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William G. Kaval
Air Force Institute of Technology

Robert A. Lake
Air Force Institute of Technology

Ronald A. Coutu Jr.
Marquette University, ronald.coutu@marquette.edu

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PVDF-TrFE Electroactive Polymer Mechanical-to-Electrical Energy Harvesting Experimental Bimorph Structure

William G. Kaval, Robert A. Lake, Ronald A. Coutu Jr.
Electrical Engineering
Air Force Institute of Technology
Dayton, Ohio 45433
Email: william.kaval@afit.edu

Abstract—Research of electrostrictive polymers has generated new opportunities for harvesting energy from the surrounding environment and converting it into usable electrical energy. Electroactive polymer (EAP) research is one of the new opportunities for harvesting energy from the natural environment and converting it into usable electrical energy. Piezoelectric ceramic based energy harvesting devices tend to be unsuitable for low-frequency mechanical excitations such as human movement. Organic polymers are typically softer and more flexible therefore translated electrical energy output is considerably higher under the same mechanical force. In addition, cantilever geometry is one of the most used structures in piezoelectric energy harvesters, especially for mechanical energy harvesting from vibrations. In

order to further lower the resonance frequency of the cantilever microstructure, a proof mass can be attached to the free end of the cantilever. Mechanical analysis of an experimental bimorph structure was provided and led to key design rules for post-processing steps to control the performance of the energy harvester. In this work, methods of materials processing and the mechanical to electrical conversion of vibrational energy into usable energy were investigated. Materials such as polyvinyledenedifluoridetetrafluoroethylene P(VDF-TrFE) copolymer films (1um thick or less) were evaluated and presented a large relative permittivity and greater piezoelectric _-phase without stretching. Further investigations will be used to identify suitable micro-electromechanical systems (MEMs) structures given specific types of low-frequency mechanical excitations (10-100Hz).

I. INTRODUCTION

Natural energy sources are attracting a rising amount of interest due to increasing environmental concerns. Electroactive polymer (EAP) research is one of the new opportunities for harvesting energy from the natural environment and converting it into usable electrical energy. Piezoelectric ceramics, such as lead zirconate titanate (PZT), materials used for mechanical to- electrical energy harvesting tend to be unsuitable for lowfrequency mechanical excitations such as human movement. Polymer materials are typically more flexible, allowing the electrical energy output to be considerably higher under the same mechanical energy input. Several applications have been identified where free, unused mechanical energy could be used to generate electrical energy and are summarized in Table I.

TABLE I Frequency and Acceleration of Various Vibration Sources [1]

Vibration source	Frequency (Hz)	Acceleration amplitude (m/s^2)
Car instrument panel	13	3
Casing of kitchen blender	121	6.4
Clothes dryer	121	3.5
HVAC vents in office building	60	0.2-1.5
Car engine compartment	200	12
Refrigerator	240	0.1
Human walking	2-3	2-3

There are various methods to convert mechanical energy from vibrating or moving objects into electrical energy. Electroactive polymers possess semi-crystalline structures in which the centers of positive and negative charges do not overlap, yielding dipoles. When subjected to mechanical vibrations, mechanical strain is applied to these materials and leads to distortion of the dipoles, creating electrical charge. The electrical energy can be harvested by storing it in capacitors or rechargeable batteries [1].

The following electroactive polymers have demonstrated piezoelectric, pyroelectric or ferroelectric properties: Nylon- 11 [2], polylactic acid (PLLA) [3], poly(lactic-co-glycolic acid) (PLGA) [4], and poly(vinylidene fluoride) (PVDF) [1]. PVDF and its copolymers have

demonstrated the best all-around electroactive properties [5][1]. Many of the interesting properties of PVDF, in particular those related with its use as a sensor or actuator, are related to the strong electrical dipole moment of the PVDF which results from the electronegativity of fluorine atoms as compared to those of hydrogen and carbon atoms [5][6]. In this way, each chain possesses a dipole moment perpendicular to the polymer chain. This semicrystalline polymer shows a complex structure and can present several distinct crystalline phases related to different chain conformations. As shown in Fig. 1, the *β*-phase possesses the highest dipole moment per unit cell when compared to the other two phases (*α* & *λ*) and is therefore the most responsive piezoelectric polymer.

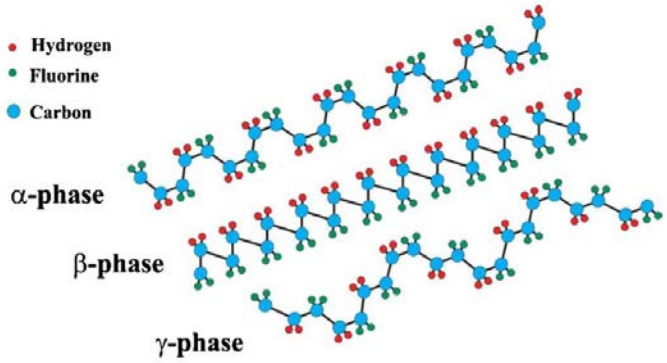

Fig. 1. Schematic representation of the chain conformation for the α, β, and λ phases of PVDF [5]

Previous processes used to manufacture PVDFs piezoelectric *β*-phase have been limited to drawn films. Therefore in order to obtain the electroactive phases of PVDF, different strategies have focused on the inclusion of specific copolymers such as Poly(vinylidene fluoride-Trifluoroethylene), P(VDFTrFE) [6][7][8][5]. As shown in Fig. 2, P(VDF-TrFE) always exhibits the ferroelectric *β* crystalline phase [1][5]. The fluorine atom from TrFE stabilizes the *β*-crystalline phase and discourages *β*-crystalline phase formation [1]. This property permits P(VDF-TrFE) copolymer to be produced in the form of thin-films by spin coating, and allows a suitable control of sample thickness which is ideal for the production of energy harvesting microstructures.

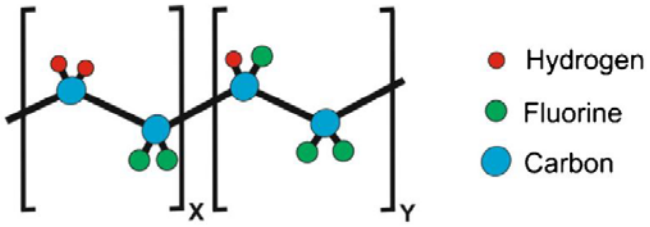

Fig. 2. Schematic representation of the P(VDF-TrFE) repeat units [5]

II. METHODOLOGY

In the case of energy harvesting using an EAP such as P(VDF-TrFE), the vibration or mechanical energy sources either have low motion frequencies or low acceleration. A thin and flat form factor allows the EAP element to readily react to the motion of the host structure. Therefore, cantilever geometry is one of the most used structures in piezoelectric energy harvesters, especially for mechanical energy harvesting from vibrations [1][9][10] (Fig. 3).

Harvester performance can be optimized to specific applications provided a known resonant frequency from Fig. 4, which is given by: $\omega_{\eta f} + \alpha_{\eta} \sqrt[2]{\frac{\mathrm{EI}}{mL^4}}$ where $\alpha_n = 1.875, 4.694\ 7.885$ [11]. Therefore the resonance frequency of a simply supported cantilever beam can be calculated using (1) where E is the Young's modulus, I is the moment of inertia, L is the length of the cantilever, w is the width of the cantilever, m is the

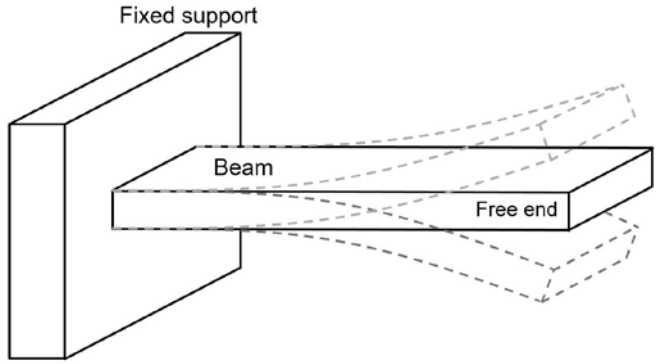

Fig. 3. Cantilever beam with rectangular cross section under free vibration mass per unit length of the cantilever beam, and $\alpha_n = 1{,}875$ is the eigenvalue for the fundamental vibration mode [1].

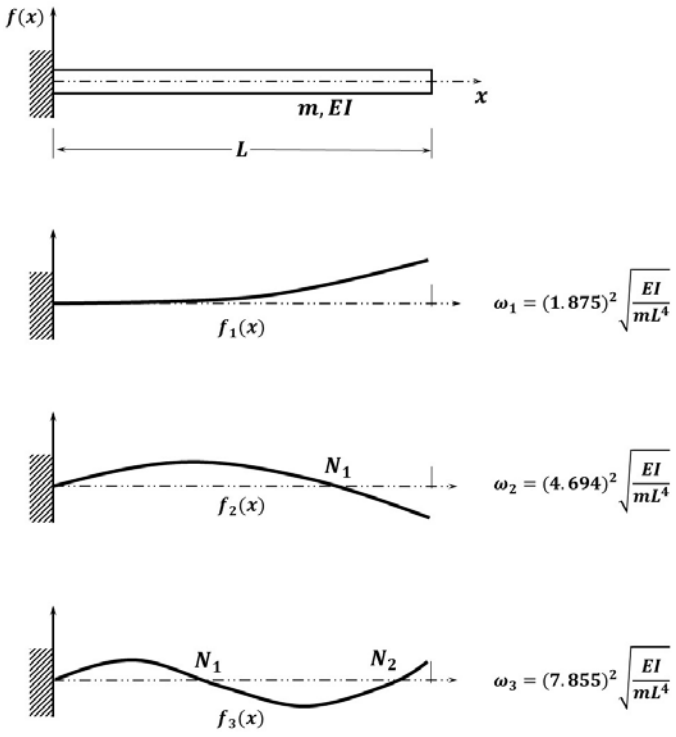

Fig. 4. The first three undamped natural frequencies and mode shapes of a cantilever beam

$$f_r = \frac{{\alpha_n}^2}{2\pi} \frac{1}{L^2} \sqrt{\frac{EI}{mw}} \quad (1)$$

$$f_\tau = \frac{{\alpha'_n}^2}{2\pi} \frac{1}{L^2} \sqrt{\frac{K}{m_e + \Delta m}} \quad (2)$$

In order to further lower the resonance frequency of the cantilever microstructure, a proof mass can be attached to the free end of the cantilever (Fig. 5). In which case (1) can be approximated by (2), to include the proof mass Δm where ${\alpha'_n}^2 = \alpha_n \sqrt[2]{0.236/3}$, $m_e = 0.236mwL$ is the effective mass of the cantilever, and K is the effective spring constant of the cantilever [1][12].

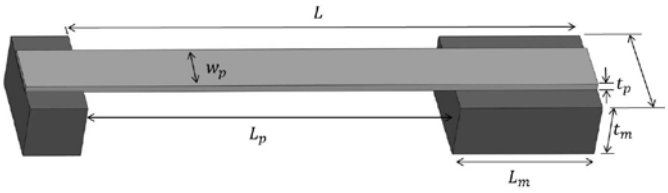

Fig. 5. Proof mass attached to the free end of a cantilever beam

III. DESIGNS AND FABRICATION

Fig. 6 shows a large bimorph structure that will be used to experimentally validate the aforementioned design rules. Energy harvester performance can be predicted based on the dimensions, mass of the cantilevers, and proof mass. In this structure, a thin layer of P(VDF-TrFE) will be deposited and patterned into a cantilever and bonded with a top and bottom electrodes serving as conductors for the generated charge. Commercially available PolyMUMPs prototyping services were used to fabricate the cantilever based devices. Since PolyMUMPs uses a predefined process and materials, postprocessing was required for deposition and patterning P(VDFTrFE) polymer for energy harvesting application. Fig. 9 shows the post processing steps for PolyMUMPs energy harvesting structures using P(VDF-TrFE) EAP.

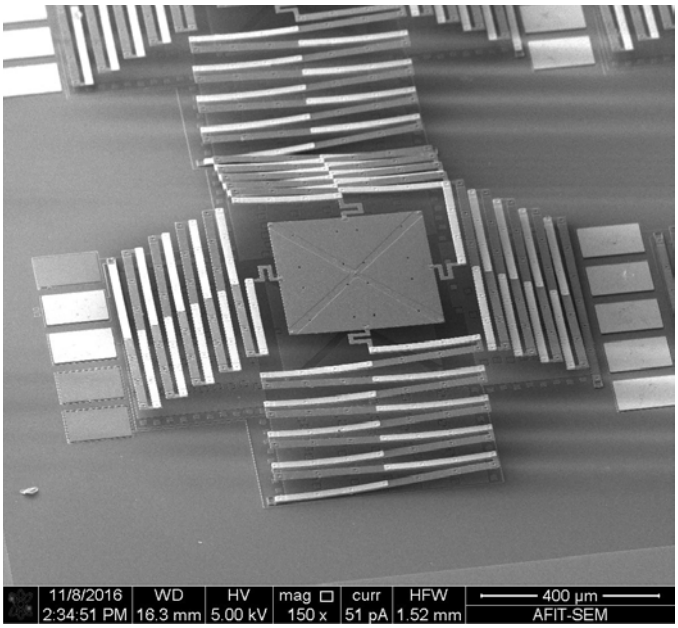

Fig. 6. PolyMUMPs design for a bimorph structure with large center proof mass for energy harvesting. Overall dimensions are 1mm x 1mm

The first step in post-processing was the deposition of 8% (weight/volume) of P(VDF-TrFE)/methyl ethyl ketone (MEK) copolymer solution. The solution was deposited by spin coating at 2000 rpm for 30 seconds resulting in a $\sim 1\mu m$ layer of P(VDF-TrFE) based on Fig. 7. The sample was then baked at 100_C in a vacuum oven for 5 hours at 50mT. The oven heat was turned off with the sample remaining and allowed to cool slowly until the sample was within $\pm 5°C$ of ambient.

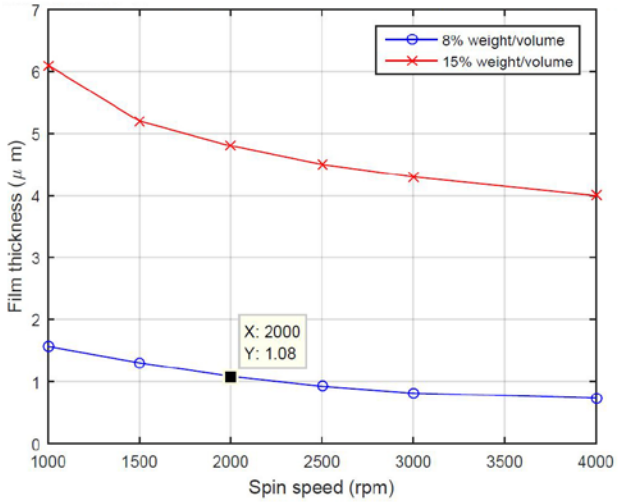

Fig. 7. Film thickness vs. spin speed with 8% and 15% weight/volume of PVDF-TrFE/MEK solution

For the top electrode, a 30Å layer of chromium was deposited followed by a 2000Å layer of gold. Photoresist was spin coat deposited followed by patterning and development. Next, the top Ti/Al electrode (2500Å thick) was patterned by wet etch. Once patterned, the top electrode

and remaining photoresist were used as an reactive ion etch (RIE)/etch stop to pattern the P(VDF-TrFE) thin film. The exposed P(VDF-TrFE) was removed by RIE dry etch performed under 75 SCCM oxygen gas environment with $100W$ RF power and $50mT$ pressure. The P(VDF-TrFE) thin film etch rate was $\sim$230nm/min. The photoresist mask atop the patterned electrodes were etched simultaneously with an etch rate of $\sim$150nm/min and dry etch was continued until the photoresist mask was fully etched. Due to the PolyMUMPs process, the final processing step requires releasing the PolyMUMPs structures by immersing the chips in a 49% HF solution. This release step removes the untrapped sacrificial oxide layers (1st Oxide and 2nd Oxide) freeing the first and second mechanical layers of polysilicon (Poly1 and Poly2) as illustrated in Fig. 8 [13].

Once processed, the P(VDF-TrFE) must be poled in order to obtain piezoelectricity. Temperature and electric field poling conditions are critical to the resulting piezoelectricity of the ferroelectric polymer [14][15]. Two widely used methods are electrode poling and corona poling. The first method involves the poling electric field being applied through two metal electrodes. The second, corona poling, is a method in which a high electric field is applied directly to the polymer film without metal electrodes. Electrode poling is the safest and easiest to conduct. However, corona poling is more efficient

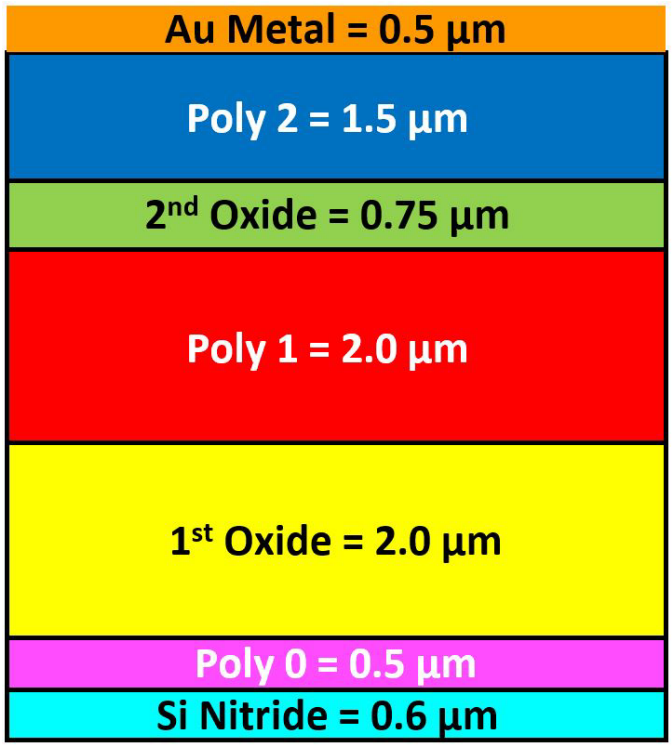

Fig. 8. A schematic illustrating the layers and their corresponding dimensions used in the PolyMUMPs process

because of the reduced risk of localized electric breakdown occurring, in which case the corona poling process would not be affected [15].

IV. RESULTS AND DISCUSSION

Since polymers are typically used in capacitive energy harvesting designs, the use of polymer materials with large relative permittivity have demonstrated the most success for mechanical to electrical energy conversion [1][16]. The characteristic equations of piezoelectric materials are $D_3 = \epsilon_{33}E_3 + d_{31}T_1$ and $S_1 = d_{31}E_3 + s_{11}T_1$, where D_3 is the electric displacement in the polarization direction, S_1 is the strain in the axial direction, ε_{33} is the dielectric permittivity of the piezoelectric material in the polarization direction at constant stress condition, E_3 is the electric field in the polarization direction, T_1 is the stress in the axial direction of the cantilever, d_{31} is the piezoelectric coefficient, and s_{11} is the compliance of piezoelectric material under constant electric field condition [17][18]. Given the area of the piezoelectric layer (*AP*), the generated piezoelectric charge can be calculated as:

$$\int^{AP} D_3 dA = d_{31}S_1/s_{11} + \epsilon_{\overline{33}}E_3 dA, \quad (3)$$

where: $\epsilon_{\overline{33}}E_3\ (1 - k_{31}^2)$ and $k_{31}^2 = (\epsilon_{33}s_{11})$ [17]

The crystal structure of P(VDF-TrFE) plays an important role in how we can characterize it as a potential electroactive polymer for energy harvesting. Consequently the crystal structure is typically related to the composition of the copolymer in addition to the annealing process. As illustrated in Fig.2, the unit cell of *β* crystalline phase of P(VDF-TrFE) is orthorhombic with each chain aligned and packed with the CF_2 groups. Figure 10 shows the XRD degree of crystallinity of P(VDF-TrFE) for different annealing temperatures (80; 90; 100; 110; 120; 140ºC) in order to obtain information on the degree of the crystalline structure.

A model representing a bimorph energy harvesting structure was designed in simulation taking into account the additional deposition steps involved. Finite element modeling was conducted using CoventorWare© to evaluate the addition of PVDF and top gold electrode deposition (post PolyMUMPS

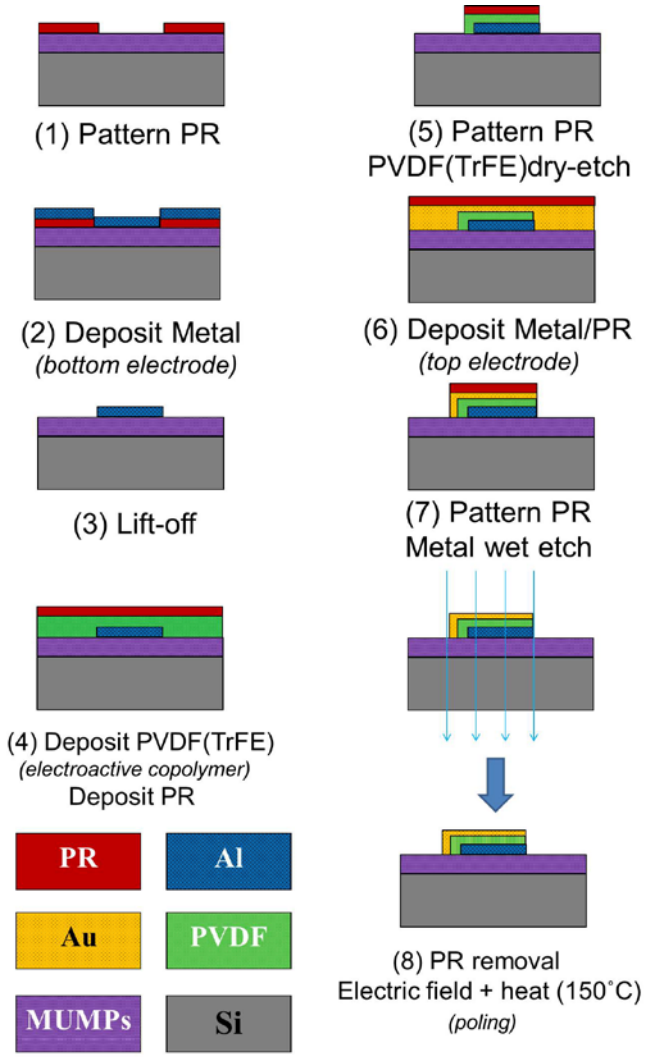

Fig. 9. PolyMUMPs post-processing fabrication steps involving the deposition and patterning of PVDF films

processing). More specifically, partial bimorph cantilever beam material properties and geometries were evaluated. In modeling and simulation, the addition of PVDF and gold reduced the deflection by approximately 66% independent of actuator length (Table II).

TABLE II Results of Cantelever Deflection With/Without Post Processing

$Length$	Deflection $(2\mu m)$ $(Poly2, Au)$	Deflection $(3.5\mu m)$ $(Poly2, Au, PVDF, Au)$
$500\mu m \rightarrow$	$24\mu m$	$8.2\mu m$
$625\mu m \rightarrow$	$37\mu m$	$13\mu m$
$750\mu m \rightarrow$	$54\mu m$	$18\mu m$
$875\mu m \rightarrow$	$73\mu m$	$25\mu m$
$1000\mu m \rightarrow$	$95\mu m$	$32\mu m$

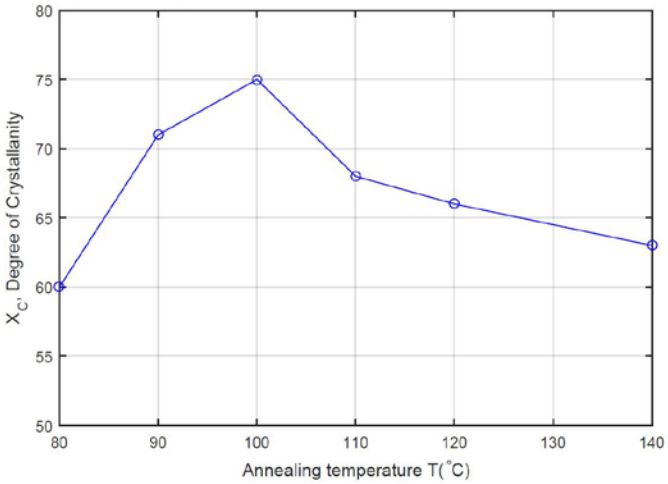

Fig. 10. Dependence of the degree of the crystalline structure as a function of annealing temperature

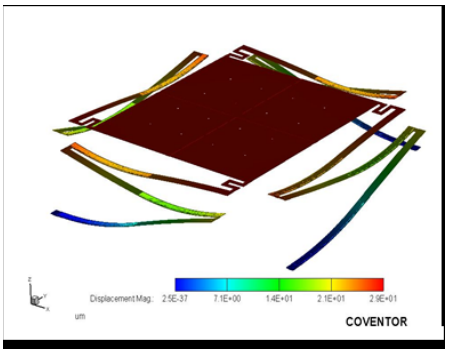

Fig. 11. MEMS large aperture actuator assembly mechanical analysis

V. CONCLUSION

The work presented in this thesis provided the framework for a unique approach to characterize P(VDF-TrFE) for energy-harvesting application. Fabrication and processing was conducted which resulted in the validation of a viable PolyMUMPs post-processing techniques toward the implementation of full scale energy-harvesting arrays capable of producing usable amounts of power.

The goal of this research was to design, model, fabricate, and test/characterize a high fill-factor, large aperture, out-of-plane, sensor/actuation assembly capable of generating electrical charge with an eventual project goal of collecting and storing usable energy. Therefore since the harvester performance is proportional to resonant frequency, a known proofmass was used to establish the dominant resonant frequency. It was also discovered that the annealing temperature play an important role in the crystal structure when processing P(VDFTrFE) for use in energy harvesting. Other applications of this research include off-grid remote sensing applications as well as a multitude of commercial systems requiring a sustained sources of power. Ultimately, knowledge gained from this research will increase the efficiency of consumable power sources.

VI. ACKNOWLEDGMENTS

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REFERENCES

[1] H. Li, C. Tian, and Z. D. Deng, "Energy harvesting from low frequency applications using piezoelectric materials," *Applied Physics Reviews*, vol. 1, no. 4, pp. 0–20, 2014.

[2] S. C. Mathur, J. I. Scheinbeim, and B. A. Newman, "Piezoelectric properties and ferroelectric hysteresis effects in uniaxially stretched nylon-11 films," *Journal of Applied Physics*, vol. 56, no. 9, pp. 2419–2425, 1984.

[3] L. Huang, X. Zhuang, J. Hu, L. Lang, P. Zhang, Y. Wang, X. Chen, Y. Wei, and X. Jing, "Synthesis of Biodegradable and Electroactive Multiblock Polylactide and Aniline Pentamer Copolymer for Tissue Engineering Applications," *Biomacromolecules*, vol. 9, no. 3, pp. 850–858, mar 2008. [Online]. Available: http://pubs.acs.org/doi/abs/10.1021/bm7011828

[4] D. J. Bryan, J. B. Tang, S. A. Doherty, D. D. Hile, D. J. Trantolo, D. L. Wise, and I. C. Summerhayes, "Enhanced peripheral nerve regeneration through a poled bioresorbable poly(lactic-co-glycolic acid) guidance channel," *Journal of Neural Engineering*, vol. 1, no. 2, p. 91, 2004. [Online]. Available: http://stacks.iop.org/1741-2552/1/i=2/a=004

[5] P. Martins, A. C. Lopes, and S. Lanceros-Mendez, "Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications," *Progress in Polymer Science*, vol. 39, no. 4, pp. 683–706, 2014. [Online]. Available: http://dx.doi.org/10.1016/j.progpolymsci. 2013.07.006

[6] Y. G. Jiang, S. Shiono, H. Hamada, T. Fujita, D. Y. Zhang, and K. Maenaka, "Reactive ion etching of poly(vinylidene fluoridetrifluoroethylene) copolymer for flexible piezoelectric devices," *Chinese Science Bulletin*, vol. 58, no. 17, pp. 2091–2094, 2013.

[7] F. Bauer, E. Fousson, Q. M. Zhang, and L. M. Lee, "Ferroelectric copolymers and terpolymers for electrostrictors: Synthesis and properties," *IEEE Transactions on Dielectrics and Electrical Insulation*, vol. 11, no. 2, pp. 293–298, 2004.

[8] H. Han, Y. Nakagawa, Y. Takai, K. Kikuchi, S. Tsuchitani, and Y. Kosimoto, "Microstructure fabrication on a *β*-phase PVDF film by wet and dry etching technology," *Journal of Micromechanics and Microengineering*, vol. 22, no. 8, p. 085030, 2012.
[9] S. Saadon and O. Sidek, "Micro-Electro-Mechanical System (MEMS)-Based Piezoelectric Energy Harvester for Ambient Vibrations," *Procedia - Social and Behavioral Sciences*, vol. 195, pp. 2353–2362, 2015. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1877042815036770
[10] S. Boisseau, G. Despesse, and B. A. Seddik, "Electrostatic Conversion for Vibration Energy Harvesting," *Small-Scale Energy Harvesting*, no. October, pp. 1–39, 2012. [Online]. Available: http://www.intechopen.com/books/small-scale-energyharvesting/electrostatic-conversion-for-vibration-energy-harvesting
[11] Y. Liu, T. Nabatame, T. Matsukawa, K. Endo, S. O'uchi, J. Tsukada, H. Yamauchi, Y. Ishikawa, W. Mizubayashi, Y. Morita, S. Migita, H. Ota, T. Chikyow, and M. Masahara, "Comparative Study of Charge Trapping Type SOI-FinFET Flash Memories with Different Blocking Layer Materials," *Journal of Low Power Electronics and Applications*, vol. 4, no. 2, pp. 153–167, 2014. [Online]. Available: http://www.mdpi.com/2079-9268/4/2/153/
[12] A. S. Y. Ho, J. S.; Poon, "Energy transfer for implantable electronics in the electromagnetic midfield (invited paper)," *Progress In Electromagnetics Research*, vol. 148, no. August, pp. 151–158, 2014.
[13] A. Cowen, B. Hardy, R. Mahadevan, and S. Wilcenski, "PolyMUMPs Design Handbook a MUMPsR process." [Online]. Available: http://www.memscap.com/fn gfn gdata/assets/pdffn gfile/0019/1729/PolyMUMPs-DR-13-0.pdf
[14] M. Wegener and R. Gerhard-Multhaupt, "Poling of piezoelectric polymer cables and assessment of their sensor properties," in *Proceedings. 11th International Symposium on Electrets*, no. 1. IEEE, 2002, pp. 379–382. [Online]. Available: http://ieeexplore.ieee.org/lpdocs/epic03/wrapper.htm?arnumber=1043023
[15] F. A. Costache, C. Schirrmann, R. Seifert, K. Bornhorst, B. Pawlik, H. G. Despang, and A. Heinig, "Polymer energy harvester for powering wireless communication systems," *Procedia Engineering*, vol. 120, no. April 2016, pp. 333–336, 2015.
[16] A. Plihon, V. Fischer, F. D. D. Santos, and R. Gwoziecki, "Printed actuators made with electroactive polymers on flexible substrates," *9th IEEE International Conference on Nano/Micro Engineered and Molecular Systems, IEEE-NEMS* 2014, pp. 68–71, 2014.
[17] L. Zhang, S. R. Oh, T. C. Wong, C. Y. Tan, and K. Yao, "Piezoelectric polymer multilayer on flexible substrate for energy harvesting," *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, vol. 60, no. 9, pp. 2013–2020, 2013.
[18] L. Technology, "Typical application," no. LT 0915 REC C, pp. 1–42, 2013.

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