Piezoelectric energy harvesting using poly (Vinylidene Difluoride-Trifluoroethylene)

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**PIEZOELECTRIC ENERGY HARVESTING USING POLY
(VINYLIDENE DIFLUORIDE-TRIFLUOROETHYLENE)**

VENKATESWARLU BHAVANASI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

Mechanical energy is available almost everywhere and at all the time in the ambient environment. Piezoelectric materials convert the ambient mechanical energy into useful electrical energy which can be used to realize the self-powered electronic devices and sensors. Ferroelectric/piezoelectric polymer, poly (vinylidene difluoride - trifluoroethylene) [PVDF-TrFE], is flexible and can sustain larger strains and strain rates (under impact stress) compared to inorganic counterparts, making it attractive for harvesting energy from the mechanical vibrations. Yet, the piezoelectric energy harvesting ability of these polymers is unsatisfactory because of lower piezoelectric coefficients and Young's modulus of the PVDF-TrFE compared to inorganic counterparts. Various strategies are employed to improve the energy harvesting performance of PVDF-TrFE by improving the properties such as piezoelectric coefficient, Young's modulus and by combining the electrostatic energy harvesting along with piezoelectricity. Firstly, combining the PVDF-TrFE films with graphene oxide (a negatively charged material with high modulus) not only enable to harvest electrostatic component along with piezoelectricity but also improves the Young's modulus and creates residual stress (under stress gradient) into the PVDF-TrFE films. This leads to the enhanced energy harvesting performance of bi-layer films over PVDF-TrFE films alone. Secondly, by synthesizing the one dimensional nanostructures of PVDF-TrFE (nanotubes/nanowires), it is obtained oriented crystal structure corresponding to (110) planes (along the length of the nanotubes) and hence lower coercive fields and higher piezoelectric coefficient values compared to film counterpart. Higher piezoelectric coefficients along with high surface area and strain confinement in the 1-D nanostructures lead to the improved energy harvesting performance over PVDF-TrFE films. Furthermore, a methodology is provided to control the alternating current (AC) type nature of the output of the piezoelectric energy harvesting devices. By employing a ferroelectric polarization charge in series with the piezoelectric energy harvesting device, an asymmetric voltage output with reduction in the voltage at one end of the AC peak is observed, a step towards realizing the DC type voltage output from the futuristic piezoelectric energy harvesting devices.

The work provided here is advantageous to develop an efficient piezoelectric energy harvester and hence to develop self-powered electronic devices or sensors.

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Abbreviations

AFM Atomic Force Microscopy

FESEM Field Emission Scanning Electron Microscopy

GO Graphene Oxide

PFM Piezo Force Microscopy

PVDF-TrFE Poly (Vinylidene Difluoride-Trifluoroethylene)

XRD X-Ray Diffraction

Chapter 1

Introduction

Limited fossil fuels and need for green energy propelled an immense enthusiasm in exploring non-conventional means of energy generation. Mechanical energy is available almost everywhere and at all the time. We choose piezoelectric polymer PVDF-TrFE to harvest the mechanical energy because of its high piezoelectric coefficient among polymers and its ability to sustain high impact stress and strains compared to inorganic counterparts. The dissertation work focuses on the strategies to improve the energy harvesting ability of the PVDF-TrFE. In this chapter, we present the problem statement and hypothesis followed by the objective of the dissertation. We further present the over view of the thesis followed by findings and originality of the dissertation work.

1.1 Hypothesis and problem statement

Piezoelectric materials are of great interest to realize self-powered systems due to their ability to harvest mechanical energy to electrical energy. Piezoelectric polymers can sustain higher strain, strain rates, impact stress compared to inorganic counter parts but their piezoelectric coefficient and Young's modulus are lower than inorganic piezoelectric materials.

The voltage output of the piezoelectric materials is given by ^{1, 2}

$$V = d_{33} \sigma t / \epsilon$$

Where d_{33} = piezoelectric coefficient, σ = stress applied ($\sigma = E \times \text{Strain}$, where E Young's modulus of the device), t = thickness and ϵ = dielectric constant

$$V = d_{33} E (\text{Strain}) t / \epsilon \dots\dots\dots (1)$$

The energy harvesting ability of (voltage and power output) PVDF-TrFE is lower due to its lower piezoelectric coefficient ($d_{33} \sim 20 \text{ pm/V}$, for PZT $d_{33} > 100 \text{ pm/V}$)^{3, 4}, lower Young's modulus ($E \sim 1\text{-}2 \text{ GPa}$)⁵ compared to inorganic counter parts. PVDF-TrFE required higher poling fields due to their higher coercive fields ($E_c \sim 50 \text{ MV/m}$ for PVDF-TrFE, $E_c \sim 1 \text{ MV/m}$ for PZT).

The energy harvesting ability of PVDF-TrFE can be improved either by improving its intrinsic properties (such as piezoelectric coefficient, Young's modulus) or combining with the hybrid cells which can harvest energy either by multiple energy stimuli (such as mechanical, wind, solar energy etc.) or by multiple ways (harvesting mechanical energy by means of piezoelectric, electromagnetic or electrostatic manner etc.).

According to equation 1, the voltage output of the piezoelectric device is proportional to the Young's modulus. However the Young's modulus of the material is directly related to the strain in the material. The higher the Young's modulus, the lower the strain. It is observed that unimorph actuators showed better performance when they combine the

piezoelectric material with the high modulus elastic material^{6, 7}. Therefore, it is hypothesized that the preparation of a bi-layer structure of PVDF-TrFE with a high modulus material can improve the energy harvesting. In addition, upon the application of force, there is a change in the thickness of the piezoelectric films. Electrostatic nanogenerators generate energy when there is a change in the thickness. A charged material can be useful to harvest electrostatic energy without any external voltage source. It is hypothesized that by fabricating the bi-layer films of PVDF-TrFE with a charged material, it is possible to harvest both electrostatic and piezoelectric energy and hence improve the energy harvesting ability.

Furthermore, the piezoelectric coefficient of PVDF-TrFE is lower in bulk and film form (~20 pm/V), mainly due to the random crystal and dipolar orientations³. In single crystal form, the piezoelectric coefficient of PVDF-TrFE is approximately 250 pm/V⁸. So the piezoelectric coefficients can be improved by achieving an oriented crystallization along with a favorable polarization orientation (when a force is applied along the polarization direction, the force can be effectively applied onto the dipoles and results in the maximum change in the dipole moment/polarization and hence leads to the higher piezoelectricity). It is reported that the oriented crystallization in PVDF-TrFE can be achieved by confined crystallization in the nanopores^{9, 10}. By synthesizing the 1-D PVDF-TrFE nanostructures in confined environment, it is hypothesized that a lower coercive field and enhanced piezoelectric coefficients can be achieved. In addition the strain confinement in 1-D geometry, together with enhanced piezoelectric coefficients of 1-D nanostructures will further lead to the enhanced energy harvesting ability of the PVDF-TrFE over films or bulk counter parts.

Piezoelectric energy harvester can be used to realize the self-powered electronic devices. The electronic devices usually require direct current (DC) voltage for operation, however, the output from the piezoelectric energy harvester is alternating current (AC) in nature. It is reported in the literature that when a charged material (formed during the growth process) is assembled at one end of the piezoelectric active material or device, it is possible to realize

DC output behavior¹¹. Since the ferroelectric materials are characterized by a fixed polarization charges on either side of the material, we proposed that by utilizing a ferroelectric material at one end of the piezoelectric device may give rise to the DC output.

1.2. Objective and scope

The objective of the present work is to improve the energy harvesting ability of the PVDF-TrFE.

Here we study the energy harvesting ability of the PVDF-TrFE by combining it with a high modulus and charged material, realizing a bilayer device. We investigated the effect of nanostructural PVDF-TrFE and compared the voltage and power outputs of the synthesized materials with film counterparts (under the same compression pressure). A strategy to curb the AC output of the PVDF-TrFE nanogenerator is delineated using the ferroelectric charge facilitator assembled at one end of the device.

1.3 Dissertation Overview

Chapter 2 presents the various mechanical energy harvesting technologies and introduces the piezoelectric energy harvesting. Various ferroelectric and piezoelectric materials and the fundamental behavior of ferroelectric materials such as polarization orientation and piezoelectric coefficient were discussed. The recent progresses in the piezoelectric energy harvesting and the methodologies to improve the performance are reviewed. Questions in the literature, which are yet to be tackled, will be identified.

Chapter 3 presents the detailed experimental methods for the preparation of the materials used, various characterization techniques such as structural and electrical characterization techniques used in this dissertation.

Chapter 4 presents the bi-layers combining PVDF-TrFE film and graphene oxide to achieve the high Young's modulus and enhancement of the energy harvesting by means of electrostatic and piezoelectric manner. It is reported that an enhanced voltage (two times) and power output (2.5 times) of bi-layer films compared to single layer PVDF-TrFE can be achieved. The enhanced energy harvesting performance is due to the electrostatic contribution, stress induced in the PVDF-TrFE films, high modulus of the bi-layer films over PVDF-TrFE films, complex interface between the PVDF-TrFE and graphene oxide layers aroused from the polarization charges and charge across the GO layer, in addition to the piezoelectric contribution of PVDF-TrFE.

Chapter 5 presents the synthesis of PVDF-TrFE nanotubes to address the lower piezoelectric coefficients and higher poling fields of the PVDF-TrFE in thin film form. Structural and ferroelectric studies were carried out to prove the ferroelectric phase formation and to study the coercive field and polarization orientation. It is shown that the nanotubes have a lower coercive field and have (110) plane along the length of the nanotube with minimal or no c-axis orientations.

Chapter 6 presents the measurements of the piezoelectric coefficient and piezoelectric energy harvesting on to the PVDF-TrFE nanotubes. It is reported the piezoelectric coefficients of nanotubes is almost two times that of the PVDF-TrFE films. The nanotubes with diameter 200 nm exhibited enhanced voltage (5 times) and power (36 times) output over the films. Further reducing the diameter of the one dimensional nanostructures from 200 nm to 50 nm, the voltage output enhanced by 1.7 times and power output by 3.6 times.

Chapter 7 presents the effect of the fixed charges on the output voltage when a layer of charge facilitator is positioned at one side of the piezoelectric energy harvesting device. It is observed that a reduction in the magnitude of the voltage at one side of the AC peak output is attained, resulted in an asymmetric AC output behavior.

Chapter 8 summarizes and concludes the thesis and lists the recommendations for future directions.

1.4 Findings and outcomes/originality of the work

The following are the findings, outcomes and originality of this work

- Superior energy harvesting performance of bi-layers combining PVDF-TrFE film and graphene oxide (Voltage output 2 times, power output 2.5 times) compared to PVDF-TrFE films
- Energy is successfully harvested by means of both piezoelectric and electrostatic manner utilizing the bi-layer films of PVDF-TrFE and graphene oxide.
- We provide an effective approach that improves the energy harvesting performance by addition of a charged dielectric layer with high Young's modulus and high dielectric constant. Our validated concept can be used for highly sensitive pressure sensors, for self-powered systems in flexible electronics, as the bi-layer films are flexible in nature.
- The PVDF-TrFE nanotubes synthesized from melt wetting followed by annealed at 135 °C have (110) planes along the length of the nanostructures with no or very minimal presence of c-axis orientations
- Provided an efficient way to synthesize nanotubes (200 nm diameter) with piezoelectric coefficients almost two times higher than that of the films and hence leads to superior energy harvesting ability (voltage output ~ 5 times, power output ~ 36 times higher than that of films). Reducing the diameter of the one dimensional nanostructures to 50 nm further improves the strain confinement and alignment of dipoles and hence leads to the improved energy harvesting (over nanostructures with 200 nm diameter).
- Mono domain and poly domain behavior corresponds to the polarization component perpendicular and parallel to the length of the nanotubes, respectively.
- The nanotubes have polarization direction at an inclination to the long axis of the nanotubes with coercive field almost three times lower than that of the bulk/ films.
- Lower poling fields for one dimensional nanostructures (~40 % lower) over film counter parts have been achieved.
- The fixed charge at one side of the piezoelectric energy harvester results in the asymmetric AC voltage with reduction in the voltage at one side of AC peak

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Chapter 2

Literature Review

In this chapter, we review the literature related to the dissertation work. We present the various mechanical energy harvesting technologies and introduce the piezoelectric energy harvesting. Various ferroelectric and piezoelectric materials and the fundamental behavior of ferroelectric materials such as polarization orientation and piezoelectric coefficient were further discussed. The recent progresses in the piezoelectric energy harvesting and the methodologies to improve the performance are reviewed. The questions in the literature, which are yet to be answered, were also identified.

2.1 Overview

2.1.1 Energy harvesting technologies

The limited fossil fuels in nature have propelled an immense enthusiasm for the exploration of non-conventional means of energy generation in the last half century. Non-conventional means of energy can be generated from various sources like solar, chemical, thermal and mechanical. Mechanical energy, which is available almost everywhere at all the time and it can be readily derived from the ambient environment. Self-powered systems are particularly important in nanoelectronics, for sensors located in remote places, medical devices implanted into the human body etc. Electrical energy can be harvested from the abundant mechanical vibration energy available in the nature, typically in the range of microwatts to milli watts per cm^3 . Harvesting this kind of energy is particularly useful in low power electronics such as to power sensors, MSN nodes, LED, cardio pacemaker, remote wireless sensing etc.

Various vibration energy harvesting technologies are developed such as electromagnetic¹, electrostatic^{2, 3} and piezoelectric⁴ means. Out of the three, piezoelectric energy harvesting is the efficient option to harvest mechanical energy to electrical energy. In the present work we concentrate on piezoelectric means of energy harvesting.

2.1.2 Piezoelectric energy harvesting

When stress is applied across a piezoelectric material, the material develops an opposite charge across the material surfaces (figure 2.1). This is called direct piezoelectric effect. Similarly, by applying an electric field across the material the strain can be created in the material. This property is called an inverse piezoelectric effect.

Using the inverse piezoelectric effect, as the material develops strain upon the application of electric field; these materials can be used for the applications of actuators. The direct piezoelectric effect can be used to harvest electrical energy from mechanical vibrations and

as pressure sensors. In the present work, we have used the piezoelectric materials to harvest electrical energy by applying a mechanical compression force.

Figure 2.1: Piezoelectric materials under the application of force

Piezoelectric materials exhibit non centro-symmetric crystal structure. Piezoelectricity arises due to the materials internal structure, consists of local separation of positive and negative charges, named electric dipole. In the crystalline phase these dipoles are aligned in one particular direction giving rise to net polarization in the material. For ferroelectric materials, the dipoles are aligned by either electrical poling or mechanical stretching or both. By the application of external force, the dipoles are distorted, producing an electrical displacement and hence develop a charge on the surface of the material. This gives rise to a potential difference across the surface of the material. By connecting the material to external circuit, the electrical energy can be used to drive external load.

Basic equations of piezoelectric energy harvesting is

$$\text{Strain } S = sT + dE$$

$$\text{Displacement current } D = dT + \epsilon E$$

Where d = piezoelectric coefficient, s = compliance of the material, T = stress, ϵ = dielectric constant

By Application of force, the voltage output from the piezoelectric materials is given by

$$V = d_{33} \sigma t / \epsilon$$

Where t = thickness,

Stress applied onto the device is given by $\sigma = E * (\text{strain})$, where E is the Young's modulus

$$V = d_{33} E (\text{strain}) t / \epsilon \quad \dots\dots (1)$$

Current output $I = d_{33}E$ A (strain rate) (2)

Power output $P = V^2/R$ (3)

The electromechanical coupling of the material (K) is given by

$K^2 = \text{Input mechanical energy converted to electrical energy} / \text{input mechanical energy}$

$K = d_{33}(E/\epsilon)^{1/2}$ (4)

2.1.3 Various piezo and ferroelectric materials

The materials such as ZnO, quartz, Rochelle salt etc. exhibit piezoelectric nature in addition to all the ferroelectric materials. Ferroelectric materials ranging from inorganic perovskite materials such as BaTiO₃, PbZrTiO₃ etc. to polymers and small molecules such as PVDF and its copolymers, odd Nylon, croconic acid and some supra molecular networks of charge transfer networks⁵ exhibits piezoelectric nature. The inorganic ferroelectrics possess excellent piezo properties (higher values of piezoelectric coefficient $d_{33} > 100$ pC/N, for PZT, BTO), ferroelectric behavior (higher remnant polarization ~ 75 $\mu\text{C}/\text{cm}^2$ for PZT, low coercive field < 1 MV/m) and pyroelectric properties compared to organic counter parts, but inorganic materials are brittle and cannot sustain high strain rates. Table 2.1 presents the piezoelectric properties of commonly known inorganic and polymeric ferroelectric materials.

The striking properties of organic piezoelectrics (/ferroelectrics) are the flexible nature, ability to sustain high impact stress, strains, strain rates and low dielectric constant compared to inorganic counterparts. In addition organic ferroelectric/ piezoelectric materials are low cost, solution processability, flexibility and easily made into nano structures as well as large areas processability. These properties make organic piezoelectric/ ferroelectric materials suitable in energy harvesting applications where the materials need to sustain high impact stress and high strains and strain rates. Among the many polymer piezoelectrics / ferroelectrics PVDF and its co-polymers attracted much attention due to their high piezoelectric coefficients (~ 20 pC/N) in addition to its high remnant polarization (8-12 $\mu\text{C}/\text{cm}^2$) and low coercive field (50 MV/m) and pyroelectric

coefficients and stable nature at ambient atmosphere⁵⁻⁸. In the present work we chose polymeric PVDF copolymers to further improve the energy harvesting performance of these materials.

Table 2.1: Properties of various piezoelectric materials

Material	Density g/cm ³	Dielectric constant	Piezoelectric const		Coupling factor	Young's Modulus (GPa)
			d (pm/V)/ (pC/N) Charge coefficient	$g \cdot 10^{-3}$ Vm/N Voltage coefficient		
PVDF	1.76	11	20 d ₃₃	200 g ₃₁	16	2
Nylon 11	1.04	4	3-14 d ₃₃	-	-	1.2
PZT-5 ⁴	7.75	1700	370 d ₃₃	11 g ₃₁	34	63
BaTiO ₃	5.7	1700	78 d ₃₁	5 g ₃₁	21	67
ZnO	5.61	10	10-12 d ₃₃	-	-	60

The piezoelectric materials such as ZnO, quartz can directly be used for the energy harvesting applications. In case of ferroelectric materials, the domains are randomly oriented in as synthesized state, and hence these materials required electrical poling, to align the domains and to use them for the energy harvesting applications. The poling field depends on the coercive field of the materials. By applying the field along the polarization direction, the domains/ dipoles can be effectively aligned.

2.1.4 Piezoelectric/ Ferroelectric PVDF and its copolymers

The polyvinylidene difluoride (PVDF) and its copolymer PVDF-TrFE (polyvinylidene difluoride- trifluoroethylene) are amongst the most studied piezoelectric polymers. In a thin film form, PVDF-TrFE/ PVDF exhibits a piezoelectric d₃₃ coefficient value of ~ 20 pm/V, with a low coercive field (50 MV/m) and high remnant polarization (8-12 $\mu\text{C}/\text{cm}^2$)^{5, 9, 10}. PVDF and its copolymers exhibit excellent thermal (up to 90 °C) and chemical stability. These superior properties enable PVDF and its copolymers to be useful for

diverse applications such as non-volatile memories¹¹, transducer¹², actuators¹³, pressure sensors¹⁴ and energy harvesting¹⁵.

PVDF exhibits piezoelectric nature when it is in ferroelectric form. Ferroelectricity in PVDF stems from the molecular dipole moment between the electro negative fluorine and electro positive hydrogen atoms. Nature of PVDF depends on conformation of the molecular back bone. The piezoelectricity of the polymer arises from the changes in the dipole moment upon application of external pressure. So it is important to synthesize the PVDF with permanent dipoles.

Figure 2.2: Structural representation of PVDF polymer (adopted from 16)

PVDF exhibits various conformations when made into thin films as shown in figure 2.2. In all trans (TTTT) conformation, the hydrogen atoms arrange at one side of the molecular back bone and the fluorine atoms at the other side. This gives rise to a net dipole moment/polarization in the chains perpendicular (along b-axis) to the molecular back bone

(c-axis). The corresponding crystal packing is termed as β -phase or form-1 structure. In trans-gauche (TGTG) conformation, the hydrogen and fluorine atoms arranged alternatively at one side of the molecular back bone. In this configuration the net dipole moment will be zero and the material is no more ferroelectric. The corresponding crystal packing is called α -phase or form-2 structure. By poling the α -phase polymer, it is possible to achieve the β -phase. Other form of weak ferroelectric molecular conformation of PVDF is TTTG configuration and the corresponding crystal structure is called γ phase or form-3. In this configuration the total dipole moment is equal to the half of the dipole moment in the form-1 configuration.

In PVDF, the dominant forces are the van der Waals forces. In all-trans configuration, the space available to the fluorine atoms, created by the two carbon atoms is less than the required space. So the all-trans phase is unstable and it favors to crystallize in alpha phase. The various crystal packing of PVDF are having almost equal energies, so it is easy to change from one form to the other form by stretching or poling. So PVDF films required stretching and poling to bring the alpha phase PVDF in to ferroelectric beta phase. Whereas PVDF-TrFE readily comes into the ferroelectric beta phase due to the extra fluorine atom. When PVDF is copolymerized with PTrFE, one of the small hydrogen is replaced by the bigger fluorine atom. Since the alpha phase is closely packed, the bigger extra fluorine atom presence makes the α -phase more unstable and makes it ready to crystallize in the beta phase¹⁷. Ferroelectric phase can be readily formed when the molar ratio of TrFE in PVDF-TrFE is in the range of 20 % to 50 %. Because of this reason we choose PVDF-TrFE, instead of pure PVDF, to further study the ferroelectric and piezoelectric properties. Lower and higher molar ratios of TrFE amount in PVDF leads to defects, reduced dipole moments and/or crystallization. It is reported, at molar ratios of 65 % VDF and 35 % TrFE, PVDF-TrFE exhibited clear hysteresis behavior with good ferroelectric and piezoelectric properties ($\sim 80\%$ crystallinity)¹⁷. In the present work, we chose PVDF-TrFE with 65 % VDF and 35 % TrFE molar ratio to further improve the energy harvesting performance of PVDF-TrFE.

Figure 2.3a shows the schematic of the unit cell in ferroelectric beta phase. It can be observed that the molecular chain corresponds to the c-axis. The polarization between the electro negative fluorine and electro positive hydrogen is along the b-axis¹⁸. In as-synthesized state, the dipoles are randomly oriented. Therefore it is important to know the alignment of b-axis (and the crystal structure) or polarization orientation in the material synthesized, as a result the electric field can be effectively applied along the polarization direction to align the dipoles to maximize the piezoelectric capability of the material.

Figure 2.3: a) Schematic of unit cell, b) Polarization direction. Reprinted by permission from Macmillan Publishers Ltd: [Nature Materials] Ref. (18), copyright (2009)

2.1.4.1 Origin of piezoelectricity

In 1969, Kawai discovered the piezoelectricity in uniaxially drawn and poled PVDF film¹⁹. It is proved that only the ferroelectric phase exhibits piezoelectricity. In general the polymers are semi crystalline in nature. The crystalline and amorphous regions exist in the polymer simultaneously. The piezoelectricity in PVDF arises from the following factors.

- The elastic constant of amorphous and crystalline regions is different. This yields a strain dependence of the polarization in a polarized sample (dimensional contribution).
- The crystalline parts have an intrinsic piezoelectricity due to the strain dependence of their polarization (crystal contribution).

For a poled PVDF, the piezoelectricity is essentially due to the electric moment of the crystalline regions⁷.

The piezoelectricity of a material is different in different crystalline directions. Since the ferroelectric PVDF is having orthorhombic crystal structure with $mm2$ symmetry, the piezoelectric tensor can be described by 5 independent piezoelectric coefficients, longitudinal piezoelectric coefficients d_{31} and d_{32} , the transverse piezoelectric coefficient d_{33} and the shear coefficients d_{15} and d_{24} .

The important coefficients among them are d_{33} and d_{31} . Here the subscripts indicate the Cartesian co-ordinates. In d_{xy} , the first subscript position, x , denotes the electrodes are perpendicular to x - direction or the applied field is along x direction. Applied stress or piezoelectrically induced strain is in y direction.

2.1.5 Basic properties of ferroelectric materials

Ferroelectrics are useful for various applications due to their multi-functionality. All the ferroelectrics are piezo and pyroelectric in nature. This functional behavior makes the material feasible for many kinds of applications.

Ferroelectrics are characterized with spontaneous polarization. It has two equally stable polarization states that can be repeatedly switched by an external electric field. The critical electric field required to reverse the polarization is called the coercive field (E_C). When plotted against field strength (E), the electric displacement (D) consequently draws a hysteresis loop (D - E loop) between opposite polarities. Ferroelectric behavior only observed below certain critical temperature called Curie temperature (T_C), above which the material behaves like a common dielectric. Figure 2.4 shows the typical D - E hysteresis loop of a ferroelectric. The poling fields required to align the dipoles primarily depends on the coercive field. Lower the coercive field of the material, lower the poling fields required.

Figure 2.4: Typical D-E hysteresis loop of a ferroelectric material

2.1.6 Piezoelectric energy harvesting: Various methodologies to improve the performance

The energy harvesting ability of the piezoelectric materials can be improved by improving the intrinsic properties (such as crystal structure) or engineering of the materials structure (dimensions of the material, porous nature, internal stress creation, mechanical alignment). The energy harvesting ability can be further improved by using hybrid cells which combine piezoelectric energy harvesting with other kind of energy harvesting technology which can harvest mechanical energy (triboelectric, electromagnetic or electrostatic) or other source of energy available in the nature such as solar, chemical energy etc.

Here we review the literatures related to improving the crystal structure, engineering of the materials and its application in energy harvesting and hybrid cells.

The voltage and power output of piezoelectric energy harvester is given by

Voltage output $V = d_{33} E \text{ strain } t / \epsilon$ and

Power output $= V^2 / R$

From the voltage and power output equations, it is observed that, the piezoelectric voltage can be enhanced by improving the piezoelectric coefficient, strain in the material, and Young's modulus of the material and using a low dielectric constant material.

The materials in single crystalline form with polarization direction in out of plane, exhibits higher piezoelectric coefficients, whereas random crystal orientations in the material leads to the lower piezoelectric coefficients²⁰. So there is a need for the materials with oriented crystallization. Oriented crystallization in the polymers can be obtained various methods such as nanoconfinement¹⁸, electro spinning²¹ and mechanical stretching²⁰. Confined crystallization has the ability to synthesize various materials with oriented crystallization in zero dimensional¹⁸, one dimensional²² form. Here we review the nanoconfinement effects on the crystal structure of PVDF-TrFE of various dimensions and its implication in various applications.

2.1.6.1 Nano confinement of PVDF-TrFE

The PVDF-TrFE thin films readily form ferroelectric beta phase when annealed at 140 °C and cooled to room temperature. The film will have b axis orientations away from its substrate surface with random orientation. This implies the films with polarization axis oriented randomly^{9, 18} and hence leads to the decrease in intrinsic performance of the films. The crystallization in thin films is initiated by the heterogeneous nucleation. The impurities act as nuclei in the bulk phase. The typical density of impurities in bulk phase is 1 per $10^5 \mu\text{m}^3$. For confined structures where the available space is less than $10^5 \mu\text{m}^3$, the crystallization takes place through homogeneous nucleation^{23, 24}. This leads to the oriented and ordered structure as reported recently by the number of authors^{18, 23}. So by confining the polymer in a dimension well below the average distance between the heterogeneous nucleation centers, it is possible to obtain highly oriented and ordered crystal structures. This could also lead to the preferred orientation by graphoepitaxial alignment of supra molecular structures/ crystals.

Recently intense research is happening in improving the formation of ferroelectric phase in PVDF/PVDF-TrFE and hence its intrinsic properties by nano confinement approach^{18, 22-30}. Z.Hu et al. reported nano imprinting of PVDF-TrFE in 100 nm cavities, which leads to the formation of nano dots of PVDF-TrFE as shown in **figure 2.5**. TEM characterization together with FTIR showed the preferential orientation with b-axis oriented out of the plane of the substrate.

This preferential crystalline behavior leads to the reduced coercive field 10 MV/m in PVDF-TrFE nanodots, five times lower than the coercive field observed for thin films of PVDF-TrFE ($E_c=50$ MV/m)¹⁸. S.J Kang et al showed low voltage operation and low gate leakage current in the polymeric ferroelectric FETs with confined crystallization of PVDF-TrFE in periodic organosilicate (OS) lamellae with 30 nm in width and 50 nm in periodicity formed from PS-PEO block copolymer. Confinement in OS trenches leads to the elimination of structural defects and preferential orientation of PVDF-TrFE, with chain axis parallel to the substrate plane with b-axis away from the substrate surface as confirmed from 2-D XRD. This enabled low voltage operation 8 V, low leakage currents and improved retention times ~ 2 hrs in ferroelectric polymer FET memory²⁵.

Figure 2.5: AFM image of the nano imprinted nanodots, with schematic showing the b-axis in out of plane direction. Reprinted by permission from Macmillan Publishers Ltd: Nature Materials, Ref. (18), copyright (2009).

M. Steinhart et al reported the formation of one-dimensional nanorods and nanotubes of PVDF using solution and melt wetting in Anodic Aluminum Oxide (AAO) templates³¹.

The formation of b-axis along the tube axis for the PVDF 1-D nanostructures is observed²³. They showed the orientation control of the nanostructures by crystallizing 1-D nanostructures by keeping the nanostructures in contact or not with the top extra polymer layer on AAO template. In the presence of extra top layer on the template, the dominant growth phase in the bulk will grow along the long axis of the nanorods and tubes. When the nanostructures are free from the top residue layer, all the crystal orientations which can grow inside the template pores are possible²³.

PVDF generally forms in non-ferroelectric α -phase. Confinement effects affect the crystal structure formed in PVDF. Ferroelectric phase formation has been reported (β or γ) in PVDF by confinement effects. M.C.G. Gutierrez et al reported the formation of gamma phase PVDF inside the AAO pores by solution wetting of PVDF³². S.J. Kang et al observed the formation of gamma-phase PVDF by confinement under a surface energy controlled top layer during melt recrystallization²⁶. The confinement (created by either the AAO walls or the top confined layer) inhibits the formation of alpha-phase crystals^{26, 33, 34}.

Enhanced beta phase formation and reduced amorphous phase is observed for the 1-D PVDF-TrFE nanostructures made from AAO pores compared to thin films. C-axis orientations are absent in the 1-D nanostructures up to a pore diameters of 50 nm (c-axis oriented in a direction perpendicular the nano rod axis)²².

Still very little information is available on the confinement effects on the orientation of the molecular chain axis (and polarization) and hence on the ferroelectric (remnant polarization, coercive field and switching time) and piezoelectric behavior in 1-D nanostructures. Based on macroscopic polarization versus hysteresis loops and XRD, it is reported that the polarization orientation occurs along the length of the nanostructures, for samples synthesized using solution wetting approach³⁴. For the nanostructures synthesized under the same conditions, another report suggests the polarization orientation perpendicular to the length of the nanotubes²⁷. There is no clear information on the polarization orientation in addition to the piezoelectric and ferroelectric properties.

2.1.6.2 Materials structuring and application in energy harvesting

It is recently reported engineering of the materials into various forms such as porous films, patterned into various shapes etc to enhance the piezoelectric energy harvesting performance. Improved energy harvesting in PVDF and its copolymers is observed by strain confinement¹⁵ and stress concentration³⁵. Some strategies along this direction is the preparation of porous PVDF films made by etching the ZnO nanoparticles or ZnO nanorods from the composite films of PVDF and ZnO nanoparticles (/nanorods). Due to the strain confinement in the porous PVDF, 6 fold increments in the voltage output can be observed compared to compact films under a sonic sound input (100db, 100 Hz)¹⁵. Enhancement in the piezoelectric energy harvesting ability is observed in micro patterned PVDF with triangle shape or saw tooth form. The sharp edges lead to the stress concentration in the PVDF-TrFE and hence an improved energy harvesting ability or force sensing ability over flat films³⁵.

Enhanced piezoelectricity has also been observed in the buckled piezoelectric ribbons. Internal stress created in the buckled ribbons lead to the strain gradient induced polarization (flexoelectric effect), which resulted in the 70 % increment in the piezoelectric response in the buckled ribbons over flat counterparts³⁶.

Transparent energy harvesters have been fabricated using graphene electrodes on both sides of the PVDF-TrFE films^{37, 38}. Polarization on to the PVDF-TrFE resulted in doping of the graphene electrodes and hence leads to the lower sheet resistance of the graphene layer. The transparent nanogenerator is successfully employed to for energy harvesting and acoustic actuator applications.

2.1.6.3 Hybrid cells

Hybrid devices are used to harvest multiple energy sources available in nature and hence improve the energy harvesting performance of the devices. Piezoelectric energy harvesters are combined with various other devices to harvest solar energy³⁹, biochemical energy⁴⁰, thermal energy⁴¹ and other kind of mechanical harvesting devices¹.

B. J. Hansen et al., fabricated a hybrid device which can harvest the mechanical energy (piezoelectric element) and chemical energy (Bio Fuel Cell) into electricity. PVDF is used as piezoelectric component. Patterned gold electrodes are coated with CNT, followed by immobilized with glucose oxidase and laccase to form anode and cathode. By immersing the hybrid device into the bio fluid such as blood, the generated current (/energy) will flow between anode and cathode as shown in figure 2.6. It is demonstrated that simultaneous harvesting of bio mechanical and bio chemical energy occurs and show the enhanced performance over individual counterparts as shown in figure 2.6a.

Figure 2.6: Hybrid device demonstration: Bio fuel cell (BFC) and the piezoelectric nanogenerator, a) Voltage output of the combined and independent operation of the Bio fuel cell and PVDF nanogenerator. (b) Circuit diagram used for integration of the hybrid bio fuel cell – nanogenerator device. (c) Schematic of integration of hybrid device (d) Conceptual design of the hybrid device. Reprinted with permission from Ref. (40) Copyright (2010) American Chemical Society.

Since the PVDF is pyroelectric as well, energy is harvested using mechanical and heat stimulus.⁴¹ In another work, solar cell is fabricated on PVDF films, to harvest the mechanical, thermal and solar energy simultaneously (figure 2.7). In the hybrid cell, PVDF harvests the mechanical and thermal energy due to its piezo and pyroelectric behavior, whereas solar cell harvests the solar energy. Piezo, tribo and / or electromagnetic nanogenerators are combined to harvest mechanical stimuli at the same time and hence improve the efficiency of the device.

Figure 2.7: a) Schematic diagram of the fabricated hybrid energy cell. (b) SEM image of the ZnO nanowire array. (c) Output voltage and current of the hybrid pyroelectric and piezoelectric nanogenerators. (d) I-V characteristics of the device under dark and light illumination conditions. The inset shows a photograph of the ZnO nanowire array-P3HT

film solar cell. Reprinted from The Lancet, Ref. (42) Copyright (2014), with permission from Elsevier.

It is recently reported that graphene oxide, which possess electrical charges⁴³, can be used to harvest mechanical energy by means of electrostatic way³. Change in the thickness of the material with the application of mechanical force, will give rise to the electrical current in the external circuit. So it is possible to combine the piezoelectric materials with graphene oxide to further improve energy harvesting capability of the device. In addition, due to the higher Young's modulus of the graphene oxide, it enhances the total Young's modulus of the device and may leads to the enhanced performance.

2.1.7 Rectified output behavior from piezoelectric energy harvester

Recently it is reported a rectified voltage output in ZnO based nanogenerator, either by modifying the morphology or utilizing a charged medium, otherwise the output is AC in nature. Inclined ZnO nanorods morphology lead to the DC output behavior^{44,45}. During the synthesis of vanadium doped zinc oxide, it resulted in two dimensional nano sheets with the nano sheets terminated by negatively charged $V(OH)_4^-$ ions. The negatively charged hydroxide ions repel the electrons flowing towards it's surface and lead to the rectified voltage output upon application of a compressive stress⁴⁶. Similarly for the ZnO nano sheets grown on aluminum foil lead to the formation of Zn:Al layered double hydroxide (Zn:AL LDH), which carries a negative charge, at the interface of aluminum and ZnO nano sheets. The Zn:Al LDH leads to the DC output from ZnO nano sheets grown on aluminum foil upon application of mechanical stress⁴⁷. In both the cases the charged layer is formed during the growth process. Ferroelectric materials usually carry a fixed charge on its surface by means of its polarization. It is interesting to test the effect of the ferroelectric polarization charges on the voltage output behavior when kept in contact with the piezoelectric energy harvester.

2.1.8 Inorganic piezoelectric materials and its composites for nanogenerator applications

In addition to the polymer materials, researchers have also studied the inorganic piezoelectric and composites of polymer and inorganic materials to improve the energy harvesting performance. Thin films of ZnO⁴⁸, or PZT⁴⁹ are grown and transferred on to the flexible substrates to harvest the mechanical energy. Nanostructures of inorganic materials have been grown to further the improve ability of the material to sustain high strain and hence to improve the performance⁵⁰. These nanorods are spread on to the flexible substrates or embedded in a polymer matrix to achieve the flexible and mechanically robust energy harvester. 0-3 composites are made by embedding the nanoparticles or nanorods in to the polymer matrix and obtained flexible and mechanically robust devices. By combining the CNT and inorganic nano particles into the matrix, the piezoelectric energy harvesting performance is further improved by efficient transfer of the voltage generated on to the piezoelectric active nanostructures⁵¹. Furthermore by improving the arrangement of nanoparticles inside polymer matrix, it is shown that the piezo performance has been further improved⁵².

2.2 Questions to be addressed in this thesis and PhD in context of literature

From the voltage output equation (equation 1) it is observed that the device output is proportional to the Young's modulus and piezoelectric coefficients.

1. The challenge is Young's modulus of the material related to strain generated in the material, which in turn affects the energy harvesting ability. Can we combine piezoelectric material with high Young's modulus material to improve the energy harvesting ability?

In addition, upon the application of force, there is a change in the thickness of the piezoelectric films. Electrostatic nanogenerators generate energy when there is a change in the thickness. So there is a possibility to improve the energy harvesting performance by combining the piezoelectric material with electrostatic nanogenerator.

- The challenge is how we can improve the energy harvesting ability by combine the piezoelectric material with high Young's modulus and charged material?
2. The energy harvesting ability is directly proportional to the piezoelectric coefficient. From the literature it is observed that nanostructures synthesized from confined environment have oriented crystallization. In addition, the voltage output is proportional to the thickness of the piezoelectric material. So can we use 1-D nanostructures synthesized in the confined environment to improve the energy harvesting performance? We aim to unravel the properties in terms of piezoelectric coefficients, ferroelectric properties and polarization orientation of these nanostructures to further utilize them in the energy harvesting application.
 3. It is observed that the rectifying output from the nanogenerators when the nanostructured piezoelectric material is terminated with a charged material. The charged material is formed during the growth process. Can we develop a universal charged layer, which can be used with any piezoelectric material and hence achieve the rectified output from the energy harvester? Since ferroelectric materials have fixed charge on the surface by means of its polarization, can we use the ferroelectric material to achieve the rectified output from the piezoelectric energy harvester? If the charge on ferroelectric leads to the rectified output in piezoelectric energy harvester, this will enable a generalized method to achieve a rectified voltage output just by coating a ferroelectric material on any piezoelectric energy harvesting device.

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Chapter 3

Experimental Methodology

The methodologies to prepare the PVDF-TrFE films, nanotubes and bi-layer films of PVDF-TrFE and graphene oxide, fabrication of energy harvesting device and testing, various important structural and electrical characterizations performed are summarized in this chapter.

3.1 Rationale for selection of materials:

Piezoelectric material

Among the many polymer ferroelectric/piezoelectric materials, polyvinylidene fluoride (PVDF) and its copolymers polyvinylidene difluoride- trifluoroethylene (PVDF-TrFE) exhibit high piezoelectric coefficients and are stable in the ambient atmosphere¹. In addition, the polymer films are flexible and easy to process. The piezoelectricity in these polymers is due to their ferroelectric nature. PVDF-TrFE readily forms into the ferroelectric phase, whereas PVDF forms non-ferroelectric alpha phase predominantly without special treatment. So we chose PVDF-TrFE as the piezoelectric active material in the present work.

High Young's modulus charged material

Graphene oxide attracted interests recently due to its versatile properties. The graphene oxide possesses charges due to the functional groups attached to it^{2, 3}. In addition free standing papers made from the graphene oxide are flexible and have high Young's modulus (32 GPa)⁴. Electrostatic nanogenerator is fabricated using graphene oxide by utilizing the charge in it³.

Therefore, we chose graphene oxide as the high modulus charged material and fabricated bi-layer films of PVDF-TrFE and graphene oxide to study the energy harvesting ability.

3.2 Typical experimental procedure

Figure 3.1 shows the flowchart of typical experimental procedures in this thesis. In the present thesis, we have fabricated PVDF-TrFE films, nanotubes and bi-layer films of PVDF-TrFE and graphene oxide. Then the energy harvesting performance of the same is measured. Voltage and power output is measured to study the energy harvesting performance of bi-layer films, nanotubes and films.

Figure 3.1: Flow of experimental of fabricating and testing the energy harvesting device

3.3 Synthesis

3.3.1 Fabrication of PVDF-TrFE films

PVDF-TrFE granules (mole ratio: 65:35) were dissolved in butanone-2 with a weight fraction of 70 mg/ml. Thickness of the films made from drop casting was 30 μm . The films were annealed at 135 $^{\circ}\text{C}$ for two hours and cooled to room temperature naturally to improve the ferroelectric crystalline phase. The thickness if the films are 30 μm . The films were then poled using ITO as the bottom electrode and sputter coated gold on to the PVDF-TrFE films as the top electrode. Energy harvesting device is fabricated in capacitor form simply by making the gold electrodes on both sides of the PVDF-TrFE films.

3.3.2 Synthesis of bi-layers combining of PVDF-TrFE and graphene oxide films

PVDF-TrFE films are synthesized as mentioned above. Graphene oxide (GO) was synthesized using modified Hummers method^{5, 6}. Pre-oxidized graphite flakes were prepared by mixing 10 g of phosphoric acid (H_3PO_4) and 10 g of potassium per sulfate ($\text{K}_2\text{S}_2\text{O}_8$) into 30 ml of concentrated sulfuric acid (H_2SO_4) containing 20 g of graphite flakes. The as-prepared mixture was stirred at 80 °C for 5 hours to obtain pre-oxidized graphite flakes. The as-produced pre-oxidized graphite flakes (~ 3 g) and about 9 g of potassium permanganate (KMnO_4) were mixed into 70 ml of concentrated sulfuric acid (H_2SO_4) solution, while keeping the reaction temperature well below 20 °C. The reaction temperature was increased to 40 °C after the completion of reaction. Thereafter, 350 ml of DI water was mixed into the solution. Then H_2O_2 -30% (7.5 ml) was added into the above solution to maximize the rate of oxidation reactions. Then the solution was kept aside for some time to allow the oxidized product to settle down. The as-obtained sediment product was washed and centrifuge with DI: HCl (10:1 by volume) and left for sonication for several hours. The as-sonicated solution was further washed with DI: HCl (10:1 by volume) and DI water, respectively, to obtain a brown solution of graphene oxide (GO) nano-flakes. The bi-layer films combining PVDF-TrFE and GO were obtained by drop-casting the GO solution onto the PVDF-TrFE film followed by vacuum drying at room temperature.

3.3.3 Synthesis of PVDF-TrFE nanotubes

Figure 3.2: Schematic of melt wetting process

1-D PVDF-TrFE nanostructures are synthesized by using melt wetting approach^{7, 8} as shown in figure 3.2. AAO templates of pore diameter 200 nm, height 60 μm commercially supplied by Whatman are used. Approximately 30 μm thick drop cast free standing PVDF-TrFE film is placed on top of the AAO template. The template is then heated above the melting temperatures at 175 °C to completely wet the walls of the AAO with PVDF-TrFE to form the nanostructures followed by annealing at 135 °C for 10 hrs to improve the formation of ferroelectric β phase and crystallinity.

3.3.4 Freestanding nanostructures: PFM characterization

Free standing PVDF-TrFE nanostructures are obtained by etching the residual layer onto the AAO templates by chemical plasma etching followed by dissolving the AAO template in 1M NaOH solution in water. The solution then is cleaned with water with centrifuged process for 5 to 6 times to remove the salts formed during the etching of AAO. The freestanding nanostructures are then transferred on to the gold coated glass substrates from the water solution. Piezo Force Microscopy (PFM) [NT-MDT] is used to study the switching behavior at nano scale and to measure the piezoelectric d_{33} coefficient. Gold coated CSG-10 tips are used during the measurement (30 nm dia, 0.15 N/m). The sample and tip contact resonant frequency is 236 KHz. Measurements are carried out at 50 KHz for piezoelectric coefficient and at resonance frequency (236 KHz) for PFM spectroscopy in a direction perpendicular to the long axis of free standing nanotubes cluster.

3.3.5 Fabrication of nanotubes nanogenerator

PVDF-TrFE nanotubes were synthesized as described previously. To fabricate the nanotubes nanogenerator, the AAO template was dissolved in 1 M NaOH in water, to obtain the PVDF-TrFE nanotubes supported on to the residual layer of PVDF-TrFE. Gold is deposited as top and bottom contact of the device. Sputter coater is used to deposit the gold electrodes. Gold is deposited at 10^{-1} mbar, 30 mA current. A thin layer of PMMA, of thickness approximately 5 μm is formed on top of the nanotubes to avoid the penetration of gold into nanotubes and short the device.

3.3.6 Fabrication of piezoelectric energy harvesting with polarization charge at end of the device

PVDF-TrFE films are prepared on both sides of the aluminum foil by drop casting the PVDF-TrFE solution on to the aluminum foil. The films are then annealed at 135 °C for 2 hr. The PVDF-TrFE film used to measure the piezoelectric response is called piezoelectric active film and the other film which is used to create the charge at one end of the energy harvester is named as charge facilitator.

Reference films are made by poling the piezoelectric active film at fields of 75 MV/m. while the charge facilitator is used as synthesized. To test the effect of charge on the voltage output behavior when placed in conjunction with the piezoelectric energy harvester, the charge is created by poling the charge facilitator film at two different fields 60 MV/m and 75 MV/m.

3.4 Characterizations

3.4.1 Piezo Force Microscopy (PFM)

Theory

Piezo Force Microscopy is used to study the polarization orientation, ferroelectric and piezoelectric properties at nano scale. Piezo Force Microscopy employs the strong coupling between the electric and mechanical nature of the ferroelectric/piezoelectric materials. Here we used gold coated conductive AFM tips (NT-MDT, CSG-10 tips). The measurements are performed at 50 kHz. The resonant frequency of the tips is 236 kHz. The AFM works in contact mode in this configuration. In PFM mode, voltage is applied between the tip and the sample, and the generated mechanical displacement in the sample at the proximity of AFM tip is measured accurately up to a pm level using a lock-in amplifier. Figure 3.3 shows the schematic of the AFM configuration for use in PFM mode.

Figure 3.3: Schematic of Piezo Force Microscopy

A voltage V_{dc} is applied between the tip and the sample together with a small AC voltage as given by the following eq.

$$V_{tip} = V_{dc} + V_{ac} \cos(\omega t + \phi)$$

Due to this applied voltage, the piezoelectric sample generates a displacement

$$A = A_{dc} + A_{1\omega} \cos(\omega t + \phi),$$

$$A = d_{33} V_{dc} + d_{33} V_{ac} \cos(\omega t + \phi)$$

Where A_{dc} = Static surface displacement, ϕ is the phase shift between the V_{ac} and the voltage induced deformation $A_{1\omega} = d_{33}^{eff} V_{AC} + \frac{\partial C}{\partial Z} (V_{DC} - V_s) V_{AC}$. The first term here is the deformation purely based on the piezoelectric response described by piezoelectric coefficient d_{33}^{eff} . The second term is the local electrostatic deformation caused by both local and non-local Maxwell stress. V_s stand for the surface potential and c is the total capacitance of the tip and the sample system.

Piezo Response and Phase Imaging:

PFM can be used for imaging of domains in a ferroelectric sample. For imaging mode, The AFM is in contact mode and a small AC voltage is applied between the tip and the sample. The lock-in amplifier gives the phase and magnitude signals of ferroelectric domains.

Here we can obtain both the magnitude and phase of the piezoelectric response in accordance with the applied AC voltage. The contrast in phase image arises due to the orientation difference of the domains with respect to the applied signal. In amplitude image, the contrast arises based on the amount of mechanical deflection a domain can create.

PFM has the ability to separate vertical deflection and lateral deflections by following the laser spot on to the photo diode. This will help in imaging the out of plane and in-plane domains. By having the vertical PFM image (utilizing vertical deflections), together with Lateral PFM images (lateral deflection of the laser spot on to the photo diode) in two perpendicular directions we can completely provide the domain orientation 3 dimensionally.

Measurements of Piezoelectric Coefficient by PFM

PFM allows us to measure the effective d_{33} piezoelectric coefficient by following the vertical deflections (out of plane of the sample), by applying a voltage between the tip and sample in out of plane direction. Also by utilizing the lateral movement of the tip, we can find the d_{15} or d_{31} coefficient.

An AC voltage (V) is applied between the conductive tip and bottom electrode of the tip. The generated out of plane piezo response (A) is extracted from the vertical- deflection given by the photo detector (z). The amplitude of the tip vibration is derived by multiplying the deflection signal with the calibration constant of photodetector sensitivity as shown below.

$$A = z * (\text{calib const}) = d_{33} V$$

Where z = vertical deflection signal of the cantilever from the photodiode (nA), V = Applied AC voltage.

The calibration constant is calculated from the slope of the force versus displacement curve of the AFM.

Here we measured the vertical piezo response signal (tip deflection) with respect to the AC voltages ranging from 0 to 10 V. The slope of this curve is used to measure the effective d_{33} piezoelectric coefficient.

d_{33} = slope of the Piezo response vs AC voltage curve * calibration const/ lock-in amplifier gain

The vertical piezo response will be used to measure the effective d_{33} piezoelectric coefficient, whereas lateral piezo response will be used to measure the d_{31} coefficient.

PFM spectroscopy (Hysteresis Loops and Coercive Field Measurement)

This option enables us to investigate the ferroelectric behavior at nanoscale. We can measure the piezo hysteresis loops by following the phase signal and the magnitude of the piezo response provides the characteristic butterfly behavior. This will in turn gives the information about the polarization orientation.

The PFM spectroscopy can be performed by sweeping a DC voltage, which is above the coercive voltage, from -ve to +ve polarity., together with an AC voltage between the tip and the sample. Using a lock-in amplifier we can measure the piezo response accurately up to a pico meter (pm).

3.4.2 X- Ray diffractometer (XRD)

The discovery of X-rays by Röntgen a German scientist, whose wavelength is of the order of crystal lattice parameter enabled scientists use them to probe the crystal structure. When X-rays incident on a material, the X-rays diffract from the atomic lattice of the material following the equation $n\lambda = 2d \sin \theta$; where, λ = wavelength of the X-rays, d = atomic spacing, θ = angle between the incident x-rays and atomic plane. Max Von Laue, William Lawrence Bragg and William Henry Bragg extensively studied the X-ray diffraction by crystals. William Lawrence Bragg and his father William Henry Bragg studied the crystal structure analysis using X-Ray diffraction.

XRD is used to study the crystal structure and the crystal planes present in the PVDF-TrFE film and nanostructures. Shimadzu X-ray diffractometer is used to carry out the crystal structure identification. In the present experiment Cu target is used to generate X-rays. The wavelength of the X-rays generated is $1.54 \text{ \AA}$. The measurements are carried out in 2θ mode in a scan range $16^\circ - 45^\circ$.

3.4.3 Scanning Electron Microscope

When the electron beam incident on a material surface, the material emits the secondary electrons, back scattered electrons, auger electrons etc. In the scanning electron microscope, by using the secondary electrons emitted from the materials surface, the morphology of the material can be imaged. In the present experiment field emission scanning electron microscope JEOL JSM-7600F is used to image the morphology of PVDF-TrFE nanostructures. Sputter coater is used to deposit the gold coating on the material surface to make the surface conducting.

3.4.4 Transmission Electron Microscope

In transmission electron microscopy mode, electrons transmitted through the material are collected onto the photographic plate to image the materials morphology. The tubular nature of the material can be identified using TEM as the electron beam pass through the material. Low voltage TEM (ZEISS) is used to view the tubular nature of the PVDF-TrFE nanostructures synthesized.

3.4.5 Energy Harvesting Measurements

The energy harvesting device is made in a capacitor mode. Top and bottom gold electrodes are made on to the piezoelectric active material using sputtering. The energy harvesting ability of the materials is measured by measuring the voltage and power output under a dynamical compression pressure applied at a frequency of 1 Hz. The compression pressure is applied by using Instron 8516. Figure 3.4 shows the schematic of the EH measurement. The energy harvesting device is placed on a movable bottom platen. The compression force is applied when the bottom platen hits the top plate. The applied force is measured by using the force sensor which located on the top platen. The bottom plate is fixed at 4 mm away from the top plate. By increasing the movement of the bottom plate above 4 mm, will lead to increased compression pressure on the sample.

The voltage output from the device is measured by using the oscilloscope (Yokogawa). The power output of the device is measured by measuring the voltage across a load resistor.

Figure 3.4: Schematic of experimental setup to measure the energy harvesting performance

3.4.6 General characterizations

The thickness of the PVDF-TrFE and GO films are measured using profilometer (KLA Tencor). Adhesion force between PVDF-TrFE and graphene oxide layers in bi-layer form is measured in tensile mode (by applying a shear force between the two layers). The Young's modulus of the films is measured by dynamical mechanical analysis (TA instruments, DMA Q800). Dielectric constant and capacitance versus voltage measurements are carried out using LCR meter (Agilent E4980A). Polarization versus electric field hysteresis loop and polarization charge measurements are carried out using radiant ferroelectric tester equipped with high voltage amplifier up to 4000 V.

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Chapter 4

Bi-layer Films of PVDF-TrFE with Graphene Oxide

Ferroelectric materials have attracted interest in recent years due to their application in energy harvesting owing to its piezoelectric nature. Ferroelectric polymers are flexible and can sustain larger strains compared to inorganic counter-parts, making them attractive for harvesting energy from the mechanical vibrations. In this chapter, the energy harvesting performance of the PVDF-TrFE is improved by creating the internal stress in the films, improving Young's modulus of the device and harvesting the electrostatic energy in addition to the piezoelectric energy by combining PVDF-TrFE with a charged material. The bi-layers films of PVDF-TrFE and graphene oxide (GO) showed improved energy harvesting performance over single films alone by means of the above mentioned reasons.

4.1 Introduction

Piezoelectric materials have attracted much interests in recent days in energy harvesting due to their ability to convert mechanical energy into electrical energy. Energy harvesting has become increasingly important as there is a need for self-powered systems particularly in miniaturization of devices. Various inorganic and organic materials exhibit ferroelectric and piezoelectric nature. In general, the inorganic materials such as lead zirconium titanate, barium titanate etc. have higher piezoelectric coefficients but are brittle, whereas the polymer ferroelectrics Poly (vinylidene difluoride - trifluoroethylene) [PVDF-TrFE] have lower piezoelectric coefficients but are flexible and can sustain larger strains compared to inorganic counterparts^{1, 2}. In the present work polymeric ferroelectric PVDF-TrFE is chosen due to its high piezoelectric coefficients among polymer ferroelectric³ and can be readily form into the ferroelectric phase⁴.

Various approaches have been employed to improve the energy harvesting performance using piezoelectric/ferroelectric materials. Hybrid devices are made to combine the various vibration energy harvesting mechanisms in one device such as electrostatic and piezoelectric energy harvesting⁵ (using ZnO nanorods and polyethylene dielectric layer), piezoelectric/triboelectric and electromagnetic approach⁶ to improve the energy harvesting performance. Piezoelectric materials are combined with photovoltaic devices to harvest energy from mechanical stimuli as well as solar energy⁷. Electrostatic doping of graphene is employed to obtain the improved energy harvesting of PVDF-TrFE using graphene/PVDF-TrFE/graphene device structure⁸. In addition, by creating the internal stress into the material, the piezoelectricity can be enhanced further by means of flexoelectricity⁹ and by aligning the molecular chains¹⁰.

Recently, Graphene oxide (GO) attracts significant interest due to its versatile functionality attributed to the different functional groups such as carboxyl, ketonic, hydroxyl, epoxy^{11, 12}. GO and functionalized GO have found applications in sensing,¹² as electrode material for supercapacitor etc.¹³ GO layers possess negative charges due to the presence of

functional groups.^{11, 14, 15} Utilizing the charge on GO, electrostatic nanogenerator has been fabricated to harvest the energy from mechanical vibrations.¹⁵

Further high performance unimorph actuators are fabricated by combining the piezoelectric material with high modulus elastic layer such as carbon fiber¹⁶ or stainless steel^{17, 18}

Piezoelectric materials generate voltage upon application of the force. The applied force in turn results in the change in thickness. By combining the piezoelectric PVDF-TrFE with a charged material, it is possible to harvest both piezoelectric and electrostatic components upon application of a force. Here, we synthesize the bi-layer films combining PVDF-TrFE and graphene oxide to harvest energy by means of both electrostatic and piezoelectric manner in order to improve the Young's modulus and create the internal stress in the PVDF-TrFE.

4.2 Results and Discussion

4.2.1 Structural characterizations and energy harvesting performance of PVDF-TrFE films

Ferroelectric beta phase formation of the PVDF-TrFE films is confirmed by X-ray diffraction measurements as shown in Figure 4.1a. The crystals are predominantly orientated corresponding to (110)/(200) planes along with (201)/(111) orientations. The films then are poled at fields of 30 MV/m at 105 °C to orient the dipoles. Sputter coated gold on top of the films was used as the top electrode and ITO as the bottom electrode during poling. The PVDF-TrFE films are released from ITO glass and then sputter coated with gold to measure the energy harvesting performance. The non-poled films did not show any voltage output, upon subjected to the compression pressure. Whereas, the poled PVDF-TrFE films showed a peak voltage output of approximately 2 V as shown in figure 4.1b, when subjected to a dynamic compression pressure of 0.32 MPa at 1 Hz. Similar voltage output values were reported for the PVDF-TrFE films in literature.¹⁹ S-H Bae et al., reported a voltage output of approximately in the range 2- 3 V for PVDF-TrFE films with

graphene as electrodes.⁸ D. Chen et al., reported a voltage output of 1-2 V for the mesoporous PVDF-TrFE films.²⁰ J-H Lee et al., reported a piezoelectric voltage output of approximately 0.7 V under 30 % stretching.²¹

4.2.2 Charge on to the graphene oxide layer

Graphene oxide was synthesized using modified Hummers method. FTIR spectra of GO films (figure 4.2a) shows the presence of functional groups such as epoxide (970 cm^{-1}), hydroxyl (1150 cm^{-1}), COO- ($1558, 1575\text{ cm}^{-1}$), ketonic (1739 cm^{-1}) and C-O groups (1030 cm^{-1}). The presence of various functional groups makes the GO intrinsically charged. Figure 4.2b shows capacitance versus voltage (C-V) measurements that are carried out on metal dielectric semiconductor capacitor (Al/P-Si/SiO₂/GO/Au), to study the nature of the charge and amount of charge present in the GO films. For the p-type silicon, the depletion region of Al/P-Si/SiO₂/Au was observed in negative voltage region. By incorporating GO films, for Al/P-Si/SiO₂/GO/Au capacitor, the depletion region of C-V curve is shifted to positive values, this suggests the charge in GO as negative. The amount of charge on GO is calculated from the shift in flat band voltage (δv) of C-V curves with and without GO layer. The measured charge on GO is approximately $1.7 \times 10^{-4}\text{ C cm}^{-3}$ ($Q = \delta v / C$, where C is the capacitance).

4.2.3 Morphological characterization of bi-layer films

Figure 4.3 shows the schematic of the energy harvesting device made from bi-layer films combining PVDF-TrFE and GO, field emission scanning electron micrographs (FESEM) of PVDF-TrFE, graphene oxide and cross section of bi-layer films. Bi-layer films are obtained by drop casting the GO solution on PVDF-TrFE films followed by vacuum drying. As shown in figure 4.3b, PVDF-TrFE films show the typical needle shaped ferroelectric beta phase. Figure 4.3c shows graphene oxide morphology. The typical corrugated surface morphology was observed. From the cross section images of bi-layer films (figure 4.3d), it is observed that there are no gaps between the PVDF-TrFE and GO layers. The thickness of the graphene oxide layer is approximately $19\text{ }\mu\text{m}$ and PVDF-TrFE layer is $32\text{ }\mu\text{m}$. The

fabricated energy harvester device made from bi-layers is flexible, bendable and rollable and is free standing as shown in figure 4.3e and f. GO films are deposited on poled and non-poled PVDF-TrFE films to obtain the bi-layer films.

The adhesion strength of the graphene oxide onto the PVDF-TrFE films are measured using pullout method (in tensile mode). Figure 4.4 shows the stress versus extension curves of the bi-layer films of PVDF-TrFE and graphene oxide. The maximum stress value represents the adhesion strength of the graphene oxide onto the PVDF-TrFE film. In bi-layer form, graphene oxide deposited on non-poled PVDF-TrFE layer exhibits an adhesion strength of 0.062 N/mm^2 whereas graphene oxide deposited on poled PVDF-TrFE films have an adhesion strength of 0.12 N/mm^2 . The adhesion of the GO films with the non-poled PVDF-TrFE films is poor because of the hydrophobicity and chemical inertness of PVDF-TrFE (measured adhesion strength 0.062 N/mm^2). On contrast, the GO films adhered well with the poled PVDF-TrFE films (with the hydrogen terminated surface); suggesting the electrostatic interaction between the poled surface of PVDF-TrFE and functional groups in the GO films (measured adhesion strength 0.12 N/mm^2). In bi-layer configuration, the GO films are in contact with the hydrogen terminated surface of the PVDF-TrFE films.

Figure 4.1. (a) X- Ray Diffraction pattern of PVDF-TrFE films, (b) Voltage output of the poled PVDF-TrFE film under a compression pressure of 0.32 MPa

Figure 4.2. (a) FTIR spectra of GO films, (b) Capacitance versus voltage measurements on Al/p-Si/SiO₂/GO/Au and Al/p-Si/SiO₂/Au capacitors

Figure 4.3. Micrographs and macroscopic images of bi-layer energy harvesting device: a) Schematic of the bi-layer films energy harvesting device, b,c) Surface morphology of PVDF-TrFE film and graphene oxide layer respectively d) Cross section image of bi-layer films e) Bi-layer and f) PVDF-TrFE film energy harvester devices (both are freestanding, flexible, bendable and rollable)

Figure 4.4. Adhesion stress versus extension for bi-layer films

4.2.4 Energy harvesting performance of bi-layer films

PVDF-TrFE and bi-layer films are tested for the energy harvesting performance by subjecting them to dynamical compression pressure at 1 Hz frequency. Poled PVDF-TrFE films exhibited a voltage output of approximately 2 V when subjected to a dynamic compression pressure of 0.32 MPa (Figure 4.5a). Bi-layer films, with non-poled PVDF-TrFE layer, showed a voltage output of approximately 0.3 V at compression pressures 0.32 MPa (Figure 4.5b). This voltage output corresponds to the electrostatic component, which is due to the change in the capacitance of the films corresponding to the thickness variation when subjected to the compression pressure.¹⁵ The bi-layer films, with poled PVDF-TrFE layer, showed a peak voltage output of approximately 4 V at a compression pressure of ~0.32 MPa applied at 1 Hz frequency as shown in Figure 4.5c (from here on, bi-layer films refers the bi-layer films obtained from poled PVDF-TrFE with GO layer on hydrogen terminated surface, unless otherwise stated). The reverse in the polarity of voltage output of bi-layer films when reversing the contacts of the device, suggests origin of the output from the device (Figure 4.6). It is also observed that the voltage output of the bi-layer films, fabricated from poled PVDF-TrFE films, is greater than the sum of voltage output from single poled PVDF-TrFE films and the electrostatic component and is approximately two times higher than that of pure PVDF-TrFE films. This clearly shows the enhanced voltage output of the PVDF-TrFE films in the presence of graphene oxide films. Kim et al.,²² and

Gupta et al.,²³ have reported a rectifying output when nanostructured (nano sheets) piezoelectric materials are in contact or terminated with a charged surface. The rectified output is due to the presence of unipolar surface, resulted from the anionic hydroxides, at one end of the piezoelectric material. In contrast, in our work, the PVDF-TrFE film is in contact with the charged material, graphene oxide, leading to the enhancement in the AC voltage output values due to the non-uniform distribution of charge in GO associated with the presence of various functional groups. As the fabricated bi-layer energy harvester device is freestanding and is flexible, bendable and rollable (figure 4.3e), the energy harvester can be easily integrated with the flexible electronic devices to obtain the self-powered system.

Figure 4.5. Working mechanism of the bi-layer films energy harvesting device: a) Piezoelectric voltage output from the poled PVDF-TrFE film, b) Electrostatic component: voltage output from the bi-layer films, with non-poled PVDF-TrFE layer, c) voltage output from the bi-layer films device consisting of both electrostatic and piezoelectric components.

Figure 4.6. Voltage output from the bi-layer energy harvesting device by reversing the contacts

The thickness of the GO layer in bi-layer films is varied between 3 μm to 30 μm (3 μm , 20 μm , 30 μm) to optimize the device performance. With 3 μm GO films, the peak voltage output of bi-layer films is approximately 3 V. The output of the bi-layer films increases to 4 V, when the GO films are of 20 μm thick. The output voltage remains the same (4 V) when increasing the thickness of the GO films to 30 μm . The increased voltage output with increased GO thickness from 3 μm to 20 μm is due to the higher charge in GO. This can be further confirmed from the energy harvesting measurements on the samples consist of solely the electrostatic components (measured from the bi-layer films formed from non-poled PVDF-TrFE films: For the 3 μm thick GO film, the voltage output is approximately 0.1 V, for the 20 μm film the voltage output is approximately 0.3 V. There is not much change in the voltage output values for even higher thickness of GO films. This may be due to the poor adhesion between the GO and non-poled PVDF-TrFE films with increasing thickness). Therefore, by further increasing the GO thickness in bi-layer films, made from poled PVDF-TrFE, the output voltage remains approximately at 4 V, due to the screening of electrical output in the graphene oxide, there is not much contribution from the electrostatic component with increasing the thickness further. Furthermore, bi-layer films are fabricated using 10 μm thick PVDF-TrFE films by keeping the GO layer at approximately 20 μm . Enhanced voltage output is still observed even with 10 μm thick PVDF-TrFE films. The 10 μm films showed a voltage output of 0.5 V (lower output voltage compared to the voltage output of PVDF-TrFE films of thickness 32 μm , since the piezoelectric voltage output is proportional to thickness), whereas the bi-layer films

showed a voltage output of approximately 1.5 V (Figure 4.7). This suggests enhanced voltage output can be observed from bi-layer films, independent of thickness of PVDF-TrFE film.

The bi-layers films obtained from depositing the GO layers on fluorine terminated (negatively poled) surface showed lower voltage output compared to the PVDF-TrFE films (Figure 4.8). The lower voltage output is either due to the poor adhesion of negatively charged GO on to the fluorine terminated surface or the electrostatic component may be just subtracted in this case.

Figure 4.7. Voltage output 10 μm thick PVDF-TrFE film: a) PVDF-TrFE film and b) bi-layer films

Figure 4.8. Voltage output from a) PVDF-TrFE film and b) bi-layer films with GO on fluorine terminated PVDF-TrFE surface

The power output of the bi-layer and PVDF-TrFE films is obtained by measuring the voltage across a load resistor. The power output measured in this method is significant, compared to the power measured from the open circuit voltage and short circuit current, which is always higher than the original power output from the device.^{24, 25} Voltage is measured across the resistors ranging from 43 k Ω to 6.7 M Ω (0.043, 0.1, 0.576, 1, 6.7 M Ω). Figure 4.9 shows the power output measured across various resistors for bi-layer films and PVDF-TrFE films. A maximum in the power output is observed across a load resistor of 1 M Ω for both bi-layer films and PVDF-TrFE films. A maximum power value of 4.41 μWcm^{-2} is observed for the bi-layer films, whereas the PVDF-TrFE films have a maximum power output of 1.17 μWcm^{-2} .

Table 4.1 summarizes the power density and output voltage of bi-layer films and PVDF-TrFE films alone. The output voltage of bi-layers films is 4 V, which is two times that of PVDF-TrFE films and power density of bi-layer films is 4.41 μWcm^{-2} , which is approximately 2.5 times that of PVDF-TrFE films.

The output voltage of the bi-layer and PVDF-TrFE films are measured with respect to the applied pressure. PVDF-TrFE films are poled with fields of 30 MV/m at 105 °C. Figure 4.10 shows the applied pressure versus voltage output of the bi-layer and PVDF-TrFE films. The voltage output is measured in the compression pressures range from 0.024 MPa to 0.32 MPa. It is observed that the voltage output increases with increasing the applied compression pressure and is almost linear in the measured compression pressure range. The increase in output voltage with applied pressure in both bi-layer and the single PVDF-TrFE films suggest that the output voltage of the samples in this work is of piezoelectric origin. This further confirms that there is no voltage originating from the sliding of the graphene sheets or sliding at the interface between the PVDF-TrFE films and GO films.

The device is tested for cycling stability. Dynamic compression pressure of 0.32 MPa is applied at a frequency of 1Hz, and corresponding voltage output is measured over 1000 cycles as shown in figure 4.11. In the measured cycles range, the output voltage is almost constant, no decrease in the performance is observed even after 1000 cycles. (The slight

change in the output voltage during the cycling is due to the changes in the applied force, limited by the instrument).

Figure 4.9. Power output of the bi-layer and PVDF-TrFE films

Table 4.1: Energy harvesting performance of bi-layer and PVDF-TrFE films

	Voltage Output (V)	Power density ($\mu\text{W cm}^{-2}$)
PVDF-TrFE film	2	1.77
Bi-layer films of PVDF-TrFE and graphene oxide	4	4.41

Figure 4.10. Compression pressure versus voltage output of bi-layer and PVDF-TrFE films

Figure 4.11. Cycling stability of bi-layer films

The increased in the voltage output in the bi-layer films compared to PVDF-TrFE alone is due to the following reasons. By applying the dynamic compression force, which leads to the change in the thickness and hence change in the capacitance, results in the voltage

output. This corresponds to the electrostatic component (figure 4.5b, due to the presence of charge on GO). In addition, it is observed that the films slightly rolled after the formation of GO layer on to the PVDF-TrFE. This suggests the residual stress created in the PVDF-TrFE layer by deposition of GO layer. Figure 4.12 shows the XRD spectra of PVDF-TrFE films before and after deposition of GO layer. It is observed a shift in the XRD peak positions to higher 2 theta values for PVDF-TrFE layer after deposition of GO. The shift in the XRD peak towards the higher 2 theta values suggests the tensile stress created in PVDF-TrFE due to the bonding of GO layers. The internal tensile stress created in the PVDF-TrFE films could have aligned the molecular chains and hence lead to the enhanced piezoelectricity^{9, 10} of the films and hence contributed to the observed enhanced piezoelectric energy harvesting performance of the bi-layer films. The rolling of the bi-layer film after deposition of graphene oxide layer further indicates the stress/strain gradient in the bi-layer film, which in turn creates the spontaneous polarization upon application of dynamic pressure (by means of flexoelectricity) and hence lead to the enhanced piezoelectricity of the bi-layer films. In addition, because of the curved nature of the films, upon application of the external pressure, the films exhibit enhanced stress. This is another factor that contributed to the enhanced energy harvesting performance of the bi-layer films.

Further, Voltage output from the piezoelectric energy harvesting device is:

$$V = g_{33} (\text{stress applied}) d$$

Where g_{33} = Piezoelectric voltage coefficient, Stress applied= Young's modulus of the device * Strain, d =thickness

$$V = g_{33} * \text{Young's modulus} * \text{Strain} * d \quad (1)$$

In the bi-layer form, the stress applied depends on the Young's modulus of the bi-layer films. The Young's modulus of bi-layer films is measured to be 2.88 GPa, whereas PVDF-TrFE films is 1.5 GPa from the stress-strain curves (Figure 4.13). Increased Young's modulus of the bi-layer films leads to the higher values of electromechanical coupling factor ($k = d_{33}[E/\epsilon]^{1/2}$, a measure of the ability, to convert input mechanical energy into electrical energy, where d_{33} = piezoelectric coefficient, E = Young's modulus, ϵ = dielectric constant) for bi-layer configuration as compared to the PVDF-TrFE films alone. In addition,

since the force is applied in compression mode, the strain in the PVDF-TrFE films is not limited by the high modulus GO layer. Enhanced Young's modulus is a contributing factor in the observed improved energy harvesting performance of the nanocomposite films²⁶⁻²⁸ (electro spin composite nanofibers of PVDF-TrFE and CNT, nanocomposite films of ZnO nanoparticles, reduced graphene oxide, PDMS and composites of PVDF and BTO nanoparticles). Enhanced electromechanical coupling observed in unimorph actuators, when the piezoelectric material is coupled with an elastic material (metal plate), whose Young's modulus is higher compared to piezoelectric material.¹⁷ In addition high performance actuators have also been fabricated using high modulus flexible carbon fiber as the support in unimorph actuators.¹⁶

Figure 4.12. XRD spectra of poled PVDF-TrFE and Bi-layer films

Figure 4.13. Stress strain curve of Bi-layer and PVDF-TrFE film

This explains the efficient conversion of mechanical energy into electrical energy for the bi-layer films compared to the PVDF-TrFE films alone. In addition, the mechanical and electrical energy efficiently transferred with-in bi-layer films due to the high Young's modulus and high dielectric constant of GO compared to the PVDF-TrFE films, following the expressions below²⁹

$$\text{Efficiency of mechanical energy transfer } \eta_{\text{mec}} = 1 / (1 + d_{\text{GO}} E_{\text{P}} / d_{\text{P}} E_{\text{GO}}) \quad (2a)$$

$$\text{Efficiency of electrical energy transfer } \eta_{\text{elec}} = 1 / (1 + d_{\text{GO}} \epsilon_{\text{P}} / d_{\text{P}} \epsilon_{\text{GO}}) \quad (2b)$$

Where d_{GO} and d_{P} is thickness, ϵ_{GO} and ϵ_{P} , are dielectric constant, E_{GO} and E_{P} are the Young's modulus of graphene oxide and PVDF-TrFE respectively. From the literature, the Young's modulus of GO monolayers is approximately 200 GPa³⁰ and that of graphene oxide paper is 32 GPa³¹, which is much higher than the Young's modulus of PVDF-TrFE films (1.5 GPa). The dielectric constant of GO films is $\sim 1.75 \times 10^3$, whereas the dielectric constant of PVDF-TrFE films is 9.25 at 1 kHz (Figure 4.14). According to equation 2, it can be understood that higher Young's modulus and dielectric constant of GO helps in efficient transfer of electrical and mechanical energy with-in the bi-layer films.

In bi-layer films, GO (negatively charged) is in contact with the hydrogen terminated (positively charged) surface of the PVDF-TrFE. At the interface of PVDF-TrFE and GO, there exists an uncompensated charge, which is the result of the aligned dipoles in the PVDF-TrFE (+ve charge due to hydrogen terminated surface) and negatively charged functional groups in GO. This results in a complex interface in the bi-layer films between the PVDF-TrFE and GO with uncompensated charge along with negative charges throughout the GO films. Such complex interface leads to enhanced piezoelectric properties as in case of bi-layer films of PVDF and nylon11.³²

The present work provides a strategy to enhance energy harvesting performance of the piezoelectric films in conjunction with the charged layer of flexible high modulus and dielectric constant. By integrating the bi-layer devices, various self-powered systems can be developed. The enhanced voltage output can be particularly useful for highly sensitive pressure sensor. As the prepared bi-layer films are flexible, bendable and rollable, the energy harvesting device can be easily integrated with the flexible electronics to achieve

self-powered systems. In addition, the energy harvester can be used for electronic skin applications with improved sensing ability.

Figure 4.14: Dielectric constant versus frequency for (a) PVDF-TrFE film, (b) Graphene oxide film

To the best of our knowledge, this is the pioneer work showing the augmentation of AC voltage output can be realized with piezoelectric film in contact with charged dielectric.

In summary, we report an effective approach to improve the energy harvesting performance of ferroelectric material (PVDF-TrFE) by the addition of a charged dielectric film (GO) with high Young's modulus and high dielectric constant. Enhanced voltage (2 times) and power (2.5 times) output for the bi-layer films of PVDF-TrFE and graphene oxide compared to only PVDF-TrFE films are presented. The enhanced performance of the bi-layer films are ascribed to the electrostatic contribution of GO films, internal stress created in the PVDF-TrFE films and increased Young's modulus of the bi-layer films. We rationalize that any charged material (with high dielectric constant and Young's modulus) interface with the ferroelectric material can lead to enhanced energy harvesting performance.

4.3 Principal Outcomes

- Superior energy harvesting performance of bi-layer films of PVDF-TrFE and graphene oxide (Voltage output 2 times, power output 2.5 times) compared to PVDF-TrFE films when subjected to the dynamic compression pressure.

- Energy is harvested by means of both piezoelectric and electrostatic means using bi-layer films of PVDF-TrFE and Graphene Oxide.
- Enhanced energy harvesting performance is due to the electrostatic component of the graphene oxide (due to the negative charges in the GO), internal tensile stress, together with the higher modulus of the bi-layer films.
- We provide an effective approach that improves the energy harvesting performance by addition of piezoelectric material with charged dielectric layer with high Young's modulus and high dielectric constant.
- Our validated concept can be used for highly sensitive pressure sensors, for self-powered systems in flexible electronics.

4.4 Conclusions

We successfully fabricated the bi-layers films of PVDF-TrFE and graphene oxide. Energy is harvested successfully by means of both piezoelectric and electrostatic manner. The bi-layer films showed enhanced energy harvesting performance with voltage output approximately 2 times and power density 2.5 times that of the PVDF-TrFE films. The enhanced voltage and power output of the films is due to the electrostatic contribution of the graphene oxide films, internal stress created in the PVDF-TrFE films, complex interface and increased Young's modulus of the bi-layer films of PVDF-TrFE and graphene oxide. It can be further concluded that, utilizing the charged material (characterized with high-k dielectric constant and high Young's modulus) interface with the ferroelectric material is an effective approach of improving the energy harvesting performance of ferroelectric materials.

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Chapter 5

Synthesis, structural and ferroelectric studies of PVDF-TrFE nanotubes

We intend to improve the energy harvesting performance of the PVDF-TrFE by improving the piezoelectric coefficient with the synthesis of one dimensional nanostructures of PVDF-TrFE. In the present study, we aim to apply compression force along the length of the nanostructures, so it is favorable to have the polarization component along the length of the nanostructures to effectively pole and to harvest the mechanical energy. In the present chapter, synthesis, structural, morphological and ferroelectric properties of the nanostructure is presented. Further polarization orientation of the nanostructures is achieved by carrying out polarization switching studies using piezo force microscopy (PFM).

5.1 Introduction

The energy harvesting ability of the piezoelectric materials primarily depends on the intrinsic properties of the material. Young's modulus, dielectric constant, piezoelectric coefficient, strain of the material affects the energy harvesting ability of the material. Among these factors, piezoelectric energy harvesting ability primarily depends on the piezoelectric coefficient.

The crystal structure of the material affects the piezoelectric coefficient. Materials in single crystal form will have higher piezoelectric coefficient values compared to the polycrystalline form or material with random orientations. It is focused to synthesize the PVDF-TrFE material with uniform crystal orientation and hence to improve the piezoelectric coefficients.

Various factors could affect the crystal structure (/orientations) such as annealing temperature¹⁻³, dimensions of the material (1-D, 2-D, 0-D) and synthesis conditions⁴⁻⁶. PVDF-TrFE ultra-thin films annealed at temperatures between above curie transition temperature and melting point resulted in (110) planes along the surface plane whereas those annealed in the melting regime resulted in (200) planes in the substrate surface plane^{1, 7}. In case of bulk films, the annealing temperature at 135 °C leads to the c-axis orientations along with (110) planes.

Confined crystallization of PVDF-TrFE in the nano environment strongly affects the crystal orientations and its properties^{4-6, 8-10}. Reduced structural defects along with oriented crystallization is observed in the nanodots of PVDF-TrFE prepared from nano imprinting. This resulted in a reduced coercive field of PVDF-TrFE⁴. Preferential crystallization of PVDF-TrFE observed for the nanostructures synthesized in the nanotrenches of organo silicates, which leads to the better transistor performance with low voltage operation and low leakage currents compared to those fabricated using thin films⁸. 1-D nanostructures of PVDF-TrFE are synthesized using melt and solution wetting approach^{5, 11, 12}. It is observed that enhanced ferroelectric phase formation with lower melting and crystallization temperatures for the 1-D nanostructures synthesized from melt wetting approach⁵. It is

reported that polarization orientation either parallel or perpendicular to the nanostructures synthesized at the same conditions^{13, 14}. Though many researchers synthesized 1-D nanostructures, there is a lack of information on the coercive field and polarization orientation of nanostructures. In the present experiment, we intend to apply the force along the length of the nanotubes, so it is desirable to synthesize 1-D nanostructures with polarization component along the length of the nanostructures to effectively pole and harvest the energy.

5.2 Results and discussion

PVDF-TrFE nanostructures are synthesized by melt wetting approach using AAO templates as detailed in the chapter 3, experimental methods. The polymer melt wets the walls of nanoporous templates avidly if the pore walls exhibit a high surface energy

$$S = T_{SG} - T_{SL} - T$$

Where T_{SG} - alumina-air (1.59 J/m^2), T_{SL} - Alumina –PVDF-TrFE liquid, (1.17 J/m^2), and T - PVDF-TrFE liquid-air interfacial tension ($32.7 \times 10^{-3} \text{ J/m}^2$) represents interfacial tensions. If $S \geq 0$, complete wetting regime, the precursor film/solution completely wets the walls in very little time. If $S < 0$, partial wetting, and the polymer melt fills the pore through capillary action, which yields nanowires or rods. In the present case, $S=0.387 \text{ J/m}^2$ and hence nanostructures are formed in the complete wetting regime^{12, 15}.

5.2.1 Morphological and structural studies

One dimensional nanostructures formation and morphology has been studied by using FESEM and TEM. As shown in figure 5.1, it is observed that the nanostructures synthesized from AAO templates with 200 nm pore diameter are nanotubes with a wall thickness of approximately 70-90 nm (figures 2b and 2f). During the complete wetting regime, if the precursor film formed is more than half of the diameter of the pore, then the formed nanostructures are wires, otherwise the nanostructures are tubes⁵. The precursor film formed in the present case may be less than 100 nm resulted in the formation of

nanotubes using AAO templates with pore diameter 200 nm. Approximately 10-30% volume of the nanostructures is the hollow space for the nanotubes.

Figure 5.1a and 5.1b shows the top view of the empty AAO templates with pore diameter 200 nm and the formed PVDF-TrFE nanotubes in AAO pores, respectively. Figure 5.1c shows the cross-section of the AAO templates with PVDF-TrFE nanotubes embedded in it. The PVDF-TrFE nanotubes supported on the residual film, after releasing from the AAO templates (figure 5.1d). The close up SEM image shows the cracks in the nanotubes along the length, but they remain as continuous nanotubes. To obtain the free standing nanotubes, first the residual layer on top of the AAO template is removed by chemical plasma etching followed by wet chemical etching in 1M NaOH. The salts formed in this process are then removed by a centrifuge process. It is observed that the nanotubes formed as bundles after drop casting onto the gold coated glass substrates as shown inset in figure 5e. The formation of bundles of PVDF-TrFE nanotubes is due to the capillary forces arising in the process of wet chemical etching of AAO template, removal of salts and/or during drying process. The hydrophobic nature of the PVDF-TrFE together with the cohesive forces between the nanotubes might have led to the formation of bundles⁵. It is also observed that the length of the freestanding nanotubes is shortened (most of the freestanding nanotubes is approximately 15- 20 μm) due to the breaking of the nanotubes at cracks during high speed centrifugation process, while cleaning the salts/impurities from the nanotubes resulted from the template etching process. The aspect ratio of the freestanding nanotubes is in the range of 75- 100, whereas the nanotubes supported on the residual film have an aspect ratio of approximately 175-200. Figure 5.1f shows the transmission electron microscope (TEM) image of the nanotubes along the length with wall thickness approximately 80 nm. From the top view images of PVDF-TrFE nanotubes embedded in AAO (figure 5.1b) and TEM images, it is observed that the wall thickness of the nanotubes is approximately 70-80 nm with an air gap approximately 40-60 nm.

Ferroelectric β phase formation of nanotubes is studied by using FTIR and XRD. Figure 5.2 shows the FTIR spectra of PVDF-TrFE nanotubes, embedded in AAO template, shows the discernable peaks around 1170, 1288, 1403 and 1430 cm^{-1} . These peaks correspond to

the ferroelectric beta phase of PVDF-TrFE. The vibrations corresponding to 1170 cm^{-1} are parallel to the a-axis orientations, the vibrations corresponding to 1290 cm^{-1} and 1428 cm^{-1} are parallel to b-axis orientation and 1403 cm^{-1} are parallel to c-axis orientation¹.

X-ray diffraction spectra further confirms the ferroelectric beta phase formation in the nanotubes. Figure 5.3 shows the XRD spectra of PVDF-TrFE nanotubes embedded in AAO template and the PVDF-TrFE film. The peak at 19.8° corresponds to the (110)/ (200) planes of ferroelectric beta phase. Since the (110) and (200) planes have nearly equal distance, it is difficult to differentiate both the planes. PVDF-TrFE films exhibits c- axis orientations at 40.88° corresponding to the (201)/ (111) planes, whereas the nanotubes samples did not have any clear peak corresponding to the c-axis orientations at 40.88° . This suggests that the nanotubes formed from melt wetting have oriented crystallization corresponding to (110)/(200) planes along the length of the nanotubes with no or minimal orientations corresponding to c-axis orientations. XRD and FTIR analysis confirms the formation of ferroelectric beta phase in 1-D PVDF-TrFE nanotubes.

Figure 5.1: (a-e) Field emission scanning electron microscopy images of PVDF-TrFE nanotubes: a) Top view of the empty AAO porous templates, b) Top view of the PVDF-TrFE nanotubes embedded in AAO templates, c) Cross section of the nanotubes interface with AAO, d) View across the length of the nanotubes released from AAO, e) Nanotubes bundles on gold coated glass (inset image shows one such bundle); (f) Transmission electron microscopy image showing the tubular nature of the nanostructures. Reproduced from Ref. (16) Copyright 2014 Wiley.

Figure 5.2: FTIR spectra of PVDF-TrFE nanotubes embedded in AAO template. Reproduced from Ref. (16) Copyright 2014 Wiley.

Figure 5.3: X-ray diffraction pattern of PVDF-TrFE nanotubes (embedded in AAO templates) and films. Reproduced from Ref. (16) Copyright 2014 Wiley.

5.2.2 Domain behavior and polarization orientation

Figure 5.4: Schematic of the piezo force microscopy and orientation of PVDF-TrFE nanotubes

Domain behavior and polarization orientation of the PVDF-TrFE nanotubes are studied by using piezo force microscopy in a direction perpendicular to the length of the nanotubes as shown in figure 5.4. The vertical PFM and lateral PFM modes are used to study the polarization components perpendicular ($P_{\perp}$) and parallel ($P_{\parallel}$) to the length of the nanotubes. Since the measurements are carried out in a direction perpendicular to the length of the nanotubes, the vertical PFM mode measures the polarization component perpendicular to the length of the nanotubes whereas lateral PFM measures the polarization component parallel to the length.

Figure 5.5 shows the domain behavior of PVDF-TrFE nanotubes corresponding to the polarization component perpendicular and parallel to the length of the nanotubes. Mono domain behavior is observed for the polarization component $P_{\perp}$ whereas poly domain behavior is observed for the polarization component $P_{\parallel}$.

Figure 5.5: a) Polarization component perpendicular to the length of the nanotubes, b) Polarization component parallel to the length of the nanostructures.

Polarization orientation of the nanotubes are measured by performing the switching measurements corresponding to the polarization components $P_{\perp}$ and $P_{\parallel}$ at a nanoscopic location on to the nanotubes. Piezoresponse, defined as the product of inverse piezoelectric amplitude and cosine of the phase (corresponds to the applied voltage and inverse piezoelectric response) [piezoresponse = $\text{mag} * \cos$], is measured by sweeping the voltage above the coercive fields from -ve polarity to +ve polarity.

Figure 5.6 shows the switching behavior corresponding to the polarization components $P_{\perp}$, $P_{\parallel}$. The switching pattern typically corresponds to the ferroelectric switching behavior. The typical ferroelectric behavior observed in the switching behavior suggests that the synthesized nanotubes are ferroelectric. In addition, typical ferroelectric switching behavior is observed for the polarization components $P_{\perp}$ and $P_{\parallel}$. Since the voltage is swept in a direction perpendicular to the length of the nanotubes and ferroelectric switching behavior is observed corresponding to both polarization components $P_{\perp}$ and $P_{\parallel}$, suggests that the nanotubes have polarization orientation at an inclination to the length of the nanotubes as shown in Figure 5.7. From this observation, it infers that the XRD peak at 19.8° corresponds to the (110) planes rather than (200), since the polarization axis is along the b-axis. As (110) planes are predominant, it is estimated that the effective polarization is at 30° inclination to the long axis of the nanotubes¹⁷.

Figure 5.6. Piezoresponse ($\text{mag} \cdot \cos$) versus voltage measurements using PFM spectroscopy, corresponding to the polarization components (a) $P_{\perp}$ (perpendicular to the long axis) and (b) $P_{\parallel}$ (parallel to the long axis), on the freestanding PVDF-TrFE nanotubes cluster on conducting substrate. Reproduced from Ref. (16) Copyright 2014 Wiley.

Figure 5.7. Schematic of polarization axis orientation in PVDF-TrFE nanotubes. Reproduced from Ref. (16) Copyright 2014 Wiley.

Figure 5.8: a,d) topography of PDVF-TrFE nanotubes, b,c) Phase images corresponding to the polarization component $P_{\perp}$, e,f) Phase images corresponding to the polarization component $P_{\parallel}$.

In addition, switching of the domains corresponding to the polarization components $P_{\perp}$, $P_{\parallel}$ is observed, when a voltage pulse is applied at a nanoscopic location on to the nanotubes as shown in figure 5.8 (red dot represents the location at which the voltage pulse applied). Phase behavior (corresponding to polarization components $P_{\perp}$ and $P_{\parallel}$) is measured after applying a voltage pulse of magnitude 25 V, of both positive and negative polarity at the same location for 2 seconds. Voltage is applied in a direction perpendicular to the length of the nanotubes (as shown in figure 5.4). Figure 5.8 shows the phase behavior after the application of voltage pulse of ± 25 V. From figure 5.8, it is observed that by reversing the voltage pulse, the domains are switched to the opposite orientation corresponding to both polarization components $P_{\perp}$ (figure 5.8b, 4.8c) and $P_{\parallel}$ (figure 5.8e, 4.8f), though the voltage is applied in a direction perpendicular to the length of nanotubes. This further

confirms the inclined nature of the polarization orientation in the nanotubes synthesized. Incline nature of the polarization orientation is particularly useful for nanoelectronics devices where there is need to apply voltage in a particular direction and to observe the polarization switching effect in a direction perpendicular to it.

5.2.3 Coercive field measurements

Coercive field of the nanotubes corresponding to the polarization switching along and perpendicular to the length of the nanotubes is measured using macroscopic polarization versus electric field (P-E) hysteresis measurements and piezo force microscopy switching measurements respectively.

Initially, P-E hysteresis measurements are carried out on PVDF-TrFE films. Figure 5.9 shows the P-E hysteresis measurements carried out on PVDF-TrFE films using Sawyer – Tower circuit. The films exhibit the typical hysteresis behavior with remnant polarization of $9.1 \mu\text{C}/\text{cm}^2$ and a coercive field of $62 \text{ MV}/\text{m}$.

Figure 5.9: Polarization versus electric field hysteresis behavior of PVDF-TrFE films

Figure 5.10: Macroscopic Polarization versus electric field hysteresis behavior measured on PVDF-TrFE nanotubes embedded in AAO template using Sawyer –Tower circuit (inset image shows the schematic of the device structure). Reproduced from Ref. (16) Copyright 2014 Wiley.

Then the polarization versus electric field measurements are carried out on PVDF-TrFE nanotubes embedded in AAO templates. The inset in figure 5.10 shows schematic of the device onto which P-E hysteresis measurements are carried out. Electric field is applied parallel to the length of the nanotubes. As the electric field is increased, the maximum polarization and polarization at zero fields are increased as shown in figure 5.10. At fields about 52 MV/m, saturation in the polarization value at zero field and saturation in the electric field value at zero polarization is observed. The corresponding saturation values represent the remnant polarization and coercive fields. From the saturated hysteresis loop behavior, it is observed a remnant polarization value of 4.7 $\mu\text{C}/\text{cm}^2$, whereas pure PVDF-TrFE films have a remnant polarization of 9.1 $\mu\text{C}/\text{cm}^2$. The observed lower remnant polarization is due to the lower pore fraction of the AAO templates (~50 % is the pore volume), which accommodates the PVDF-TrFE nanotubes. The nanotubes exhibited a coercive field of 18.6 MV/m, whereas the films have a coercive field of 62.9 MV/m. This clearly shows that the nanotubes have a lower coercive field approximately three times

lower than that of the films. This coercive field corresponds to the polarization component parallel to the length of the nanotubes.

Using the PFM switching, the coercive field corresponding to the polarization switching in a direction perpendicular to the long axis of the nanotubes is measured (figure 5.6a). Since the voltage is applied in a direction perpendicular to the long axis of the nanotubes, the switching measurements data corresponds to polarization component $P_{\perp}$ gives the coercive field value. From the figure 5.6a, the coercive voltage value is 10 V, which corresponds to a coercive field ~ 40 MV/m. Due to the air gap in the nanotubes, only part of the voltage will be applied on to the nanotubes walls. By considering the nanotubes wall and air gap, as capacitors connected in series as shown in figure 5.11, the coercive field is approximately 13.2 MV/m ($\epsilon_{\text{PVDF-TrFE}} = 8$). Since the measurements are carried out on nanotubes bundles, the coercive field of the nanotubes will be in the range 13.2 MV/m to 40 MV/m, which corresponds to the polarization component perpendicular to the long axis of the nanotubes.

Figure 5.11. Schematic of the model used to calculate coercive field

[Capacitors in series:

$$q = CV \text{ with } V_1 = q/C_1, V_2 = q/C_2$$

$$\text{where } V = V_1 + V_2, q = q_1 = q_2 \text{ and } V_1/V_2 = C_2/C_1$$

$$V_{\text{PVDF-TrFE}}/V_{\text{air}} = C_{\text{air}}/C_{\text{PVDF-TrFE}}$$

Thickness of the nanotubes cluster = 250 nm

By considering 20% air gap, thickness of PVDF-TrFE shell- 200 nm and thickness of Air gap = 50 nm.

$$\epsilon_{\text{PVDF-TrFE}} = 8 \text{ (is measured)}, \epsilon_{\text{air}} = 1$$

$$V_{\text{PVDF-TrFE}}/V_{\text{air}} = (\epsilon_{\text{air}} * d_{\text{PVDF-TrFE}}) / (d_{\text{air}} * \epsilon_{\text{PVDF-TrFE}}) = (1 * 200) / (50 * 8)$$

$$= 1 : 2 \text{ (for } \epsilon_{\text{PVDF-TrFE}} = 8)$$

$$V_{\text{PVDF-TrFE}} = 3.33 \text{ V} \rightarrow EC = 13.2 \text{ MV/m (for } \epsilon = 8)$$

Table 5.1: Coercive field value of PVDF-TrFE

PVDF-TrFE		Coercive Field Ec (MV/m)
PVDF-TrFE Film		62.9
200 nm melt wet nanotubes bundle	Parallel to the long axis	18.6
	Perpendicular to the long axis	40 ~13.2 (by considering the voltage drop across air gap with $\epsilon_{\text{PVDF-TrFE}} = 8$)

Table 5.1 summarizes the coercive field values of the PVDF-TrFE nanotubes and films. From the table, it is clearly observed that the coercive field of the nanotubes is almost three times lower than that of the films. In the thermodynamic limit, the coercive voltage is given by $V_c = 5 \beta \sigma_{\text{wall}} \pi^2 / 8 P_s$, where V_c : coercive voltage, β : proportionality coefficient (of the order of unity), σ_{wall} : domain wall energy, P_s : spontaneous polarization^{4, 18}. By considering equal polarization value for films and nanotubes, the reduced coercive voltage value indicates the lower domain wall energy or domain wall barrier for nanotubes.

Reduced coercive fields of the nanotubes can be interpreted from the difference in the nucleation mechanism for films and 1-D nanotubes. In case of films, nucleation originates from the impurities or defects. Typical density of impurities in PVDF-TrFE is 1 per $10^5 \mu\text{m}^3$ ^{6, 19}. These nucleation centers randomly placed or oriented giving rise to the molecular chains orientated in different directions and lead to the random crystal orientations. In case

of nanotubes, synthesized in confined environment, the available space is much lower ($\sim 0.47 \mu\text{m}^3$) and hence the nanotubes formation in confined region might be due to either homogeneous nucleation or by heterogeneous nucleation on to the AAO template walls. It is also reported that one dimensional nanostructures synthesized from melt wetting approach will have reduced structural defects along with oriented crystallization due to the confined environment in side AAO pores^{5, 13}. This might have led to the observed reduced coercive fields for the nanotubes. Since the nanotubes have (110) planes along the length of the nanotubes with minimal or no c-axis orientations, the field effectively applied onto the nanotubes and hence the lower coercive fields to switch the polarization compared to bulk or films.

5.3 Principal outcomes

- The PVDF-TrFE nanotubes synthesized from melt wetting followed by annealed at 135 °C have (110) planes along the length of the nanostructures with no or very minimal presence of c-axis orientations
- Mono domain and poly domain behavior corresponds to the polarization component perpendicular and parallel to the length of the nanotubes respectively
- The nanotubes have polarization direction at an inclination to the long axis of the nanotubes with coercive field almost three times lower than that of the bulk/ films. These nanotubes are particularly useful where there is need to apply field in one direction and need to switch the polarization in a perpendicular direction.

5.4 Conclusions

PVDF-TrFE nanotubes are successfully synthesized by melt wetting approach with (110) planes along the length of the nanotubes with no or minimal c-axis orientation. The nanotubes have inclined polarization orientation with coercive fields almost 3 times lower than that of the films. Since the nanotubes have part of the polarization component along the length, the nanotubes can be easily poled and can expect effective harvesting of electrical energy by applying mechanical stimuli along the length of the nanotubes.

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Chapter 6

Piezoelectric energy harvesting performance of PVDF-TrFE nanostructures

The PVDF-TrFE nanotubes with preferential orientation corresponding to (110) planes without (or with minimal) c-axis orientations along the length are successfully synthesized. It is expected that the preferential orientation in these nanotubes will lead to the enhanced piezoelectric coefficients and hence better energy harvesting performance over films. In this chapter we present the piezoelectric coefficient and piezoelectric harvesting performance of the nanotubes synthesized.

6.1 Introduction

Polymeric piezoelectric materials are suitable to harvest electrical energy from the mechanical energy sources such as human motion, sound waves and air flow etc that are available in our daily life to realize self-sustainable low power electronics¹⁻³. The piezoelectric energy harvesting performance of the polymers is yet unsatisfactory (Table 1). The piezoelectric energy harvesting primarily depends on the piezoelectric coefficients. A higher piezoelectric coefficient gives higher voltage and power output ($V \propto d_{33}$, $P \propto d_{33}^2$) from the piezoelectric energy harvesting device^{4, 5}. In thin films form, PVDF-TrFE exhibits a piezoelectric coefficient ~ 20 pm/V⁶, whereas single crystal like PVF-TrFE can have a piezoelectric coefficient ~ 250 pm/V⁷. Lower piezoelectric coefficient of the films is due to the poly crystalline nature with random crystallite orientations⁸. Oriented crystallization in PVDF-TrFE is obtained by confined crystallization of polymers. Various nanostructures such as nano dots⁹, nano trenches¹⁰, 1-D nanostructures¹¹⁻¹³ with oriented crystal structure have been reported. In the present study, PVDF-TrFE nanotubes are successfully synthesized as described in the previous chapter with preferential orientation corresponding to (110) planes along the long axis of nanotubes. In addition the nanotubes exhibited lower coercive fields of almost three times lower than that of thin films. It is expected that the nanotubes with preferential orientation corresponds to (110) planes with minimal/ absence of c-axis orientations along the long axis will lead to enhanced piezoelectric coefficients.

In addition, 1-D nanostructures exhibit strain confinement due to their limited size in other two dimensions¹. This leads to the enhanced strain along the length of the nanotubes and hence can lead to enhanced piezoelectric performance ($V \propto \text{strain}$)¹³. It is hypothesized that the preferential orientation of (110) planes along with the strain confinement in nanotubes will lead to the improved energy harvesting over films.

Table 6.1: Literature status on energy harvesting performance of PVDF-TrFE

Work done on PVDF-TrFE	V_{out}	Power	Analysis	Reference
Direct write PVDF-TrFE fiber	5- 30 mV	2.5- 90 pW	- nano fiber mat of PVDF-TrFE fabricated by electro spinning - first nanogenerator paper on PVDF-TrFE	14
PVDF-TrFE fiber	0.6V	-	-electrospinning-method used	15
Gold nanoparticle	280mV peak to peak	-	-Gold nano particle electrode used to increase the surface area	16
Graphene multilayer film	3V	1.11 μWcm^{-2}	- increase the carrier concentration of the graphene by poling	17
Spring type device	88mV	-	-demonstate a new spring type device structure	18
Aligned nanofiber	1V	3 nW	-Highly sensitive pressure sensor demonstrated -fabricated freestanding array of aligned nano fiber of PVDF-TrFE	19
Surface controlled porous structure	2V	0.6 μW	-enhancement voltage output due to surface compressibility	20
sandwich structure of (graphene-PVDF-TrFE – CNT) -stretching mode d_{31}	0.7V(piezo) 0.4V(pyro) 1.4V(combined effect)	-	-demonstrate piezoelectric, pyroelectric effect and combined effect	21

Flexible PVDF-TrFE on PET substrate Measured by bending mode d_{31}	7V	$3.92 \mu\text{Wcm}^{-2}$ (58 nA)	- Highest voltage output report so far - However effective working area of the device is very small. The device area is selectively chosen at a place where there is maximum strain	22
PZT (Tested under a periodic pressure of 0.53 MPa)	209 V	4.91 mWcm^{-2}	Flexible fiber nanogenerator (multi layers of vertically aligned nanofiber mat)	23
ZnO (Tested under a periodic pressure of 1 MPa)	58 V	7.7 mWcm^{-2}	Vertically aligned ZnO nanowires with process optimization of fabrication methodology	24

6.2 Results and discussion

6.2.1 Piezoelectric d_{33} coefficient of PVDF-TrFE nanotubes

As detailed in the previous chapters (section 3.6 of chapter 3, chapter 5) PVDF-TrFE nanotubes with 200 nm diameter are synthesized by melt wetting approach followed by annealing at 140 °C. To compare the piezoelectric coefficients of nanotubes, PVDF-TrFE thin films are prepared as a reference. PVDF-TrFE thin films with approximately 200 nm in thickness are prepared by spin coating the PVDF-TrFE solution (prepared by dissolving PVDF-TrFE granules at a weight ratio of 30 mg/ml in methyl ethyl ketone solvent), followed by annealing the thin films at 135 °C for two hours. From the X-ray diffraction pattern (figure 6.1), it is observed that thin films prepared have (110)/ (200) planes in out of substrate plane corresponding to the ferroelectric beta phase. The synthesized nanotubes have mainly (110) crystal planes along the length of the nanotubes with minimal/absence of c-axis orientation (figure 6.1). The thin films prepared have typical needle-like surface morphology, as can be seen from the atomic force microscopy (AFM) image (figure 6.2a),

which typically corresponds to the ferroelectric beta phase of PVDF-TrFE films²⁵. Figure 6.2b shows the synthesized nanotubes cluster on to which the piezoelectric coefficients are measured.

Figure 6.1: X-ray diffraction pattern of PVDF-TrFE thin film of thickness 200 nm and PVDF-TrFE nanotubes of diameter 200 nm embedded in AAO templates

Figure 6.2: AFM image of (a) PVDF-TrFE film, (b) Nanotubes cluster

Among the various measurement techniques (laser vibrometry²⁶, direct measurement by applying the force and measuring the voltage²⁷ or vice versa) available for the measurement of piezoelectric coefficients, piezo force microscopy (PFM) is particularly useful to characterize the nanostructured samples. The piezoelectric coefficient is measured utilizing inverse piezoelectric effect. Voltage is applied at a nanoscopic location of the

(nanostructured) material using a conducting AFM tip and the corresponding strain is measured. Figure 6.3 shows the schematic of piezo force microscopy, nanotubes orientation for the measurement of piezoelectric coefficient. The conductive AFM tip is kept in contact with the sample. AC voltage is swept between the conducting tip and the sample, and corresponding piezoelectric response is measured. The slope of this curve multiplied by detector sensitivity gives the effective d_{33} value²⁸.

Figure 6.3: Schematic of piezo force microscopy to measure the piezoelectric coefficients

For reference, the d_{33} of PVDF-TrFE thin film is measured initially. Poling is performed by applying a voltage, well above the coercive value, across the thin film using the conducting AFM tip. The piezoresponse is measured with respect to the applied AC voltage on to the poled thin film as shown in figure 6.4. The measured d_{33} values of poled PVDF-TrFE thin film at various locations are in the range of $\sim 18 - 24 \text{ pmV}^{-1}$. The measured d_{33} values are in well agreement with the literature⁶. The d_{33} coefficient of nanotubes is then measured in a direction perpendicular to the tube axis as shown in the figure 6.3. In the as synthesized state the nanotubes exhibited piezoelectric behavior, with a piezoelectric coefficient $\sim 3 \text{ pmV}^{-1}$. The d_{33} values measured at various locations on the nanotubes bundle gave similar values. The poling of the nanotubes is then performed by

biasing the AFM probe tip well above the coercive voltages (~ 70 MV/m), at particular location on the nanotubes bundle. The piezoresponse of the poled nanotubes bundle with respect to the applied AC voltage is represented in figure 6.4. The nanotubes showed an effective d_{33} of 44 pmV^{-1} . d_{33} values are then measured at various locations on the nanotubes bundle and observed similar values in the range $40 - 44 \text{ pmV}^{-1}$.

Figure 6.4: Piezoresponse of the poled nanotubes of diameter 200 nm (poled at fields ~ 70 MV/m) and poled PVDF-TrFE film (poled at fields ~ 75 MV/m) with respect to the AC voltage. Reproduced from Ref. (11) Copyright 2014 Wiley.

Table 6.2: Piezoelectric d_{33} coefficient

PVDF-TrFE	$ d_{33} $ (pm/V)
Film	18-24
1-D nanotubes (200 nm diameter, measured perpendicular to the tube long axis)	41- 44

Table 6.2 summarizes the d_{33} values measured on poled films and poled nanotubes clusters. It can be clearly observed that the effective piezoelectric coefficient of the nanotubes is

almost two times that of the films. V.Cauda *et al.* measured a piezoelectric coefficient of $\sim 22 \text{ pmV}^{-1}$ and 8 pmV^{-1} for the nanowires embedded in AAO templates with the diameters 10 nm and 200 nm respectively^{29, 30}. Since we carried out the measurements on the free standing nanotubes drop casted on to the gold coated substrates, the constraints of AAO wall on the piezoresponse of nanotubes have been eliminated. In addition, the melt wet process might have effectively reduced the defects in the nanostructures¹² leading to the improved piezoelectric coefficient values.

6.2.2 Energy harvesting performance of the PVDF-TrFE nanotubes

Nanotubes nanogenerator is fabricated, as described in the experimental methods (Chapter 3, section 3.5), to realize the enhanced energy harvesting performance by taking the advantage of higher piezoelectric coefficient of PVDF-TrFE nanotubes over films. Freestanding nanotubes supported on the residual PVDF-TrFE film is obtained by etching the AAO templates in 1 M NaOH solution. Figure 6.5a shows the cross section of the nanotubes samples supported on the residual film. The nanotubes samples thickness is approximately 30 μm . Figure 6.5b shows the top view of the freestanding nanotubes samples. It is observed that, the nanotubes vertically aligned up to some extent, and after that they collapsed and lied on each other to form a mat of nanotubes as shown in figure 6.5b. Figure 6.6a, shows the schematic of nanogenerator device fabricated to test the energy harvesting performance. The energy harvesting performance is measured by applying a dynamic compression pressure of maximum 0.075 MPa at 1 Hz. The nanotubes nanogenerator shows a maximum voltage output of 4.8 V ($V_{\text{avg}} = 3.75 \text{ V}$). By interchanging the contacts, a change in the polarity of the output voltage is observed, as shown in figure 6.4c and 6.4d, this confirms the output voltage is of piezoelectric origin. The response time of the nanogenerator device is $\sim 9 \text{ ms}$. The energy harvesting performance of the nanotubes device is compared with PVDF-TrFE film counter parts poled at 60 MVm^{-1} at room temperature ($\sim 20 \text{ MVm}^{-1}$ at 110°C). On the contrary, the films exhibited a voltage output of $\sim 0.3 \text{ V}$ at 0.075 MPa and a maximum voltage output of 0.8 V at 0.3 MPa.

Figure 6.5: (a) cross sectional view of free standing PVDF-TrFE nanotubes, (b) top view of freestanding PVDF-TrFE Nanotubes

Figure 6.6: Energy harvesting performance of the PVDF-TrFE nanotubes nanogenerator. a) Schematic of the fabricated energy harvesting device, b) Power output measured across a load resistor under a cyclic pressure of 0.075 MPa applied at 1 Hz, c) and d) Polarity change of the voltage output of the PVDF-TrFE nanotubes energy harvesting device by interchanging the connections of the device. Reproduced from Ref. (11) Copyright 2014 Wiley.

Figure 6.6b, shows the output power density of the nanotube samples and film, obtained by measuring the voltage across various load resistors ranging from 50 k Ω to 1 M Ω (50, 330, 576, 816, 1000 k Ω). Measuring the power density across the load resistor is more meaningful than measuring the power from open circuit voltage and short circuit current, which is always higher than the actual power output of the device³¹. The nanotubes have a maximum power output of 2.2 μWcm^{-2} and the film counterparts have a peak power output of 0.06 μWcm^{-2} across a load resistance 576 k Ω under a compression pressure of 0.075 MPa.

To further study the effect of diameter of the 1-D nanostructures on the energy harvesting performance, 1-D nanostructures with 50 nm diameter are synthesized by melt wetting approach using commercial AAO templates with 50 nm pore diameter. The nanostructures synthesized have (110)/ (200) planes along the length of the nanostructures with minimal or absence of c-axis orientations, similar to the case of nanostructures with 200 nm diameter (figure 6.7a). Figure 6.7b shows the field emission scanning electron microscopy image of the nanostructures synthesized from AAO templates with 50 nm pore diameter. The 1-D nanostructures appear to have roughened surfaces, open pore could not be found indicating the formation of a solid core nanowires instead of nanotubes. To measure the energy harvesting performance of the nanostructures with 50 nm diameter, the energy harvesting device is fabricated and poled at ~35 MV/m as detailed earlier.

The energy harvesting device made with 1-D nanostructures with 50 nm diameter are then subjected to the dynamic compression pressure. Figure 6.8 shows the voltage output from the nanostructures upon subjected to a compression pressure of 0.075 MPa applied at 1 Hz. It is observed that the nanostructures have a maximum voltage output of approximately 8.2 V (V_{avg} : 7.2 V). It is further observed that switching in the polarity of the voltage output occurs with interchanging the contacts of the device suggests the voltage output from the device is of piezoelectric origin (figure 6.8). Further the power output from the device is measured by measuring the voltage across a load resistor. It is observed a maximum power output of ~ 7.96 μWcm^{-2} across a load resistor of 576 k Ω .

Figure 6.7: (a) X-ray diffraction pattern of 1-D nanostructures of PVDF-TrFE and films, (b) Morphology of 1-D nanostructures with 50 nm diameter

Figure 6.8: Energy harvesting performance of the one dimensional nanostructures with 50 nm diameter under the application of dynamic compression pressure of 0.075 MPa. (a) and (b) voltage output by reversing the contacts of the device

Table 6.3: Energy harvesting performance of PVDF-TrFE nanotubes and films

Material (Device area 0.785 cm²)	Max Voltage (V)	Power density (μWcm⁻²) (at 576 kΩ)
PVDF-TrFE film (unpoled and poled at 30 MV/m at RT)	No Voltage	--
Poled PVDF-TrFE film (60 MV/m)	0.8	0.06
PVDF-TrFE nanotubes (unpoled) (200 nm diameter)	0 - 0.02	--
PVDF-TrFE nanotubes (Poled) (200 nm diameter)	4.8	2.2
PVDF-TrFE nanowires (unpoled) (50 nm diameter)	0.2	-
PVDF-TrFE nanowires (poled) (50 nm diameter)	8.2	7.96

Table 6.3 summarizes the energy harvesting performance of 1-D nanostructures of PVDF-TrFE and films measured under dynamic compression pressure at 1 Hz. It is clearly observed that the nanotubes with 200 nm diameter (4.8 V, 2.2 μWcm⁻²) have superior energy harvesting performance over films (max 0.8 V, 0.06 μWcm⁻²). The voltage output of the nanotubes is 6 times that of the films whereas power output of nanotubes is 36 times that of the films. The enhanced energy harvesting performance of the nanotubes is attributed to the following reasons: Improved piezoelectric coefficient values (voltage $\propto d_{33}$, power $\propto d_{33}^2$), enhanced strain along the length of the nanotubes caused by the strain confinement due to the one dimensional geometry (voltage $\propto$ strain) and/or improved surface area (current $\propto$ surface area, power $\propto$ surface area) of the nanotubes over films. These factors led to the observed enhanced energy harvesting performance in the nanotubes over films. It is further observed that the energy harvesting performance increased with decreasing the diameter of the one dimensional nanostructures. The nanostructures with 50 nm diameter (max 8.2 V, 7.96 μWcm⁻²) have a voltage output of approximately 1.7 times

that of the 200 nm nanotubes and power output approximately 3.6 times higher than the 200 nm nanotubes. The high performance of the nanostructures with 50 nm diameter over 200 nm diameter is due to the stronger strain confinement effect with decreasing the diameter of the nanostructures. Further it is observed that the nanostructures with 50 nm diameter showed a voltage output (200 mV) even before poling suggests the alignment of the dipoles in the nanostructures in addition to the oriented crystallization. This led to the observed enhanced energy harvesting performance of one dimensional nanostructures with 50 nm diameter over nanostructures with 200 nm diameter.

Since the polymeric PVDF-TrFE is ferroelectric in nature, the samples required to be poled to align the domains/dipoles to achieve the best energy harvesting performance. Energy harvesting device fabricated from the one dimensional nanostructures with 200 nm diameter exhibited a voltage output of approximately 0-20 mV and the energy harvesting device fabricated from the nanostructures with 50 nm nanometer diameter exhibited a voltage output of approximately 200 mV, prior to poling. The energy harvesting device fabricated from one dimensional nanostructures is then poled at a maximum electric field of 35 MVm^{-1} at room temperature for one hour duration. This gives rise to the above mentioned voltage and power output in the energy harvesting device made from nanostructures. Whereas, the PVDF-TrFE films prior to poling and poled at field 30 MVm^{-1} did not show any voltage output. PVDF-TrFE films showed voltage output only when poled at fields 60 MVm^{-1} . Similar poling fields have been used to pole PVDF earlier¹. This suggests the lower poling fields ($\sim 35 \text{ MVm}^{-1}$) required for the nanostructured samples. The reduced poling fields for the nanostructured samples are due to their lower coercive fields of 18.6 MVm^{-1} , over films ($\sim E_c$ films: 50 MVm^{-1}) as obtained from macroscopic P-E hysteresis loop measurements (Chapter 5).

Enhanced piezoelectricity (piezoelectric coefficient and energy harvesting performance) of the nanotubes is due to the preferential crystallization with (110) planes along the length of the nanotubes with minimal or absence of c-axis orientations. This led to the effective utilization of the applied voltage or force. It has also been reported that the 1-D nanostructures synthesized from melt wetting would have reduced structural defects along

with oriented crystallization due to the confined nature of the AAO walls¹². For ferroelectric nanotubes, the piezoelectricity is due to intrinsic (volume change) and extrinsic factors (domain wall motion)³². The reduced coercive field implies the reduced domain wall energy barrier which might have contributed to the enhanced piezoelectric coefficients. The improved piezoelectric coefficient values in 1-D nanotubes are due to the preferential orientation corresponding to (110) planes along the long axis of the nanotubes, difference in nucleation mechanism together with confinement effects on the molecular chain which have led to the reduced structural defects. The enhanced piezoelectric coefficients, strain confinement due to the 1-D geometry and improved surface area of the one dimensional nanostructures over films lead to the observed superior energy harvesting performance.

6.3 Principal Outcomes

- Successfully provided an efficient way to synthesize the one dimensional nanostructures with enhanced energy harvesting performance over films.
- One dimensional nanostructures exhibited lower poling fields (~40 % lower) over film counter parts. Confined crystallization of 1-D nanostructures in AAO pores lead to the nanostructures with (110) planes along the length with minimal or absence of c-axis orientation which further lead to the lower coercive fields and hence lower poling fields in case of 1-D nanostructures. This is because of the effective utilization of the applied electric field on to the dipoles in the PVDF-TrFE nanostructures.
- Preferential orientation of (110) planes along the length of the nanostructures with minimal c-axis orientations further lead to the enhanced piezoelectric coefficients over films because of the efficient electromechanical coupling.
- Further proved enhanced piezoelectric coefficients together with strain confinement and improved surface area would lead to enhanced piezoelectric energy harvesting efficiency.
- Reducing the diameter of the one dimensional nanostructures further improves the strain confinement (because of the 1-D geometry) and alignment of dipoles and hence leads to the improved energy harvesting.

6.4 Conclusions

In summary, the nanotubes synthesized exhibits improved piezoelectric coefficient values almost twice that of the film counterparts. In addition, the nanotubes (diameter 200 nm) exhibited superior energy harvesting performance (voltage output 6 times, power output 36 times higher) over films. Reducing the diameter of the nanostructures further improved the energy harvesting performance (voltage output 1.7 times, power output 3.6 times higher compared to 200 nm nanotubes). Improved piezoelectric coefficients, strain confinement in the nanotubes and improved surface area of the PVDF-TrFE nanotubes or nanowires have led to the observed superior energy harvesting performance of the one dimensional nanostructures.

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Chapter 7

Control of the AC nature of piezoelectric voltage output

The voltage output from the piezoelectric materials upon application of the dynamic force is alternating current (AC) in nature. Usually electronic devices require a DC (direct current) voltage, therefore the nanogenerator requires the use of a diode in conjunction to realize the self - powered electronic device. Therefore, it is important to achieve a rectifying output from the piezoelectric energy harvester. In this chapter, we show that by using ferroelectric polarization charge in conjunction with the piezoelectric energy harvesting device, an asymmetric AC output with reduction in the voltage output at one side of the AC peak can be achieved, pathing the way for DC output.

7.1 Introduction:

Energy harvesting from ambient atmosphere is useful for the self-powered electronic devices particularly for those which are kept in remote locations, difficult to access etc. the power output of the piezoelectric energy harvesters typically few microwatts, which is sufficient to power the sensors and low power electronic devices. The electronic devices usually operate on DC voltage. The voltage output from piezoelectric energy harvesting device is AC in nature. This necessitates the use of diodes to rectify the voltage output from the piezoelectric generators and for use in self-powered devices.¹ The rectifier circuit reduces the effective voltage output and further makes the device bulky, because of the additional components.^{2, 3} Harvesting direct current voltage output from the piezoelectric energy harvesting device is advantageous to directly combine the energy harvester with the electronic devices.

Rectifying voltage output is observed from ZnO nanogenerators either by alteration of the morphology of the nanostructures or by introducing a charged layer at one end of the nanostructured ZnO material. It is reported a DC voltage output by growing inclined nanorods in the ZnO based nanogenerator instead of the vertically aligned nanorods. The inclination of the nanorods lead to the direct current behavior.⁴ Another way of realizing the rectifying voltage output is to have a fixed charge at one end of the piezoelectric active material; this resulted in the rectifying voltage output. During the growth of ZnO nano sheets on aluminum substrate, the interface between Al and ZnO resulted in AlZn: layered double hydroxide which carried a negative charge. This interlayer in turn resulted in the DC voltage output by opposing the flow of electrons towards it². M.K Gupta et al reported DC voltage output from the vanadium doped ZnO nanosheets. The vanadium doped ZnO nano sheets are terminated by $V(OH)_4^-$. The negatively charged hydroxide opposed the flow of electrons towards it and resulted in the DC output³.

In both cases, the charged layer onto the piezoelectric nanostructures is formed during the growth mechanism. It is useful if we can have a universal charged layer which can be transferred/deposited on to any piezoelectric materials and hence to harvest the DC voltage

output. Ferroelectric materials are characterized by two stable polarization states even at zero fields with its surface terminated by positive and negative charges on either side of the material⁵. Furthermore, the charge on the material surface can be changed from positive to negative by applying a field above its coercive field value. Earlier, this behavior has been used to demonstrate the ferroelectric memory devices.⁶ PVDF-TrFE is a well-known ferroelectric material as we have shown in the previous chapter with a polarization charge of approximately $9 \mu\text{Ccm}^{-2}$.^{7, 8}

Since PVDF-TrFE is piezoelectric as well as ferroelectric polymer, in this work we used PVDF-TrFE for both as an active piezoelectric material and as a fixed charge facilitator by utilizing its piezoelectric behavior and polarization charge. We fabricated a piezoelectric energy harvesting device of PVDF-TrFE with one side of the device terminated with a PVDF-TrFE layer of fixed charge. We then measured the energy harvesting performance to study the effects of the polarization charge on the voltage output behavior.

7.2 Results and discussion

7.2.1 Structural characterization of PVDF-TrFE films

Figure 7.1 shows the XRD pattern of PVDF-TrFE film (on Al foil) annealed at 135°C . The peak at 19.7° corresponds to the (110)/(200) planes and the peak at 40.8° corresponds to the (201)/(111) planes of ferroelectric beta phase and confirms the formation of ferroelectric phase in PVDF-TrFE films. In the present experiment PVDF-TrFE film is fabricated on both sides of aluminum foil.

Figure 7.1: XRD spectra of PVDF-TrFE film with Al foil as substrate

The polarization of the PVDF-TrFE (ferroelectric material) is zero in as-synthesized state because of the random orientations of the dipoles. This further leads to the zero piezoelectricity in PVDF-TrFE films in as-synthesized state. PVDF-TrFE (or in general ferroelectric materials) exhibits a positive or negative charge on its surface only when the films are poled at voltages above its coercive voltage.

7.2.2 Polarization charge of PVDF-TrFE films

Figure 7.2 shows the hysteresis behavior of PVDF-TrFE film. As seen here, in as-synthesized state, at zero fields, the polarization of the PVDF-TrFE is zero. The polarization of the material increased as the field is increased and reached a maximum. The material exhibits a stable polarization value after removing this field. The stable polarization value can be either positive or negative depending on the polarity of the voltage applied as can be seen from the hysteresis loop behavior. PVDF-TrFE films exhibits a maximum remnant polarization charge of $9 \mu\text{C cm}^{-2}$.

Figure 7.2: Polarization versus electric field: Hysteresis loop behavior of PVDF-TrFE with increasing the maximum field applied

7.2.3 Voltage output behavior of piezoelectric energy harvesting device in series with polarization charge

Figure 7.3 shows the schematic of the device proposed in order to study the effect of fixed charges on the output voltage behavior of the PVDF-TrFE piezoelectric energy harvesting device. PVDF-TrFE films are deposited on both sides of the aluminum foil as shown in the figure 7.3. PVDF-TrFE film on one side of the aluminum foil is used as the piezoelectric active material. The other side of the PVDF-TrFE (charge facilitator) on aluminum foil is used to create charges on the piezoelectric energy harvesting device.

For reference sample, only the piezoelectric active part is poled whereas the film used to create fixed charges is not poled. The film used for the piezoelectric active element is poled at fields of 75 MV/m at room temperature. This resulted in fluorine molecules towards the gold electrode side (positive poling field on to the gold electrode) and hydrogen molecules towards the aluminum electrode (negative poling field onto the aluminum electrode) side as shown in the figure 7.3. Figure 7.4 shows the voltage output from the reference samples upon subjected to a dynamic compression pressure of 0.3 MPa. It is observed that a typical AC voltage output from the piezoelectric energy harvesting device

is obtained when subjected to the dynamic compression force, in agreement with the general behavior of the piezoelectric materials.

Figure 7.3: Schematic of the reference energy harvesting device

Figure 7.4: Typical AC voltage output from the PVDF-TrFE film

The generation of voltage output from the piezoelectric energy harvesting device on application of the dynamic compression force can be explained by the creation of piezo potential and the flow of free charge carriers in the external connections. The crystalline β phase in the semi-crystalline PVDF-TrFE gives rise to the piezoelectric properties. The all trans (TTTT) conformation β phase contains negatively charged fluorine atoms, which are arranged on one side and the positively charged hydrogen atoms on one side of the carbon molecular backbone. This gives rise to a net dipole moment, due to the non-overlapping of

the positive and the negative charge centers. Before poling these dipoles are randomly oriented giving rise to a net zero polarization. After the film is subjected to poling, the electric dipoles are aligned in the direction of the electric field. The dynamic compression stress changes the dipole moment which in turn creates a change in the potential across the film. Now the free-charge carriers in the electrode will flow from the negative potential region to the positive potential across the external connection in order to nullify the potential. This flow of electron will give rise to a positive peak. When the stress is released, the potential across the film becomes zero. So, the electron returns back to the bottom electrode which in turn will give rise to a negative peak.

To study the effect of the fixed charge at one side of the piezoelectric device on to the voltage output of the energy harvesting device, the PVDF-TrFE film coated on the bottom side of aluminum foil, which functioned as the charge facilitator, is poled at various poling fields from 60-80 MV/m in such a way that +ve charge (terminated with hydrogen molecules, negative poling field is applied on aluminum foil) is created at the interface of the piezoelectric device as shown in figure 7.5. As shown in figure 7.6, the polarization or fixed charge on the PVDF-TrFE will increase with increasing the applied poling fields in the measured range of 60 MV/m to 80 MV/m.

Figure 7.5: Piezoelectric energy harvesting device with positive fixed charge at the aluminum foil

Figure 7.6: Polarization/Surface Charge versus Poling field on to the PVDF-TrFE

Figure 7.7: Voltage output from the energy harvesting device with fixed charge at one end of the piezoelectric energy harvesting device: by poling the fixed charge facilitator at (a) ~60 MV/m, (b) 75 MV/m

Figure 7.7 shows the voltage output from the piezoelectric device with fixed positive charge at the one end of it. It is observed that the presence of the fixed charge leads to the reduction in the magnitude of the voltage output at one side of the AC peak (~0.8 V). It is further observed that with increasing the amount of fixed charge, the magnitude of the voltage output at one end of the AC peak is further reduced (~0.5 V).

For the case that fixed positive charge at one end of the piezoelectric energy harvesting device (figure 7.5), when a compression force is applied the piezo potentials develop in such a way that the gold electrode side becomes more negative and the aluminum side becomes more positive. This leads to the flow of electrons from gold electrode to the aluminum electrode side. When the compression force is removed, piezo potentials will become zero and this will cause reverse in the flow of electron. In the presence of charge facilitator, the fixed positive charge (on the charge facilitator) restricts the flow of electrons moving away from the aluminum electrode surface and this leads to the reduction in the voltage output at one side of the AC peak.

Similar results were observed even with the negative fixed charge at one end of the piezoelectric energy harvesting device. Negative fixed charge on aluminum electrode of the piezoelectric energy harvesting device is realized by poling the charge facilitator by applying a positive field of ~ 60 MV/m on the aluminum electrode. This resulted in Fluorine terminated surface of PVDF-TrFE onto the aluminum electrode and hence a fixed negative charge on to the piezoelectric energy harvesting device as shown in figure 7.8. This fixed negative charge on to the energy harvesting device further resulted in an asymmetric AC voltage output with reduced voltage at one end of the AC peak, when subjected to the dynamic compression pressure, as shown in figure 7.9. The negative fixed charge at the aluminum electrode opposes the flow of electrons towards the aluminum electrode. This causes the asymmetric AC voltage output from the energy harvesting device.

Figure 7.8: Piezoelectric energy harvesting device with negative fixed charge at the aluminum foil

Figure 7.9: Voltage output from the energy harvesting device with fixed negative charge at one end of the piezoelectric energy harvesting device: by poling the charge facilitator at 60 MV/m.

For the reported ZnO based piezoelectric nanogenerator in reference 2, the negatively charged hydroxide at one end of the piezoelectric material resulted in the completely rectifying output. In our work, for the piezoelectric energy harvesting device, when its interface is in contact with a fixed polarization charge, only a reduction in the magnitude of the voltage at one side of the AC peak is observed. It is expected, in ideal case, the fixed positive polarization charge (on the charge facilitator layer) allows the flow of electrons towards the electrode that is interfaced with charged facilitator layer, but opposes the electrons going away from this electrode. Since the ferroelectric PVDF-TrFE is used to facilitate the fixed charge, the dipoles in the PVDF-TrFE will be affected when there is an application of force. This will cause change in the fixed positive polarization potentials. This change in the fixed potential might have led to the observed asymmetric AC behavior instead of complete rectification as observed in case of ZnO:V nanogenerators. It is believed that by using a dielectric material with a fixed charge, it is possible to achieve DC output from the PVDF-TrFE piezoelectric energy harvester.

The results proves that the fixed charge at the interface of the piezoelectric energy harvesting device converts the typical AC voltage output of piezoelectric energy harvesting device to asymmetric nature of AC output. This is a step towards realizing the DC output

from the piezoelectric energy harvesting device. We further believe that by utilizing a dielectric material with unipolar charged surface at the interface of the piezoelectric energy harvesting device, will enable to realize the completely rectified (DC type) voltage output. These results are particularly useful because the charge facilitator (ferroelectric or dielectric with unipolar surface charge) used in the present work can be deposited on any piezoelectric energy harvesting device made with a range of ferro or piezoelectric active materials to achieve the rectified output and hence to realize the self-powered electronic devices without usage of any complex or bulky rectifying circuits.

7.3 Principal outcomes

1. We prove that the fixed charge at one end of the piezoelectric device, realized by utilizing the ferroelectric material, controls the AC nature of the piezoelectric energy harvesting device voltage output. The fixed charge onto the piezoelectric energy harvesting device controls the flow of the electrons towards the electrode that is interfaced with this fixed charge, and hence leads to the asymmetric voltage output, a step towards realizing a piezoelectric energy harvesting device with complete rectifying voltage output.
2. We provide an effective approach to realize the asymmetric type voltage output from piezoelectric energy harvesting devices, irrespective of the piezoelectric material used, just by coating the unipolar charged material (ferroelectric or any other dielectric with unipolar charged surface) at one end of the device.

7.4 Conclusions

We successfully provided an effective approach to control the AC output nature of the piezoelectric energy harvesting devices by utilizing a ferroelectric material as fixed charge interface with the piezoelectric energy harvesting device. Polarization charge on the ferroelectric materials is successfully employed to create the fixed charge at the interface of the piezoelectric energy harvesting device. Furthermore, the fixed charge on the piezoelectric energy harvester leads to the asymmetric AC voltage output, with reduction

in the magnitude of voltage output at one side of the AC peak, a step towards realizing the complete rectifying voltage output behavior. We believe that a dielectric material with unipolar charged surface interface with the piezoelectric energy harvester will lead to the complete rectifying voltage output and hence enable to realize the self-powered electronics without usage of additional rectifying components.

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Chapter 8

Conclusions and recommendations

This chapter summarizes the concluding remarks of the work presented in this dissertation followed by the future recommendations. In this dissertation, we have emphasized the strategic steps to enhance the energy harvesting performance of PVDF-TrFE piezoelectric materials. The main hypothesis is to enhance the energy harvesting performance by improving the intrinsic properties of the material and by combining with alternative energy harvesting mechanism. The corresponding approaches are as follows; (1) Addition of piezoelectric material with a charged high Young's modulus material to combine the electrostatic energy harvesting with piezoelectric means (2) Improve the piezoelectric coefficients of the material by synthesizing the nanotubes of PVDF-TrFE in the confined environment. Furthermore, it is showed that by using a fixed charged layer (polarization charge of ferroelectric material) in series with the energy harvesting device, the typical alternating current (AC) voltage output behavior of the device can be controlled. An asymmetric AC voltage output with reduction in the magnitude of the voltage at one end of the AC peak is realized, which is a step towards realizing the complete rectifying voltage output from the futuristic piezoelectric energy harvesting devices and hence the self-powered electronic devices without the usage of any additional rectifying components.

8.1 Conclusions

Bi-layer films of piezoelectric PVDF-TrFE and high Young's modulus material with fixed charge is fabricated to harvest the energy by means of both the electrostatic and piezoelectric manner in addition to improve the Young's modulus of the device. Flexible graphene oxide films are used as high modulus material with fixed charge. The charges present on the graphene oxide, by means of the functional groups, enabled the bilayer film to harvest the electrostatic energy. The high Young's modulus of the graphene oxide film lead to the improvement of the Young's modulus of the bilayer film device. In addition, incorporation of graphene oxide onto the PVDF-TrFE leads to the creation of internal stress in the PVDF-TrFE films which enhanced the piezoelectricity by aligning the molecular chains. The roll-up of the bi-layer film after deposition of graphene oxide layer further indicates the stress/strain gradient in the bi-layer film, which in turn creates the spontaneous polarization (by means of flexoelectricity) and hence enhanced piezoelectricity of the bi-layer films. The bi-layer films showed enhanced energy harvesting performance with voltage output approximately two times and power density 2.5 times that of the single layer PVDF-TrFE films. The enhanced voltage and power output of the bilayer films is due to the electrostatic contribution of the graphene oxide films, reduced depolarization field, complex interface and increased Young's modulus of the bi-layer films of PVDF-TrFE and graphene oxide. The high modulus and high dielectric constant of the graphene oxide lead to the efficient transfer of the mechanical and electrical energy in the bi-layer films. It can be further concluded that, utilizing the charged material (characterized with high-k dielectric constant and high Young's modulus) interface with the ferroelectric material is an effective approach of improving the energy harvesting performance of ferroelectric materials.

It is further shown that the crystal structure and dimensions of the PVDF-TrFE affects the energy harvesting performance. PVDF-TrFE nanotubes are successfully synthesized by template approach. The nanotubes synthesized have the (110) orientations with minimal or no c-axis orientations along the length of the nanostructures. The synthesized nanotubes have a polarization orientation at an inclination to the long axis with coercive fields almost three time lower than that of bulk or film counterparts. These nanotubes further showed a

piezoelectric coefficient values almost two times that of PVDF-TrFE films. The nanotubes nanogenerators showed an enhanced energy harvesting performance (voltage output 6 times that of films and power output 36 times that of films) over films. The improved energy harvesting performance of the nanotubes is due to the improved piezoelectric coefficients, strain confinement due to the one dimensional geometry and improved surface area of the nanotubes over films. Reducing the diameter of the one dimensional nanostructures further showed improved energy harvesting performance because of the stronger strain confinement effects (because of the 1-D geometry) and alignment of the dipoles in the as-synthesized nanostructures with (110) planes along the length of the nanostructures with minimal or absence of nanostructures. Using 50 nm nanowires, voltage output 1.7 times and power output 3.6 times that of 200 nm nanostructures have been achieved.

Rectifying voltage output is important to realize the self-powered electronic devices without having the additional rectifying circuit. In the thesis, it is showed that by having a fixed dipolar charge at one end of the energy harvesting device, reduction in (approximately 50%) the magnitude of voltage at one side of the AC peaks can be achieved. The piezoelectric energy harvesting device showed clear symmetric AC peaks, without any charge at the interface. By introducing the polarization charge, facilitated by PVDF-TrFE layer coated at one end of the piezoelectric energy harvesting device shows a reduction in the magnitude of the voltage output at one side of the AC peak. The asymmetric AC output is further augmented (with further reduction in unipolar voltage output) with increasing the polarization charge. Though it is still AC kind of behavior, the fixed polarization charge in conjunction with the piezoelectric energy harvesting device has led to the asymmetric voltage output behavior. By choosing a proper dielectric with uni-polar charge of appropriate amplitude may further lead to the rectifying voltage output in piezoelectric energy harvester.

8.2 Future work

- **Ultra-thin one dimensional nanostructures of PVDF-TrFE for energy harvesting**

The template approach gives the ability to synthesize the one dimensional nanostructures with various diameters by changing pore diameter of the templates. From the literature it is observed that confinement effect will be stronger in the nano pores of diameter < 50 nm.¹ So decreasing the diameter will lead to the oriented crystallization and hence may lead to the formation of single crystals of PVDF-TrFE. In addition it is observed that the nanowires of diameter 5 nm and 10 nm exhibited piezoelectric behavior without poling,² which is the critical step in the usage of ferroelectric materials for the energy harvesting applications. So the 1-D nanostructures synthesized from nano pores of diameter < 100 nm is of interesting to further improve the energy harvesting and to remove or lower the poling fields.

- **One dimensional PVDF nanostructures for the energy harvesting**

The polarization of the PVDF is higher than that of PVDF-TrFE, but in general it crystallizes in non-ferroelectric alpha phase. So by fabricating the ferroelectric phase we can achieve higher piezoelectric coefficients in PVDF over PVDF-TrFE. PVDF in general requires stretching and poling to achieve the ferroelectric phase. But it is recently reported that by synthesizing the PVDF nanostructures in nano confined environment ferroelectric PVDF nanostructures can be formed.^{2, 3} So by synthesizing the ferroelectric PVDF nanostructures will enable to improve the piezo energy harvesting further. In addition, the ultra-thin nanostructures can be synthesized by further reducing the pore dimeters and can use them for the energy harvesting applications.

- **Triboelectric nanogenerators using the ferroelectric polarization**

Triboelectric nanogenerators have attracted research due to their ability to generate higher voltage outputs. Due to the tribo nature almost all the dielectric materials carries either a positive or negative charge.⁴ The typical charge generated by the tribo electricity is of the order of 10^{-4} C/m².^{5, 6} The developed charge on to the material leads to a potential

difference between the two materials in triboelectric energy harvester. The change in the potential difference caused by the contact separation leads to the voltage output.

Compared to dielectric materials, the ferroelectric polymer PVDF or PVDF-TrFE possesses high charge on to the surface $\sim 10^{-1} \text{ C/m}^2$, which is almost 1000 times higher than that of the charge on to the typical dielectric materials (caused by triboelectricity). The polarity of the polarization charge further may tune the triboelectric nature of the PVDF-TrFE (to triboelectric positive or negative). In addition the breakdown strength of the PVDF is high compared to the many other polymer materials. By properly designing the strategies, the ferroelectric polymers can be used to further improve the energy harvesting by triboelectric means.

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