Study of printed polymeric flexible energy harvesting elements – impact of the electrode materials and patterns

M Aleksandrova¹, R Aepuru², G Dobrikov¹

¹Technical university of Sofia, Department of Microelectronics, Sofia, Bulgaria
²University of Concepcion, Department of Materials Engineering, Concepcion, Chile

m_aleksandrova@tu-sofia.bg

Abstract. In this paper is presented study of flexible pressure piezoelectric energy harvesting developed with an screen-printing of polyvinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) ink on three different metal electrodes (silver, gold and aluminium) with three different topologies – rectangular, meander and side comb. The influence of the electrode type and pattern is studied in terms of polymer coating distribution and morphology, piezoelectric voltage generation and stability at multiple bending, as well as piezoelectric coefficient. The elements are studied at low mass loading of up to 100 g and frequency up to 50 Hz. They produce voltage between 916 and 362 mV from active area of 1 cm² and piezoelectric polymer film of 3 µm, according to the electrode metal nature and shape. It was found that the silver electrode with meander shape is the optimal for electrical performance and mechanical stability giving superior piezoelectric coefficient of 0.332 V.m/N to the reported values and only 8.6 % decrease of the piezoelectric voltage at 1500 repeating bending cycles.

1. Introduction

Nowadays, the demands on the portable, thin and light-weight energy harvesting devices from the ambient processes continuously increase, because they tent to serve as alternatives of the conventional batteries in the miniaturized devices (nanoelectronic or nanoelectromechanic). In contrast to the macro-piezoelectric harvesters, where loading of tenth of kilograms need to be stand and few Watts power are generated as a result, the typical efficiency of the single piezoelectric harvesting unit with area of few square centimetres and films thickness about 1-2 µm is low (not greater than few hundreds of nW or maximum few µW at higher thickness and depending on the dielectric permittivity of the piezoelectric materials) [1,2]. Therefore, few general approaches are usually applied in order to gain the piezoelectric response, such as: multilayer stack structure with intermediate electrodes, coupled in parallel; composites between piezoelectric oxides, each with high piezoelectric modulus and dielectric permittivity, multiple coated substrates connected in parallel (or series), and etc. [3]. Due to the requirements for environmental friendly technologies, lead-free, strontium-free and zirconium-free materials are recently preferred for energy device fabrication. They are characterized with much lower piezoelectric coefficients compared with the rest piezo-oxides. Piezoelectric polymers based on PVDF (polyvinylidene fluoride) replace the lead-free oxides because of the similarity in the piezoelectric modulus and dielectric permittivity, but advantageously possesses high strain resistance and great durability at bending/twisting. Additional consideration should be the high sensitivity of the piezoelectric transducers, because some of the typical applications related to health care uses mechanical stimuli with equivalent mass load not greater than 100-200 g and low frequency (for example hearth beating and breathing processes).
Recently, a lot of reports can be found about ferroelectric composite oxide-polymer or purely polymer-based transducers [4-6]. Some of the researches are devoted to chemical synthesis of new materials of chemical modification of the existing ones for enhancement of the piezoelectric constant and durability [7,8]. Another reports aim to tune the electrical properties, such as increase of the permittivity, decrease of the loss factor, increase the dipole mobility, polarization, and etc. [9,10]. In the same time, information lacks about the influence of the metal electrodes on the electrical charge collection ability and compatibility with the piezoelectric materials processing technologies (deposition and annealing).

The poly[(vinylidenefluoride-co-trifluoroethylene] (PVDF-TrFe) is modification of the conventional PVDF ensuring better ferroelectric properties and enhanced piezoelectric constant than the PVDF [11], therefore, the materials has attracted the researchers’ attention almost ten years ago, when it has been incorporated as a coating in the non-volatile memory cells [12]. The next promising applications reported more recently are inkjet-printed piezoelectric actuator with polymer P(VDF-TrFe) thin film [13] and flexible piezoelectric transducers relying on thin 200 nm polymer functional film [14]. Based on the numerous studies, one can be concluded that the material has favourable polarizing properties, good processing ability and good compatibility with the most of the used materials and technologies in the microfabrication.

In some typical micro- and nanoelectromechanical elements like sensors, or actuators, the involved metals and geometrical patterning of the electrodes are crucial for the optimization of the device electrical performance. Therefore, study of the impact of the electrodes material and configuration is strongly necessary. The literature overview showed that there is no complete investigation related to this issue. For the application of piezoelectric polymer PVDF-TrFe reports, showing the effect of the electrodes on the piezoelectric performance has not been found. Moreover, for flexible energy harvesting based on PVDF-TrFe additional considerations due to adhesion problems should be also taken into account, in addition to the technological compatibility with the substrate and piezoelectric materials.

In this paper, new formulated PVDF-TrFe ink was printed between three different electrode materials (gold, silver and aluminium) with three different patterns (square, meander and side-comb shapes (the last with non-mutually overlapped “fingers”). Comparison between the two different sets of samples was made in terms of piezoelectric output voltage and long-term stability of the signal. In this way, complex and expensive multilayer structures with inner electrodes are avoided and in the same time the collecting of the output charge is improved due to lack of internal coupling and interfacial strain problems.

2. Experimental section
Polyethylene naphthalate (PEN) plastic substrates 125 µm were cleaned and pieces were cut for bottom electrode deposition. The sizes were considered according to the calculated equivalent area of the films due to the different patterns. Three different metals were considered with small thickness in order to avoid ductility problems. Gold films with thickness of 50 nm and sheet resistance 4.5 Ω/sq was DC sputtered in vacuum at plasma current of 35 mA. Silver and aluminium films with the same thickness and sheet resistance of respectively 3.4 Ω/sq and 5.6 Ω/sq were thermally evaporated in vacuum. Standard photolithographic processes were applied - direct photolithography for the gold films with potassium iodide etching solution for patterning and reverse photolithography (lift-off process) in order to avoid etching in nitric acid and phosphorous acid, respectively for the silver and aluminium films. Square, meander and side-comb shapes were obtained. Suitable contact pads were produced in order to connect neighbouring segments in series and make the active functional area equal.

P(VDF-TrFE) ink was screen printed (printer model S300V) on metal coated PEN substrates, which were selected to avoid thermal stress during annealing of the piezoelectric coating. Screen with mesh count of 180 n/cm and wire diameter of 30 µm was used and the deposition parameters were squeegee speed of 200 mm/s and pressure of 3 bars. The annealing of the samples was done in furnace at 135°C per 15 minutes in order to stabilize the prints and guarantee interruption of the rheological
behaviour of the print. At these deposition and annealing conditions it was found that homogeneously distributed and crystallized P(VDF-TrFE) films could be produced on any of the metals coating the plastic substrate without cracks and other defects. The film thickness was approximately 3 μm, measured by profilometer. After deposition and patterning of the top electrodes polling was performed by applying a constant electric field of 50 V/μm. Top electrodes of the same type with the same patterns were realized. Photos of the bottom electrodes and the completed prepared samples are shown in figure 1 a-c.

![a) bottom electrode patterns b) flexed PEN/Au c) completed structure](image)

Figure 1. Photos of the prepared samples.

The electromechanical testing setup (described elsewhere [15]) provides single point clips and free standing opposite side of the sample (cantilever type testing in dynamic mode), thus apply precisely controlled strain. The way of fixing and strain applying with respect to the electrodes places (capacitor type structure) results in a g_{31} measurement mode. The magnitude of the vibration equivalent to mass load provides maximum load of 100 g and broad range of frequencies from 2Hz to 2 MHz. The produced piezoelectric voltage was monitored by oscilloscope Tektronix TDS 1012B and the surface morphology of the coatings was observed by Dino-Lite digital microscope at magnification of 500. In order to gain the current produced from a unit element it was not tested single structure (except for the rectangular one), but multiple smaller elements were connected in parallel by the conductive lines and pads, shaped during the photolithography.

3. Results and discussion

The effect of the different metal electrodes and their shapes on the piezoelectric behaviour was compared and summarized in figure 2. It can be observed that no matter of the electrode pattern, the samples with silver electrodes produced the greatest piezoelectric voltage, showing that the silver could be the most suitable for coupling with PVDF-TrFe. Depending on the electrode shape, the piezoelectric voltage decreased with the decrease of the bottom and top electrodes overlapping area and this is common trend for all three studied metals. Thus, at maximal mass load of 100 g and bending frequency of 50 Hz, it can be observed that the silver rectangular electrodes could produce piezoelectric voltage (U_{pe}) of 916 mV, the meander electrodes could give 840 mV and the side comb electrodes – 446 mV. In comparison to the silver, the gold is the next possible solution, due to the very close results in term of piezoelectric voltage – 800, 768 and 362 mV - produced from rectangular, meander and side comb shaped electrodes, respectively. Although the technological compatibility of the aluminium, which is preferable electrode in most of the microelectronic device, here its weak piezoelectric response and high sensitivity to the electrodes shape make it not preferable for interfacing with PVDF-TrFe.

The shape of the generated piezoelectric signal from PEN/Ag/PVDF-TrFe/Ag sample at relatively small load of 80 g with frequency of 50 Hz is shown in figure 3 as an example for strong signal, although the distortions presence. It could be seen that the maximal voltage at this relatively low bending intensity was 664 mV (effective value rms was 265 mV), which is sufficient to drive some specialized power management circuits for accumulation of charge, such as ADP5090 ultralow power boost regulator that can be used for low power consumer supply [16].
Figure 2. Comparison of the metals and their pattern suitable for PVDF-TrFe piezoelectric flexible elements at maximum mass load of 100 g and 50 Hz.

For the determination of optimal performance of all nine produced combinations, the long term stability should be also considered. The results are presented in figure 4 a-c. When the samples are shacked and tested after 1500 repeating bending cycles, the speed of degradation is strongly dependent on the electrode shape. As can be seen from figure 4, the side comb configuration exhibited the most stable behaviour with variation of the piezoelectric voltage (not greater than 1.9 % from its initial value).

Figure 3. Piezoelectric voltage generated from PEN/Ag/PVDF-TrFe/Ag sample with rectangular electrodes at mass load of 80 g and frequency of 50 Hz.

Figure 4. Stability of the piezoelectric voltage produced from PVDF-TrFe samples with different metal electrodes and different patterns of the electrodes at maximum mass load of 100 g and low frequency of 20 Hz: a) silver; b) gold; c) aluminium.

Electrical stability of the samples is strongly dependent on the wetting ability of the different electrode materials from the ink and the screen printed polymer coating morphology. As could be seen from the microscopy images in figure 5, the density of the PVDF-TrFe coating is relatively low, as compared to coating with the same thickness printed on silver or aluminium. This can explain the greatest instability of the piezoelectric voltage \( \Delta U_{PE} @1500 \text{ bends} \) generated from the samples with gold electrodes after 1500 bends, despite of the pattern. The sample with gold rectangular electrode exhibited 17.5 % decrease in the piezoelectric voltage, the meander shaped gold electrodes showed 11.4 % decrease, and the side comb - 1.9 %. For comparison, the same data about the aluminium are as follows: 16.4 %, 9.5 % and 1.7 % respectively. The samples with silver electrodes demonstrated the most stable behaviour with decrease in the piezoelectric voltage, respectively 12.3 % for rectangular electrode, 8.6 % for meander shape and 1.5 % for side comb pattern. As a general trend, the samples with side comb structures are characterized with the greatest stability of the piezoelectric signal after multiple bending, due to the smallest contact zones between electrode and polymer films. However, due to the poor coverage, the collected charge was the lowest possible from the three available
patterns and the produced voltage barely reached amplitude beyond 480 mV. On the other hand the high density rectangular electrodes ensured high piezoelectric voltage up to 1 V, but it gradually decreased almost twice at the end of the test. The meander shaped electrodes accept intermediate position in the cases of all three studied metals with regards of piezoelectric yield and durability.

As can be seen from figure 5a the polymer printed on gold electrode is characterized with relatively low density coating, figure 5b shows finer granular and more homogenous structure of the PVDF-TrFe with higher density when printed on aluminium electrode and the coating in figure 5c, which is printed on silver exhibits the highest regularity and density. Although some point defects could be noted, the film in between them is smooth. This is a precondition for stable and uniform contact formation at the interface between the piezoelectric polymer and metal electrode with absence of strain effects which tent to peel of the polymer and corrupt the electrical connection between the coatings, resulting in piezoelectric voltage instability.

![Microscopic images](image)

**Figure 5.** Microscopic images of PVDF-TrFe screen printed on a) gold, b) aluminium and c) silver electrodes.

In all cases of patterns and variety of metals with different electrical conductivity, the overall conductivity of the samples was limited by the piezoelectric material and was in the range between 7 and 24 nA at the studied low mass loading and frequency of bending. Therefore, working as energy harvesting, these elements are able to produce electrical power $P$ in the range of 6.3 µW and 22.8 µW which could be successfully accumulated in the micro-supercapacitors specially designed for work with high impedance energy harvesting systems.

Considering the relation between the piezoelectric coefficient $g_{31}$, the voltage generated $V$ when stain $\sigma$ is applied to piezoelectric film with thickness $t$ ($g_{31} = \frac{V}{\sigma t}$) it could be calculated that the maximum possible coefficient is 0.332 V.m/N when silver electrode is implemented in the harvesting design and give 930 mV at 100 g/cm² (0.098 N/m²) over PVDF-TrFe coating with thickness of 3 µm. To the best of our knowledge, this value has not been previously reported and it is superior to this one of commercial thick film convertors which highest value is 0.06 V.m/N [17]. This result can be ascribed to the well-arranged high density polymer coating onto silver electrode, which form uniform and adherent interface at bending.

Based on the above achieved results the following comparison of the piezoelectric energy harvesting performance could be made (Table 1).

**Table 1.** Comparison of the basic properties of piezoelectric harvester with three types of metal electrodes and patterns.

|                      | Ag electrode | Au electrode | Al electrode |
|----------------------|--------------|--------------|--------------|
|                      | rectang.     | meand.       | s.comb       | rectang.     | meand.       | s.comb       | rectang.     | meand.       | s.comb       |
| $U_{PE}$, mV         | 916          | 840          | 446          | 800          | 768          | 362          | 528          | 400          | 258          |
| $\Delta U_{PE}$ @1500 bends, % | 12.3         | 8.6          | 1.5          | 17.5         | 11.4         | 1.9          | 16.4         | 9.5          | 1.7          |
| Polymer microstructure | Smooth, uniform and dense coating | Relatively low density coating | Fine granular, homogeneous |
| $P$, µW              | ~22.8        | ~13          | ~6.3         |
4. Conclusions

Flexible polymer based energy harvesting elements were produced by simple processing and great compatibility with variety of substrates and electrode materials. They were investigated in terms of electrode effect on the piezoelectric behavior, according to the metal type and electrode patterns. It was found that the silver electrodes are more favorable in terms of produced piezoelectric voltage and quality of the printed polymer coating on them. It was also demonstrated that the side comb shape electrodes provide the highest stability of the piezoelectric voltage after great number of repeating bending cycles, despite of the electrode material nature. As a general conclusion, the meander electrodes could be a balanced compromise between electrical performance and mechanical stability. Another key outcome of the experimental work is the obtaining of a well controllable screen printed coating on surfaces with different wettability with new piezoelectric polymer ink, based on P(VDF-TrFE) material. Future work will be focused on experimental study of the frequency and temperature dependences of the dielectric permittivity and loss factor of flexible energy harvesting with screen printed PVDF-TrFe films with the proposed electrodes topologies.

5. References

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Acknowledgments

This work was financially supported by Bulgarian National Science Fund, grant number DH07/13.