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William G. Kaval

Robert A. Lake
Air Force Institute of Technology

Ronald A. Coutu Jr.
Marquette University

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William G. Kaval[1], Robert A. Lake[1] and Ronald A. Coutu Jr.[2]
[1]Air Force Institute of Technology, 2950 Hobson Way, Wright-Patterson, OH 45419, U.S.A.
[2]Marquette University, 1637 W. Wisconsin Ave, Milwaukee, WI 53233, U.S.A.

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 polyvinyledenedifluoridetetra-fluoroethylene P(VDF-TrFE) copolymer films (1um thick or less) were evaluated and presented a large relative permittivity and greater piezoelectric β-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).

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 low frequency 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.

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 semi-crystalline polymer shows a complex structure and can present several distinct crystalline phases related to different chain conformations. 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

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(VDF-TrFE) [6,7,8,5]. As shown in figure 1, P(VDF-TrFE) always exhibits the ferroelectric β crystalline phase [1,5]. The fluorine atom from TrFE stabilizes the β-crystalline phase and discourages α-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.

Figure 1. Schematic representation of the P(VDF-TrFE) repeat units.

THEORY

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].The resonance frequency of a simply supported cantilever beam as shown in figure 2 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 mass per unit length of the cantilever beam, and $\alpha_n = 1.875$ is the eigenvalue for the fundamental vibration mode [1,11].

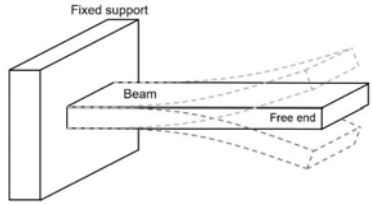

Figure 2. Cantilever beam with rectangular cross section under free vibration.

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

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

Figure 3 shows a large bimorph structure that was 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, post-processing was required for deposition and patterning P(VDF-TrFE) polymer for energy harvesting application.

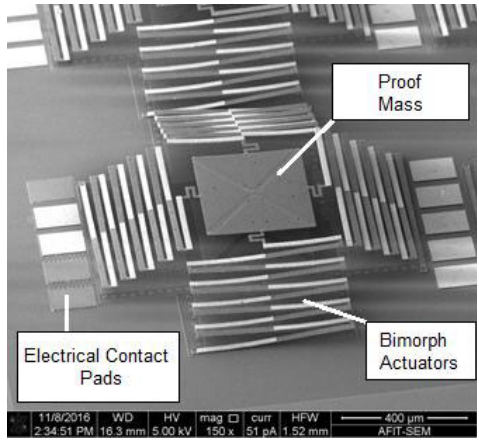

Figure 3. PolyMUMPs design for a bimorph structure with large center proof mass for energy harvesting. Overall dimensions are 1mm ×1mm.

FABRICATION

The first step in post-processing was the deposition of 8% (weight/volume) of P(VDF-TrFE)/methyl ethyl ketone (MEK) copolymer solution on top of the Cr/Au bottom electrode. The solution was deposited by spin coating at 2000 rpm for 30 seconds resulting in a ~1µm layer of P(VDF-TrFE. The sample was then annealed at 100°C in a vacuum oven (50mT) for 5 hours. The sample was allowed to cool slowly until the sample was within ±5°C of ambient. The top electrode, consisted of a thin adhesion layer of chromium followed by a 2000Å layer of gold and patterned by wet etch. 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 at an etch rate was of ~230nm/min. The remaining photoresist mask atop the patterned electrodes were dry etched simultaneously with an etch rate of ~150nm/min and dry etch was continued until the photoresist mask was fully etched. Due to the PolyMUMPs process, the final processing step required releasing the PolyMUMPs structures by immersion in a 49% HF solution. This release step removed the untrapped sacrificial oxide layers (1st Oxide and 2nd Oxide) freeing the first and second mechanical layers of polysilicon (Poly1 and Poly2).

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 [1,11]. The characteristic equations of piezoelectric materials are $D_3 = \varepsilon_{33}E_3 + d_{31}T_1$ 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 [11]. Given the area of the piezoelectric layer (AP), the generated piezoelectric charge can be calculated using (3).

$$\int^{AP} D_3 dA = d_{31}S_1/s_{11} + \bar{\varepsilon_{33}}E_3 dA \quad \textbf{(3)}$$

As illustrated in figure 1, the unit cell of β crystalline phase of P(VDF-TrFE) is orthorhombic with each chain aligned and packed with the CF2 groups. Consequently the degree of crystallinity of P(VDF-TrFE) showed a relationship to the annealing process. Figure 4 shows the XRD degree of crystallinity of P(VDF-TrFE) for different annealing temperatures (80,90,100,110,120,140°C) in order to obtain information on the degree of the crystalline structure.

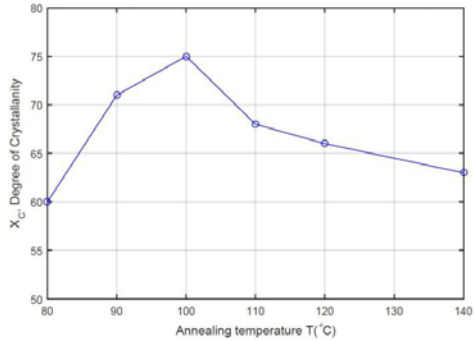

Figure 4. Dependence of the degree of the crystalline structure as a function of annealing temperature.

RESULTS

A noticeable decrease in the initial deflection of the bimorph structures was noticed with the addition of the PVDF layer due to the increase structural rigidity of the arms increasing with the additional thickness. The measured deflections are recorded in Table 1 for different lengths of bimorph arm for both with and without the additional PVDF layer.

Table 1: Results of bimorph cantilever deflection with and without PVDF layer.

Length	Deflection without PVDF	Deflection with PVDF
500 μm	24 μm	8.2 μm
625 μm	37 μm	13 μm
750 μm	54 μm	18 μm
875 μm	73 μm	25 μm
1000 μm	95 μm	32 μm

In order to obtain voltage response, the bimorph structures were cycled at varying frequencies ranging from 2Hz to 20Hz and the response was recorded via the oscilloscope. The results are summarized in Table 2.

Table 2: Bimorph electrical response from 2 to 20 Hz cycle rate.

Bimorph Cycle Frequency (Hz)	dB Gain
2	55
5	45
10	35
20	25

CONCLUSIONS

This study provides the framework 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 the goal of collecting and storing usable energy. It was demonstrated that through post processing, MEMS devices originally intended for uses other than energy harvesting can be modified so that they generate electricity while they are being operated for their original purpose, in this case a high deflection vertical actuator. 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 exhibit potential to increase the efficiency of consumable power sources.

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