & 0
\end{pmatrix}.
\]  

(5.37)

It has been shown that piezoelectric coupling in a device can be modeled using a transformer [257]. This modeling offers separate electrical and mechanical analyses for the device, as if they are not coupled. Figure 5.8 shows a circuit model representing the electromechanical coupling for a piezoelectric generator, while the mechanical and the electrical domains of the piezoelectric system are modelled as circuit elements [251]. The mechanical domain of the equivalent circuit consists of inductor, resistor and capacitor, which represents the mass of the generator, \( m \), the mechanical damping, \( d_m \), and mechanical stiffness, \( Y \), respectively. At the electrical domain, \( C_P \) is the capacitance of the piezoelectric device and \( V \) is the voltage across the piezoelectric layer, while \( n \) is the equivalent turn ratio of the transformer which is proportional to the piezoelectric charge constant \( d_{31} \).

The right side of Figure 5.8 is an open circuit which means no electrical load has been considered for the system. In this case, no power is actually transferred.
Researchers usually consider a resistive load in the electrical circuit to develop a simple model for predicting the power output of the harvester. Figure 5.9 shows the circuit representation of the system with a simple resistive load, $R_L$, applied.

At the electrical side of the model, $V$ and $i$ represent the voltage across the piezoelectric element and the current through the circuit, respectively, which are analogues to the stress and strain at the mechanical side of the model, respectively. Using this electrical model and assuming a harmonic excitation of the mechanical structure, the steady state voltage over the resistive load $R_L$ has been calculated as

$$V = \frac{-j\omega Y d_{31} h_p B}{\sigma_{in} \left[ \frac{1}{R_L C_p} \omega_n^2 - \left( \frac{1}{R_L C_p} + 2\zeta \omega_n \right) \omega^2 \right] + j\omega \left[ \omega_n^2(1 + k_{31}^2) + \frac{2\zeta \omega_n}{R_L C_p} - \omega^2 \right]} \quad (5.38)$$

where $j = \sqrt{-1}$, $\omega$ is the exciting frequency, $\omega_n$ is the resonance frequency of the cantilever beam, $h_p$ is the thickness of the piezoelectric layer, $B$ is a constant related
to the neutral axis of the structure, and $\zeta_t$ is the total damping of the device [251].

As Eq. 5.38 shows, the strain ($\delta$) generated in the electrode-covered piezoelectric layer plays an important role in designing of the energy harvester. Hence, the electromechanical energy conversion of the device depends on the relation between this strain and the tip displacement of the cantilever beam.

The root mean square (rms) power is defined as the square of the voltage peak ($V_{\text{peak}}$) divided by $2R_L$. Hence, using output voltage given by Eq. 5.38, the power output of the resistive load when excited at the resonance frequency will be described as [251]

$$P = \frac{V_{\text{peak}}^2}{2R_L} = \frac{R_L C_p^2}{\omega_n^2} \left( \frac{Y d_{31} h_p B}{\epsilon} \right)^2 \left[ 4\zeta_t^2 (R_L C_p \omega_n)^2 + 4\zeta_t k_{31}^2 (R_L C_p \omega_n)^2 + 4\zeta_t^2 \sigma_m \right]. \quad (5.39)$$

In order to maximize the energy transform from mechanical to electrical domain, an optimum resistive load should be used. By substituting Eq. 5.38 into 5.39 and optimizing the resultant equation with respect to $R_L$, the optimum resistive can be calculated. Assuming that the frequency of input vibration, $\omega$, is equal to the natural frequency of the beam, $\omega_n$, analytic expressions for electrical damping factor and optimal load resistance of the cantilever beam have been derived in [251] as follows

$$\zeta_e = \frac{\omega_n k^2}{\sqrt{\omega_n^2 + (R_L C_p)^2}} \quad (5.40)$$

$$R_{L,\text{opt}} = \frac{1}{\omega_n C_p \sqrt{4\zeta_m^2 + k^4}} \quad (5.41)$$

Eq. 5.41 shows that the optimal load is a function of parasitic mechanical damping. By proper selection of the load resistance, $R_{L,\text{opt}}$, given in Eq. 5.41, $\zeta_e$ will be equal to the mechanical damping ratio $\zeta_m$. 

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5.3 Designing of PVEH

The unimorph cantilever beam structure, introduced in section 5.2.4, has been used for fabrication of the PVEH device. Mechanical to electrical energy conversion, using the cantilever beam, follows steps below:

- Input vibration creates acceleration in the cantilever beam.
- The created acceleration will be converted into force through the effective mass.
- The cantilever beam bends according to the created force which in turn results in strain along the piezoelectric layer.
- The generated stress in the piezoelectric layer will be converted into electrical charge.
- Electrodes collect the generated charge.

The main parameters that affect the power output are amplitude and frequency of the input vibration, effective mass of the beam, stiffness and damping coefficient of the beam, effective electromechanical coupling coefficient, and size of the electrodes. Except the input vibration, other structural parameters can be optimized to maximize the power output. In addition, keeping the design simple guarantees the printability of the multilayer device with minimum print inconsistencies.

In order to achieve a design that satisfies all the criteria, simulation-based design (SBD) was used. SBD is a powerful approach in all the major engineering fields such as electrical and mechanical engineering. In this method, various designs will be tested simultaneously to arrive to the optimized design that meets all the criteria. COMSOL Multiphysics is finite element method (FEM) software that can be used for simulating coupled or multiphysics phenomena. This software not only provides an effective tool for optimal designing of mechanical/electrical devices but also saves
cost and time due to its parametric sweep analysis. Hence, COMSOL has been used to verify the PVEH design.

5.3.1 Introduction to COMSOL

COMSOL Multiphysics is simulation software for modeling and solving multiphysics problems based on partial differential equations (PDEs). The software works based on FEM analysis in which a variety of numerical solvers are used to run the finite element analysis using adaptive meshing of the model. In COMSOL, the user can define physical quantities such as material properties based on which a set of PDEs will be complied to represent and analyze the generated model. For more detailed information, one can use references [258] and [259].

From various built-in modules in COMSOL, *Structural Mechanics* and *Piezoelectric Devices* were used for simulation of the PVEH device. These two modules are explained below.

1. **Structural Mechanics Module:** this module can be used for solving problems in structural and solid mechanics where strain-stress analysis can be performed for 2-D and 3-D models. Different variables such as stress, strain, displacement, rotation and traction in all directions can be studied by using this module. In our case, this module was used to analyze the generated stress, strain, displacement, and stored energy in the PVEH device.

2. **Piezoelectric Devices Module:** this module can be used for solving a wide range of problems such as sensors, actuators, and ultrasonic devices in which piezoelectric materials are used. Different variables such as electric charge and voltage can be studied using this module. In our case, this module was used to analyze the generated charge, voltage, and stored electrical energy in the PVEH device.
5.3.2 COMSOL Simulation of Unimorph Cantilever Beam

5.3.2.1 3-D Model and Materials

The 3-D model of a unimorph cantilever beam consisting of substrate and piezoelectric layer was created in COMSOL Multiphysics 5.0 as shown in Figure 5.10. Polyethylene terephthalate (PET) was used as substrate and PVDF was used as piezoelectric material.

![3-D model of the simulated PVEH.](image)

5.3.2.2 Boundary Conditions

The boundary conditions were set such that one end of the beam is fixed while the other end is free to move. The fixed constrained boundary condition was applied to the vertical face of both PET and PVDF layers, while other faces were free to move. In order to use $d_{31}$ mode of the device, floating potential and ground were applied to the upper and lower faces of the PVDF layer, respectively, while all other faces of the piezoelectric layer were kept at zero charge constraint. A body load was applied as an input to the upper face of PVDF layer to induce strain.
5.3.2.3 Meshing

The created model was then meshed using the physics-controlled mesh feature with fine element size as shown in Figure 5.11.

![Meshed 3-D model](image)

Figure 5.11: Meshed 3-D model.

5.3.2.4 Eigenfrequency Analysis

Eigenfrequency analysis was conducted to study the effect of structural size on the resonance frequency of the cantilever beam. A cantilever beam has an infinite number of natural frequencies that can be determined based on its structural characteristics. Figure 5.12 shows the first six natural frequency modes of the cantilever beam shown in Figure 5.10.

Using parametric sweep analysis, the first resonance frequency of the beam was calculated for different values of beam length (Figure 5.13(a)), beam width (Figure 5.13(b)), substrate thickness (Figure 5.13(c)) and piezoelectric layer thickness (Figure 5.13(d)).

As it can be concluded from Eq. 5.28, resonance frequency of the cantilever beam is inversely proportional to the square of beam length. As shown in Figure 5.13(a), by increasing the beam length from 1 to 5 cm, the resonance frequency decreases from around 2.8 kHz to less than 100 Hz. However, as the beam length becomes bigger the change in frequency is reduced.
Figure 5.12: First six natural frequency modes of the cantilever beam shown in Figure 5.10.

Figures 5.13(b) shows that the resonance frequency slightly increases as the beam width increases. Figures 5.13(c) and 5.13(d) show that resonance frequency increases
Figure 5.13: Effect of (a) beam length, (b) beam width, (c) substrate thickness, and (d) piezoelectric layer thickness on beam’s resonance frequency.

as beam thickness increases. However, the absolute value of the rate of change in these cases is much smaller than the curve in Figure 5.13(a), which means that the beam length plays the key role in determination of its resonance frequency. The desired resonance frequency can be achieved for the unimorph cantilever beam considering these effects in design parameters.

5.3.2.5 Stationary Analysis

The effect of structural parameters on mechanical and electrical performance of the beam was also studied using stationary analysis. Figure 5.14 shows the tip displacement as the length and width of the beam change. As the beam length increases, the tip displacement increases (Figure 5.14(a)). In opposite, increasing the beam width decreases the tip displacement (Figure 5.14(b)). By comparing the rate of change for these two results, one can observe that the beam length has the major role on tip
Figure 5.14: Effect of beam (a) length and (b) width on tip displacement of the cantilever beam.

Figure 5.15 shows the relation between the stored energy density and the length and width of the beam. As the beam length increases the stored energy density increases (Figure 5.15(a)). In opposite, increasing the beam width decreases the stored energy density (Figure 5.15(b)).

Figure 5.16 shows the relation between the elastic strain energy and the length and width of the beam. As the beam length increases the elastic strain energy increases (Figure 5.16(a)). In opposite, increasing the beam width decreases the elastic strain energy (Figure 5.16(b)).

Figure 5.17 shows the relation between surface charge density of the piezoelectric
and the length and width of the beam. As the beam length increases the surface charge density increases (Figure 5.17(a)). In opposite, increasing the beam width decreases the surface charge density (Figure 5.17(b)).

Figure 5.18 shows the relation between output voltage across the piezoelectric layer and the length and width of the beam. As the beam length increases the output voltage increases (Figure 5.18(a)). In opposite, increasing the beam width decreases the output voltage (Figure 5.18(b)).

Based on the simulation results obtained in Figures 5.14, 5.15, 5.16, 5.17, and 5.18, more power can be generated by increasing the length of the cantilever beam and decreasing the width of the beam. However, in the simulation process, the
Figure 5.18: Effect of beam (a) length and (b) width on output voltage across the piezoelectric layer.

physical constraints of the device such as minimum and maximum allowed length width, thickness and fabrication process limitations are not taken into accounts. On the other hand, it should be noted that the effect of mechanical damping has not been considered in these simulations. By increasing the length of the beam, the mechanical damping of the beam increases. As it was previously shown in Eq. 5.23, the maximum power output is proportional to the inverse of damping ratio, which means that increasing the length of the beam might have adverse effect on the performance of the PVEH device. Hence, devices with different sizes have been fabricated and tested in this project.

5.3.3 Unimorph Cantilever Beam with Proof Mass

Having the beam vibrating at resonance frequency, the heavier and stiffer the beam the more energy can be generated in the structure. The most conventional approach for increasing the effective mass is to add a proof mass at the end of the beam. In order to study the effect of mass on the generated stress in the piezoelectric layer, COMSOL multiphysics was used to simulate two cantilever beams with/without a proof mass. Figure 5.19 shows the 3-D models for these cantilever beams. The effective mass for the cantilever beam with proof mass is 7 times of the beam without cantilever beam. The size of the beams has been chosen such that they both have the same natural
frequency. Both cantilever beams have been excited using the same input vibration and resulted von Mises stress and elastic strain energy density have been simulated as shown in Figures 5.20 and 5.21, respectively.

![Figure 5.19: 3-D models of cantilever beams (a) without and (b) with proof mass built in COMSOL Multiphysics.](image)

As shown in Figures 5.20 and 5.21, the resulted stress and elastic strain energy density for the cantilever beam with proof mass are almost 5 and 29 times of the beam without proof mass, respectively. It should be noted that adding of the proof mass not only increases the effective mass of the beam but also decreases the air damping of the structure significantly. As it was previously shown in Eq. 5.23, the maximum power output is proportional to the inverse of damping ratio which means that the
Figure 5.21: COMSOL simulation results for elastic strain energy density created in cantilever beams (a) without and (b) with proof mass.

beam with proof mass generates more power.

5.4 Fabrication and Characterization of First Generation PVEH

5.4.1 Chemicals and Materials

Flexible PET film (Melinex ST 329) from DuPont Teijin Films was used as substrate. Ag ink (Electrodag 479SS) from Henkel was used as the metallization ink for the bottom and top electrode layers. PVDF ink from SOLVENE™ was used for the fabrication of the piezoelectric layer.

5.4.2 Device Fabrication Process

The PVEH device was designed with different dimensions. These dimensions were selected based on the simulation results obtained in Section 5.3 such that the fabricated cantilever beam has resonance frequency of less than 200 Hz. Figure 5.22 shows the design file which was used to create the stainless screen required for fabrication of PVEH devices with different dimensions. As shown in this figure, PVEH device with dimensions of 3 cm × 3 cm, 3 cm × 2 cm, 3 cm × 1 cm, 2 cm × 3 cm, 2 cm × 2 cm, and 2 cm × 1 cm have been fabricated.
The fabrication of the PVEH device has been performed through the following steps, as shown in Figure 5.23:

1. PET substrate was cleaned using IPA (Figure 5.23(a)).

2. Ag ink was screen printed on the PET substrate as bottom electrode. Printed Ag ink was then cured at 120 °C for 5 minutes (Figure 5.23(b)).

3. PVDF ink was screen printed on top of the bottom electrode as piezoelectric layer leaving out the contact pad of the electrode. The printed PVDF film was then cured at 130 °C for 5 hours. Two more layers of PVDF ink were screen printed and each layer was cured for 5 hours at 130 °C (Figure 5.23(c)). Multilayer PVDF structure was used in order to reduce the possibility of getting
short circuit between the bottom and top electrodes.

4. Ag ink was then screen printed onto the piezoelectric layer as the top electrode. Printed Ag ink was then cured at 120 °C for 5 minutes (Figure 5.23(d)). Figure 5.24 shows a photograph of the fabricated 3 cm×3 cm first generation PVEH.

![Figure 5.23: Schematic for the fabrication of the first generation PVEH device: (a) cleaning substrate, (b) screen printing bottom electrode onto substrate, (c) screen printing piezoelectric layer on bottom electrode, and (d) screen printing top electrode onto piezoelectric layer.](image)

![Figure 5.24: Photograph of the fabricated 3 cm×3 cm first generation PVEH.](image)

### 5.4.3 Characterization of Printed Layers

A Bruker vertical scanning interferometer microscope (CounterGT) was used to characterize the thickness and roughness of the printed conductive bottom electrode
and piezoelectric layer. Figure 5.25 shows the profilometry image of printed bottom Ag electrode on PET substrate. The average thickness of the bottom electrode was measured to be around 12 µm. The root mean square (rms) roughness of the Ag layer on PET substrate was around 0.6 µm. The surface roughness of the printed Ag layer plays a key role in the successful fabrication of the device. The smoother the printed bottom electrode is, the lower the chance of short circuit between the bottom and top electrodes would be. Figure 5.26 shows the profilometry image of the printed PVDF layer over the Ag bottom electrode. The average thickness of the PVDF layer was measured to be around 10 µm. The rms roughness of the printed PVDF layer on PET substrate was around 0.4 µm.

Figure 5.25: Profilometry scan of screen printed Ag electrode on PET substrate illustrating an average thickness (∆Z) of 12.1 µm.
5.4.4 Polarization of Piezoelectric Film

The PVDF layer obtains its piezoelectric characteristics when polarized by applying an electric field, typically between 60 to 200 V/µm across the layer. The alignment of the dipoles, in the material, can be improved by heating the layer during the poling process and cooling it down to room temperature. By heating the piezoelectric material, it loses its polarity and a new poling direction appears along the applied voltage. Figure 5.27 shows the polarization setup which was used in this process. An air gun was used to heat the PVEH device. The heated device was poled by applying an electric field of 80 V/µm for 1 hour. The PVEH device was then cooled down to the room temperature before the external voltage was removed.
5.4.5 Electromechanical Testing Measurement

Figure 5.28 shows the equivalent electrical model of the PVEH connected to power storage system. The PVEH operates as an AC current source in parallel with a resistor, $R_p$, and capacitor, $C_p$. Mechanically resonating the device at its resonance frequency, $\omega_n$, results in a time-varying mechanical stress, $\sigma(t)$, alternating from tensile to compressive, to be applied to the piezoelectric film. This in turn generates a time-varying charge, $Q(t)$, within the piezoelectric layer, which is the source of the AC current $I_p(t) = dQ(t)/dt$. A rectifying circuit and electrical storage capacitor, $C_S$, were used to rectify and store the electrical energy generated within the PVEH.

In order to measure the output characteristics of the fabricated PVEH, a base shaking system was employed. The block diagram of the experimental setup used for testing of the fabricated PVEH device is shown in Figure 5.29. As shown in this figure, the PVEH is mounted on a shaker using a custom-built clamp. The shaker is excited by a function generator through a power amplifier. The output of the PVEH is connected to a bridge rectifying circuit and a storage capacitor followed by
a resistive load. A digital oscilloscope is used to monitor the output voltage of the PVEH and the resistive load.

Figure 5.30 shows the implemented experimental setup. The PVEH device was mounted on a shaker (Vibration Test System, Model No. VG 100-8) using a custom-built clamp. The shaker is connected to a function generator through a power amplifier (Techron, Model No. 7705). The output of the PVEH is connected to a bridge rectifying circuit followed by a resistive load. The bridge rectifying circuit consists of four small signal Schottky diodes (STMicroelectronics® 1N5711) and a 500 nF storage capacitor. A digital oscilloscope (Tektronix TDS5104B Digital Phosphor Oscilloscope) is used to monitor the output voltage of the PVEH and resistive load.
5.4.6 Experimental Results

The first step in measuring power generation capability of PVEH is to measure its resonance frequency. For this purpose, a sinusoidal signal with frequency sweeping from 0 to 0.5 kHz was used to excite the shaker. Simultaneously, the output voltage of the PVEH was monitored at different frequencies. The frequency that results in the largest output voltage is the first resonance mode of the PVEH. The highest output power can be obtained by exciting the PVEH at this resonance frequency. Table 5.1 shows the resonance frequencies obtained for PVEH with different dimensions. As shown in this table, resonance frequency of the cantilever beam is more dependent on beam length than beam width. Also, results show that larger beam lengths result in lower resonance frequencies. Similar results were previously observed through COMSOL eigenfrequency analysis of the cantilever beam in Section 5.3.2.4.

Table 5.2 summarizes various vibration sources in terms of the frequency and acceleration magnitude of the fundamental vibration mode. Information about the potential vibration sources plays a key role in the designing of vibration energy harvesters. First, the device should be designed to resonate at the fundamental vibration
frequency, which is quite low and may be difficult to obtain within small volumes. Second, the higher vibration frequency modes are lower in acceleration magnitude than the low frequency fundamental mode. As mentioned before in modeling of vibration energy harvester, the potential output power is proportional to \( A^2/\omega \) where \( \omega \) is the frequency of the vibration mode. Therefore, the design should target the low frequency fundamental mode. As shown in this Table 5.2, most of the available vibration sources have vibration frequencies less than 200 Hz. Obtained results in Table 5.1 show that selected PVEH dimensions can be used to harvest energy from vibration sources available in the environment surrounding us.

Table 5.2: Acceleration magnitude and frequency of fundamental vibration mode for various sources [3].

<table>
<thead>
<tr>
<th>Vibration Source</th>
<th>( A ) (m/s²)</th>
<th>( F_{\text{peak}} ) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Car engine compartment</td>
<td>12</td>
<td>200</td>
</tr>
<tr>
<td>Base of 3-axis machine tool</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>Blender casing</td>
<td>6.4</td>
<td>121</td>
</tr>
<tr>
<td>Clothes dryer</td>
<td>3.5</td>
<td>121</td>
</tr>
<tr>
<td>Person nervously tapping their heel</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Car instrument panel</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>Door frame just after door closes</td>
<td>3</td>
<td>125</td>
</tr>
<tr>
<td>Small microwave oven</td>
<td>2.5</td>
<td>121</td>
</tr>
<tr>
<td>HVAC vents in office building</td>
<td>0.2-1.5</td>
<td>60</td>
</tr>
<tr>
<td>Windows next to a busy road</td>
<td>0.7</td>
<td>100</td>
</tr>
<tr>
<td>CD on notebook computer</td>
<td>0.6</td>
<td>75</td>
</tr>
<tr>
<td>Second story floor of busy office</td>
<td>0.2</td>
<td>100</td>
</tr>
</tbody>
</table>

After determining the resonance frequencies of the fabricated PVEHs, each PVEH was excited at its resonance frequency and its voltage output was monitored. Fig-
Figure 5.31 shows the voltage outputs of PVEHs described in Table 5.1. As shown in this figure, the peak-to-peak voltage response of the fabricated PVEHs on PET substrate is lower than 0.1 V. These generated voltage responses of the PVEHs fabricated on PET substrate are not high enough to be rectified and then be used to power electronics. The reason behind these low voltage responses is the ineffective polarization of the PVDF film due to the large thickness of the substrate. Hence, the author fabricated a second generation of PVEHs by eliminating the PET substrate as described in Section 5.5.

Figure 5.31: Voltage responses of fabricated (a) 1 cm (width) by 3 cm (length), (b) 2 cm (width) by 3 cm (length), (c) 3 cm (width) by 3 cm (length), (d) 1 cm (width) by 2 cm (length), (e) 2 cm (width) by 2 cm (length), and (f) 3 cm (width) by 2 cm (length) PVEHs when excited at their resonance frequencies.

5.5 Development of Second Generation PVEH

As described in Section 5.4, the poor polarization of the PVDF films in fabricated PVEHs on PET substrate resulted in voltage responses which were not high enough
to be rectified and then be used to power electronics. Hence, the second generation of PVEHs was fabricated by eliminating the PET substrate. The following sections describe the fabrication process and experimental results of the second generation PVEHs.

5.5.1 Chemicals and Materials

Plate glass from Corning and flexible Metglas (2605SA1) were used as the substrate and metallization layers, respectively. PVDF ink from SOLVENE™ was used for the fabrication of the piezoelectric layer.

5.5.2 Device Fabrication Process

Initially, the glass substrate was cleaned using IPA. Then, three layers of PVDF ink were screen printed onto the glass substrate. After printing each layer, the PVDF film was kept at room temperature for 10 minutes and then cured for 5 hours in a VWR 1320 temperature controlled oven at 130 °C. A Bruker vertical scanning interferometer microscope (CounterGT) was used to characterize the printed PVDF layer. The average thickness of the PVDF layer was measured to be around 12 µm, as shown in Figure 5.32.

The fabricated PVDF film was then peeled off from the glass substrate. The peeled-off PVDF film was then polarized using the process described in Section 5.4.4. The polarized PVDF layer was then sandwiched between two pieces of Metglas as bottom and top electrodes using conductive tape. The fabricated PVEH is shown in Figure 5.33.

5.5.3 Electromechanical Testing Measurement

The experimental setup described in Section 5.4.5 was used to test the voltage and power generation capability of the fabricated PVEH shown in Figure 5.33. Initially,
the PVEH mounted base shaker was excited with a sinusoidal voltage of varying frequencies between 10 Hz to 200 Hz and the tip displacement was monitored. A first resonance frequency of 54 Hz was obtained for the cantilever beam structure. Then, the base shaker was used to apply vibrations to the PVEH device at its first resonance frequency of 54 Hz and its voltage output was measured. Figure 5.34 shows the response of the PVEH device while being excited at 54 Hz. It was observed that the fabricated PVEH device generated a peak-to-peak voltage output of $\sim 10$ V. The high peak-to-peak voltage of the fabricated PVEH is due to the highly effective
polarization of the $\sim 12 \mu m$ thick PVDF film. The non-ideal sinusoidal behavior of the generated voltage is due to the non-ideal bonding between the three layers of the PVEH device.

![Figure 5.34: Unrectified voltage response of the PVEH device for a sinusoidal vibration of 54 Hz.]

Then, the PVEH device was connected to the bridge rectifying circuit with a resistive load across the storage capacitor. The shaker was then again excited at 54 Hz, while the load voltage was measured as a function of load resistance. Figure 5.35 shows the load voltage and the power delivered to the load for different values of load resistance. It was observed that the load voltage increased with increase in load resistance, up to $\sim 1.4$ V at 10 M$\Omega$. However, the power delivered to the load does not increase indefinitely. A maximum power output of $\sim 0.3$ µW with a 0.53 VDC voltage was obtained for the 1 M$\Omega$ load, after which the electrical power decreased with increase in load resistance. Thus, for the fabricated PVEH device, the power density was calculated to be $\sim 11.7$ µW/cm$^3$.

The results obtained for second generation PVEH showed the potential of the printed device to be used as vibration energy harvester. However, there were some issues that needed to be addressed. For the fabrication of the PVEH, even though
Figure 5.35: Load voltage and power delivered to the load versus load resistance.

Conductive tape was used for bonding between the peeled-off PVDF film and the conductive electrodes, the adhesion of the conductive tape degrades over the time, thus resulting in separation of the layers. Also, the non-ideal bonding between the three layers of the PVEH results in a non-ideal sinusoidal behavior of the generated voltage and lower power output. Direct printing of conductive inks, such as silver, onto the peeled-off PVDF film not only improves the bonding between the device layers but also increases the contact area between the piezoelectric film and the conductive electrodes, thereby increasing the amount of electric charge that can be collected during the vibrations. The PVEH device would thus be able to generate more power at lower accelerations. Hence, the author fabricated a third generation of PVEHs by direct printing of silver ink onto the PVDF film as described in Section 5.6.

5.6 Development of Third Generation PVEH

The fabricated PVEH in Section 5.5 demonstrated the proof-of-concept of a self-supported fully printed PVEH device. Experimental results showed the voltage and power generation capability of the PVDF film. In order to address the issues of the second generation PVEH, a third generation PVEH was fabricated as described
5.6.1 Chemicals and Materials

Ag ink (Electrodag 479SS) from Henkel was used as the metallization ink for the bottom and top electrode layers. PVDF ink from SOLVENE™ was used for the fabrication of the piezoelectric layer. Aluminum block was machined and used as a mold.

5.6.2 Device Fabrication Process

Figure 5.36 shows the fabrication process of the third generation PVEH. First, PVDF ink was poured into the aluminum mold. The poured ink introduces bubbles, which were removed by setting aside at room temperature overnight. The whole setup was then cured for 5 hours in a VWR 1320 temperature controlled oven at 130 °C and was cooled down to room temperature. The cured PVDF film was then peeled off from the mold. A Bruker vertical scanning interferometer microscope (CounterGT) was used to characterize the peeled-off PVDF film. The average thickness of the PVDF film was measured to be around 140 µm, as shown in Figure 5.37.

![Figure 5.36: Schematic for fabrication of the third generation PVEH: (a) PVDF ink poured in aluminum mold and cured, (b) peeling off cured PVDF film, (c) screen printing top Ag electrode on PVDF film, and (d) screen printing bottom electrode on second side of PVDF film.](image-url)
Figure 5.37: Profilometry scan of the peeled-off PVDF film formed in aluminum mold.

Ag ink was screen printed on one side of the peeled-off PVDF film as bottom electrode. Printed Ag ink was then cured at 120 °C for 5 minutes. Finally, Ag ink was screen printed onto the other side of the PVDF film as top electrode and was cured at 120 °C for 5 minutes. Figure 5.38 shows a photograph of the fabricated 3 cm × 3 cm self-supported PVEH. It should be noted that in the following discussion, the first and second numbers of dimensions represent the width and length of the PVEHs, respectively. For example, a PVEH with 3 cm × 2 cm dimensions has a width of 3 cm and a length of 2 cm. The PVDF film was then polarized using the process described in Section 5.4.4.

5.6.3 Electromechanical Testing Measurement

The experimental setup described in Section 5.4.5 was used to test the voltage and power generation capability of the fabricated PVEHs. In order to determine
the first resonance frequency of the fabricated PVEHs, each PVEH was mounted on the shaker and the shaker was excited with a sinusoidal voltage of varying frequencies between 10 Hz to 200 Hz while monitoring the generated voltage of the excited PVEH. Table 5.3 summarize the first resonance frequencies of fabricated PVEHs with different dimensions.

Table 5.3: Summary of first resonance frequencies for third generation PVEHs with different dimensions.

<table>
<thead>
<tr>
<th>Width (cm)</th>
<th>Length (cm)</th>
<th>Resonance Frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1</td>
<td>253</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>53</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>197</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>39</td>
</tr>
</tbody>
</table>

Then, the base shaker was used to apply vibrations to each PVEH at its first resonance frequency and its voltage output was measured. Figure 5.39 shows the responses of fabricated PVEHs with different dimensions while being excited at their resonance frequencies. As shown in this figure, the voltage outputs of the third generation PVEHs were closer to sinusoidal signal when compared to the voltage outputs of
the first and second generations PVEHs. It was observed that the fabricated PVEHs generated peak-to-peak voltage outputs as high as \( \sim 9 \) V. The lower peak-to-peak voltages of the fabricated PVEHs when compared to the second generation PVEH is due to the thicker PVDF films used for fabrication of the third generation PVEH. Higher voltages can be achieved by using thinner PVDF film. However, thinner PVDF film tends to bend during the curing process of the printed Ag electrodes thus resulting in a bent PVEH, due to different temperature coefficients of expansion. Printing Ag ink on curved PVDF film is not practical.

Each fabricated PVEH was connected to the bridge rectifying circuit with a resistive load across the storage capacitor. The shaker was then excited at the resonance frequency of the mounted PVEH, while the load voltage was measured as a function of load resistance. Figure 5.40 shows the load voltage and the load power versus the load resistance for PVEHs with different dimensions. Similar to the second generation PVEH, it was observed that the load voltage increased with increase in load resistance. However, the power delivered to the load did not increase indefinitely.

Table 5.4 shows the summary of the results obtained for third generation PVEHs. In this table, optimal load resistance (\( R_{opt} \)), maximum power (\( P_{max} \)) delivered to \( R_{opt} \), voltage (\( V_{out} \)) across \( R_{opt} \), and approximation of power density for each fabricated PVEH are shown. Maximum power output of 0.6 \( \mu \)W, 2.5 \( \mu \)W, 1.5 \( \mu \)W, 0.4 \( \mu \)W, 1.5 \( \mu \)W, and 0.6 \( \mu \)W, were obtained for 3 cm \( \times \) 1 cm, 3 cm \( \times \) 2 cm, 3 cm \( \times \) 3 cm, 2 cm \( \times \) 1 cm, 2 cm \( \times \) 2 cm, and 2 cm \( \times \) 3 cm PVEHs, respectively. For maximum generated power output, the voltage output of 0.9 V, 1.8 V, 1.4 V, 0.4 V, 1.4 V, and 0.9 V were obtained for 3 cm \( \times \) 1 cm, 3 cm \( \times \) 2 cm, 3 cm \( \times \) 3 cm, 2 cm \( \times \) 1 cm, 2 cm \( \times \) 2 cm, and 2 cm \( \times \) 3 cm PVEHs, respectively. As shown in this table, for the 3 cm wide PVEHs, the maximum power (2.5 \( \mu \)W) was generated by the one with length of 2 cm. Similar result was observed for the 2 cm wide PVEHs, i.e., the maximum power (1.5 \( \mu \)W) was generated by the one with length of 2 cm. As
Figure 5.39: Unrectified voltage response of third generation PVEHs with different dimensions.

discussed in Section 5.3.2.5, by increasing the length of the cantilever beam from 2 cm to 3 cm, the mechanical damping of the beam increases, thus reducing the generated power. Among all the fabricated third generation PVEHs, the 3 cm by 2 cm PVEH generated the maximum power output of 2.5 μW with a 1.8 VDC voltage for the 1320 kΩ load. For this PVEH, power density of \( \sim 27 \, \text{µW/cm}^3 \) was calculated, which is \( \sim 130\% \) improvement when compared to the second generation PVEH. This power density can be even improved either by reducing the thickness of the PVDF film or
Figure 5.40: Load voltage and power versus load resistance for third generation PVEHs with different dimensions.

by improving the polarization process of the PVDF film.

Table 5.4: Summary of the results obtained for third generation PVEH with different dimensions.

<table>
<thead>
<tr>
<th>Width (cm)</th>
<th>Length (cm)</th>
<th>$R_{opt}$ (kΩ)</th>
<th>$P_{max}$ (W)</th>
<th>$V_{out}$ (V)</th>
<th>Power Density (µW/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1</td>
<td>1320</td>
<td>0.6</td>
<td>0.9</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1320</td>
<td>2.5</td>
<td>1.8</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>1320</td>
<td>1.5</td>
<td>1.4</td>
<td>10.9</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>462</td>
<td>0.4</td>
<td>0.4</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1320</td>
<td>1.5</td>
<td>1.4</td>
<td>24.3</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>1320</td>
<td>0.6</td>
<td>0.9</td>
<td>6.4</td>
</tr>
</tbody>
</table>
5.7 Summary

In this chapter, the author introduced a novel piezoelectric-based vibration energy harvester. A brief background and introduction to the need for fully printed piezoelectric-based vibration energy harvester was provided. The piezoelectric-based device was then modeled and its performance was investigated using COMSOL multiphysics simulation. A detailed account of the experimental tasks involved in this work was then presented. This includes the materials and devices to use, fabrication of the devices and the experiment used. Finally, the capability of the printed energy harvesters was investigated by measuring the DC output voltage and the power output delivered to varying load resistances.

In summary, three generations of PVEHs were developed and tested. For the first generation, the screen printing technique was used to deposit all piezoelectric and conductive layers of the device. In this device, a PVDF layer was sandwiched between two printed silver electrodes all fabricated on a PET substrate. PVEHs in different dimensions were fabricated and tested. Test results showed that this fabrication process, along with the polarization setup used in this project, were not able to provide large enough piezoelectric coefficients for the vibrated PVEH to generate large enough voltage output to pass the rectifying circuit and power the resistive load. For the second generation, PVDF ink was screen printed onto a glass substrate. Then, conductive Metglas was tapped on both sides of the PVDF film peeled-off from the glass substrate. For this generation of PVEH, a maximum power output of 0.28 µW with a 0.53 VDC voltage was obtained for the 1MΩ load. Thus, for the fabricated PVEH device, the power density was calculated to be 11.67 µW/cm³. However, there were some issues that needed to be addressed. For the fabrication of the PVEH, even though conductive tape was used for bonding the peeled-off PVDF film to the conductive electrodes, the adhesion of the conductive tape degrades over time, thus resulting in separation of the layers. Also, the non-ideal bonding between the three
layers of the PVEH results in a non-ideal sinusoidal behavior of the generated voltage, thus reducing the generated power output. Therefore, the third generation of PVEHs was fabricated by direct printing of silver ink onto PVDF film. In this approach, an aluminum mold was used to form a $\sim 140 \mu m$ PVDF film. Then, the screen printing technique was used to deposit silver ink onto both sides of the PVDF film. PVEHs in various dimensions were fabricated and tested. Among all the fabricated third generation PVEHs, the 3 cm (width) by 2 cm (length) PVEH generated the maximum power output of 2.5 $\mu W$ with a 1.8 VDC voltage for the 1320 k$\Omega$ load when excited at 80 Hz. For this PVEH, power density of 27 $\mu W/cm^3$ was calculated, which is $\sim 130\%$ improvement when compared to the second generation PVEH. The response of the fabricated PVEHs demonstrated the potential of using additive print manufacturing processes for the fabrication of cost-efficient, lightweight flexible vibration energy harvesters. Further research is underway to enhance the power output of the printed PVEH by reducing the thickness of the device as well as improving the polarization process to achieve higher piezoelectric coefficient.

In the following chapter, the author concludes this dissertation with a summary of the projects performed and provides some suggestions for possible future work.
CHAPTER VI

CONCLUSION AND FUTURE WORK

6.1 Conclusion

In this dissertation, the author has developed a surface enhanced Raman spectroscopy (SERS) substrate to be used in detection of explosive compounds in the vapor phase, a flexible touch-sensitive skin to be used in touch and force sensing applications, and a piezoelectric-based vibration energy harvester by using conventional printing technique. The dissertation was organized and pursued in three projects in order to achieve the research outcomes.

In the first project, an efficient SERS substrate was fabricated by gravure printing a thin film of silver nanoparticle ink on flexible polyethylene terephthalate (PET) sheet. The feasibility of the printed substrate to be used as a SERS substrate for the detection of explosive materials such as DNT was demonstrated. An enhancement factor of three and four for the peaks at 1350.13 cm\(^{-1}\) was obtained for the SERS based response of the printed SERS substrate toward DNT solution and vapor, respectively, when compared to target molecules adsorbed on bare PET. The effect of temperature on the intensity of Raman spectrum was also examined. An 85\% decrease in the Raman intensity was observed at 65 °C when compared with the intensity of Raman spectrum at 25 °C. The effect of bending on the SERS response was also investigated. The intensity of the Raman spectrum was increased as the SERS substrate was bent by different radius of curvature. Further research is underway for the development of a gravure printed SERS substrate using different substrates such as paper to be used in hand-held SERS based systems for the detection of a wider range of bio/chemicals. Moreover, the fabricated SERS substrates have the promising potential to be used
as a cost-effective substitution in commercialized SERS detection applications. The outcome of this research project was published in [260].

In the second project, piezoelectric-based touch sensors were successfully fabricated on flexible PET and paper substrates by using the screen printing technique. The capacitive devices were fabricated using Ag and PVDF inks as the metallization and piezoelectric layers, respectively. Characterization of the substrates and various printed layers of the touch sensor were performed. The proper formation of the β-phase crystals in the cured PVDF film was investigated using XRD measurements. The effective polarization of the printed piezoelectric PVDF layer was verified using capacitance-voltage analysis. A sensitivity of 1.2 V/N and 0.3 V/N, with correlation coefficient of 0.9954 and 0.9859, was obtained for the PET and paper based printed touch sensors, respectively. Piezoelectric-voltage analysis demonstrated that the printed sensor can be used as both touch and force sensors. The advantage of fabricating touch sensors on flexible substrates is the ability to fold and place the sensor on nearly any platform or to conform to any irregular surface, whereas the additive properties of printing processes allow for a faster fabrication process, while simultaneously producing less material waste in comparison to the traditional subtractive processes. It is believed that this technology has a significant potential for use in flexible electronics where light weight sensing devices can be attached conformably onto the surface to improve user-device interactions. The outcome of this research project was published in [261, 262].

In the third project, three generations of novel piezoelectric-based vibration energy harvesters were fabricated and tested. For the first generation, the screen printing technique was used to deposit all piezoelectric and conductive layers of the device. In this device, a PVDF layer was sandwiched between two printed silver electrodes, all fabricated on a PET substrate. PVEHs in different dimensions were fabricated and tested. Test results showed that this fabrication process along with the polarization
setup used in this project were not able to provide large enough piezoelectric coefficients for the vibrated PVEH to generate large enough voltage output to pass the rectifying circuit and power the resistive load.

For the second generation, PVDF ink was screen printed onto a glass substrate. Then, conductive Metglas was tapped onto both sides of the PVDF film peeled-off from the glass substrate. For this generation of PVEH, a maximum power output of 0.28 µW with a 0.53 VDC voltage obtained for the 1MΩ load. Thus, for the fabricated PVEH device, the power density was calculated to be 11.67 µW/cm³. However, there were some opportunities to improve the performance of the fabricated PVEH. For the fabrication of the PVEH, even though conductive tape was used for bonding the peeled-off PVDF film to the conductive electrodes, the adhesion of the conductive tape degrades over the time thus resulting in separation of the layers. Also, the non-ideal bonding between the three layers of the PVEH results in a non-ideal sinusoidal behavior of the generated voltage, thus reducing the generated power output. Therefore, the third generation of PVEHs was fabricated by direct printing of silver ink onto PVDF film. In this approach, an aluminum mold was used to form a ∼200 µm PVDF film. Then, the screen printing technique was used to deposit silver ink onto both sides of the PVDF film. PVEHs in various dimensions were fabricated and tested. Among all the fabricated third generation PVEHs, the 3 cm (width) by 2 cm (length) PVEH generated the maximum power output of 2.5 µW with a 1.8 VDC voltage for the 1320 kΩ load when excited at 80 Hz. For this PVEH, power density of 27 µW/cm³ was calculated which is ∼130% improvement when compared to the second generation PVEH. The response of the fabricated PVEHs demonstrated the potential of using additive print manufacturing processes for the fabrication of cost-efficient, lightweight flexible vibration energy harvesters. Further research is underway to enhance the power output of the printed PVEH by reducing the thickness of the device as well as improving the polarization process to achieve
higher piezoelectric coefficient. The outcome of this research project was published in [263].

6.2 Future Work

Based on the knowledge and experiences gained during this dissertation work, the author believes that there are several possibilities and opportunities to improve upon the current projects in terms of fabrication process and performance. The details of suggested future work for each project is provided below.

- **Vapor-Phase Detection of Explosives Using SERS:**
  - Various substrates such as paper can be used for development of the printed SERS substrate. Performance of different substrates can be compared for optimum “hot-spots” formation.
  - The explosive detection capability of the printed SERS substrate in the presence of other non-explosive compounds can be studied and improved.
  - Results of the developed sensing system can be compared with commercially available systems for explosive vapor sensing.
  - SEM images of the printed SERS substrate can be used to further investigate the proper formation of the “hot-spots”.
  - Treating of the substrate can improve the quality of printed SERS substrate, thus providing larger enhancement in the Raman spectra.
  - The size of the silver nanoparticles can be selected according to the wavelength of the laser source to achieve a larger enhancement factor in the Raman spectra.
  - Utilizing different printing techniques, such as screen, flexography, and inkjet printing on different substrates, such as different papers for fabrica-
tion of high efficiency SERS substrates can be investigated. The performance of each of the sensing systems can be compared for optimum system performance.

- **Screen Printing of Flexible Piezoelectric-Based Touch Sensor:**

  - The Ag ink can be replaced with a transparent conductive ink to fabricate a transparent touch sensitive device to be used in touch screens.
  
  - Other printing techniques such as gravure and flexo printing could be employed to fabricate the bottom electrodes in order to achieve a smoother surface, thus resulting in a more uniform PVDF layer which in turn reduces the change of short circuit occurrence between the bottom and top electrodes. This would increase the yield of using printing techniques for fabrication of flexible touch sensitive devices.
  
  - Integrating the printed touch sensors with a more complicated readout circuit, including a microcontroller in order to develop a pressure sensing system.
  
  - Using mathematical algorithms in order to reduce the crosstalk issue between adjacent touch sensing spots, therefore, resulting in better performance for the printed touch sensors.
  
  - Depositing a protective encapsulating layer over the printed areas to improve the stability and durability of the printed sensors.
  
  - The flexible printed touch sensor can be fabricated in a larger area size to be placed over a football helmet for detection of the concussion to the head of a football player during a football game.
  
  - Similar materials and fabrication processes can be used to develop a piezoelectric heart rate monitor. Much larger piezoelectric coefficients are required to fabricate the reliable heart rate monitor.
- The polarization process can be optimized by conducting a series of capacitance-voltage analysis for various polarization parameters. An optimized polarization process can improve the sensitivity of the touch sensitive device significantly.

- **Development of Piezoelectric-Based Vibration Energy Harvester:**

- Reducing the thickness of the PVDF film in order to increasing the effect of polarization process on alignment of the dipoles in the piezoelectric material. A more effective polarization process results in a higher piezoelectric coefficient, which in turn increases the power density of the energy harvester. The challenge related to using a thinner PVDF film is that PVDF material tends to bend during the curing of the deposited conductive ink. The thinner the PVDF film is the more challenging the fabrication process would be. Also, a bent PVDF film decreases the effect of polarization, thus reducing the power generating capability of the energy harvester.

- Multiple printed energy harvesters can be connected in different configurations in order to generate higher power and voltage output.

- Computer based optimization algorithms can be used to optimally design the structural parameters of the printed energy harvester. This would increase the power density of the energy harvester.

- Integrating the printed energy harvester with a CMOS based rectifying circuit can increase the voltage output and the power delivered to the load.

- Other piezoelectric materials such as PZT can be used instead of PVDF for fabrication of the piezoelectric material. PZT has larger piezoelectric coefficient when compared to PVDF which in turn results in higher power density.
- Improving the polarization process for the piezoelectric material can dramatically increase the power density of the printed energy harvester. A polarization setup in which the temperature of the PVDF film can be controlled throughout the polarization process results in better alignment of the dipoles in the piezoelectric material.

- As explained in Section 5.3.3, adding a proof mass would increase the resultant stress and elastic strain energy density of the cantilever beam, thus resulting in more power output. The design of the energy harvester can be modified to include a proof mass at the tip of the cantilever beam.
APPENDIX

LIST OF PUBLICATIONS, HONORS, AND AWARDS

A.1 Inventions


A.2 Honors and Awards

1. Graduate Student Travel Grant, Graduate College, Western Michigan University, March 2016

2. All University Graduate Research and Creative Scholar, Graduate College, Western Michigan University, April 2016

3. Graduate Student Research Grant, Graduate College, Western Michigan University, March 2015
A.3 Publications

Journal Papers:


Conference Papers:


Biosensors (BIOSENSORS), May 27-30, Melbourne, Australia, pp. 120-121, 2014.


substrates”, Flexible and Printed Electronics Conference (FlexTech), February 4-6, Phoenix, Arizona, USA, pp. 45, 2014.


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[67] Ian R Lewis, Nelson W Daniel, and Peter R Griffiths. Interpretation of raman


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David Rancourt, Ahmadreza Tabesh, and Luc G Fréchette. Evaluation of


[181] Eric J Houser, Todd E Mlsna, Viet K Nguyen, Russell Chung, Robert L Mow-


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