

DESIGN OF FLEXIBLE PIEZOELECTRIC ENERGY HARVESTING DEVICE WITH OPTIMIZED PERFORMANCE

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Abstract

In this paper, we demonstrate fabrication of environmental friendly flexible piezoelectric generator and propose optimization strategy for its performance by a formation of stress concentrators in the piezoelectric material. The entire structure is characterized with improved electrical response to mechanical stimuli, although the thickness of the used piezoelectric film is in nanosized range. Piezoelectric oxide films are grown by vacuum sputtering and patterned in a specific way by applying lift-off microfabrication technology. The design is based on simulation analysis, showing a concentration of peak stress in specific areas, causing enhanced charge generation. As a result, the piezoelectric coefficient of 11.28 pC/N is achieved and it is superior, compared to the device without concentrators. This value is competitive to devices using lead-containing lead zirconium titanate (PZT), as well as to devices with millimeter thickness of the piezoelectric material. Vibrational dynamic test in the low- frequency range up to 50 Hz shows that the generated voltage after patterning increases with 12.8 %, reaching ~677 mV. In addition, the device with concentrators can stand 187 000 bends without failure and the useful capacity, which is greater than 250 pF, decreases by 7%.

Keywords: energy harvesting, flexible piezoelectric device, nanocoatings, stress concentrators, optimized mechanical behavior

1. INTRODUCTION

Over the last years, energy harvesting devices have attracted huge attention due to the continued miniaturization and self-sustainability of the micro- and nanodevices. One of the most popular applications, requiring such devices are wearable sensors for health monitoring [1, 2]. That is why the researchers investigate methods to scavenge and store energy from the ambient for replacement of the battery power supply. For this purpose, few approaches were developed, such as piezoelectric, thermoelectric and triboelectric nanogenerators [3-5]. Among them, the piezoelectric generators (PEG) are the most widely used due to their ability to convert a great variety of mechanical stimulus (vibrations, movements, sound, hearth beating, pulse, etc.) into electrical energy with relatively high power density (0.01–10 mW/cm²). Although a lot of studies are currently available regarding wearable PEG, the problems with the durability of the flexible system and improvement of the conversion efficiency at continuous dimensions reduction are still partially solved. There are several ways to enhance the piezoelectric coefficients, such as using nanocomposites, tuning the resonant frequency, doping the lattice by atoms substitution, crystallographic orientation varying with the synthesis procedure and optimizing the geometrical parameters of the harvesters by nanostructuring [6-8].

In this study we propose an easy and effective path for enhancement of the generated voltage by macro-level control of the stress, causing the piezoelectric response over the films, by inserting stress concentrators. Technological flow for fabrication of such device is given and the effect of the concentrators' size among the piezoelectric film is investigated. The main electro-mechanical parameters and characteristics of the energy harvesting device are compared for two types of generators - with dense, continuous piezoelectric films and with formed concentrators. It was proved that the proposed construction modification leads to significant improvement of the piezoelectric coefficient at feasible mechanical stability.

2. MATERIALS AND METHODS

2.1. Design and simulation

A detailed study of the mechanical behavior, in particular, the mechanical stresses in piezoelectric layers of PEG samples was conducted. First, the PEG design was developed as a full surface dense, continuous layer with linear size of 15 x 15 mm square. As the samples are stuck to a metal beam with a trapezoidal shape for testing, this setup was replicated in simulation environment of SolidWorks. The beam was cycled at low frequencies (below 50 Hz) and subjected on a pure bend (without twisting) with a force of 12 N at the console end. The value was experimentally established so that at electrode layers of gold, tensions reaching the yield strength limit of the material are generated. In the same time, this value is never passed over, so plastic deformations do not occur and PEG durability is not affected. The simulation showed a revealed stress in the piezoelectric layer of the order of 2.3-2.4 MPa. It is assumed that the piezoelectric film is uniformly deposited on the electrode coated flexible and the total piezoelectric area is 225 mm².

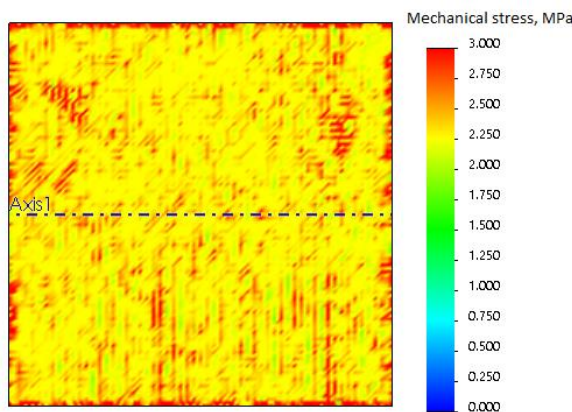


Fig. 1. Shape of PEG and stress distribution in the dense piezoelectric layer at pure bending of the beam

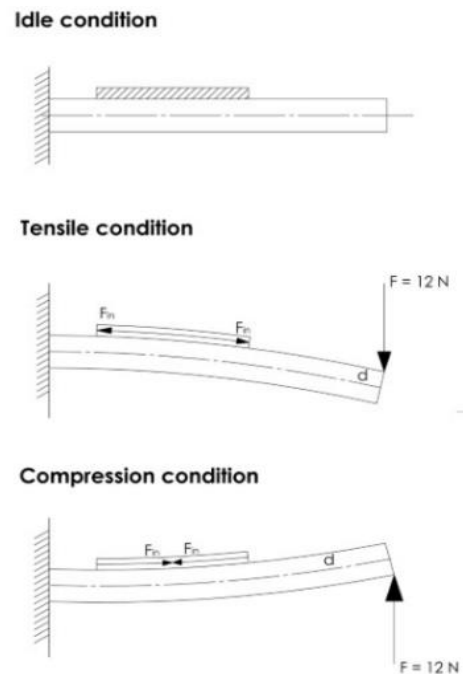


Fig. 2. Action of the internal mechanical forces in PEG

As can be seen in Fig. 1, the mechanical stress is uniformly distributed across the piezoelectric layer. It means that each randomly selected point on the sample generates mechanical stress of the order of 2.3-2.4 MPa. Through a series of simulations, it has been found that it does not matter where the PEG will be placed on the beam of the experimental set-up. The mechanical loading of PEG results from the fact that it follows the deformation line of the set-up because it is stuck. It is placed on the top of the beam, which is subject to pure bending. In this case, in fact, the sample is subjected to tension/compression over the longitudinal axis of the assembly (Fig. 2). Pure bending stretch or shrink the sample after the beam is loaded thus forms a deformation line and it is no longer in an idle state. We can conclude that the piezoelectric layer experiences equal stress over its entire area based on the theoretical assumption that uniform tension over the entire area of the loaded object of tension/compression can be delivered. [9,10]. This condition is valid when the object is with a constant cross-section.

It is typical for the piezoelectric materials behavior that they generate larger values of electrical voltage when larger area is affected by mechanical stress – as higher the mechanical load is as larger electricity is generated. Software simulations were conducted by SolidWorks to increase the efficiency of PEG by finding a suitable design for enhancing the stress effect without to increase the sample size. A variant is being tested, where the actively loaded area is reduced and the mechanical loads on the piezoelectric layer are increased locally. This could be realized if the samples are constructed by placing stress concentrators, facilitating generation of local peak values of the mechanical stresses [11]. Stress concentrators are actually cavities (or vias) in the piezoelectric and top electrode films. They cause sharp change in the cross-section, thus increasing the stress, but only in the zone nearby the cross- section change. Therefore, in order to create such local peak values, the piezoelectric layer (squared 15 x 15 mm) is deposited with N number of vias formed in it. Although vias with a wide variety of shapes, starting from typically simple ones - square, rectangle, circle, etc. could be patterned, the simulation showed that the circle shape gave the best results in term of stress concentration and uniform stress distribution across the micro-areas around the vias. In the concrete case, peak stress of 16-18 MPa could occur at a pure tension of 12 N. It cannot attenuate in depth in the piezoelectric layer, due to its small thickness of 340 nm.

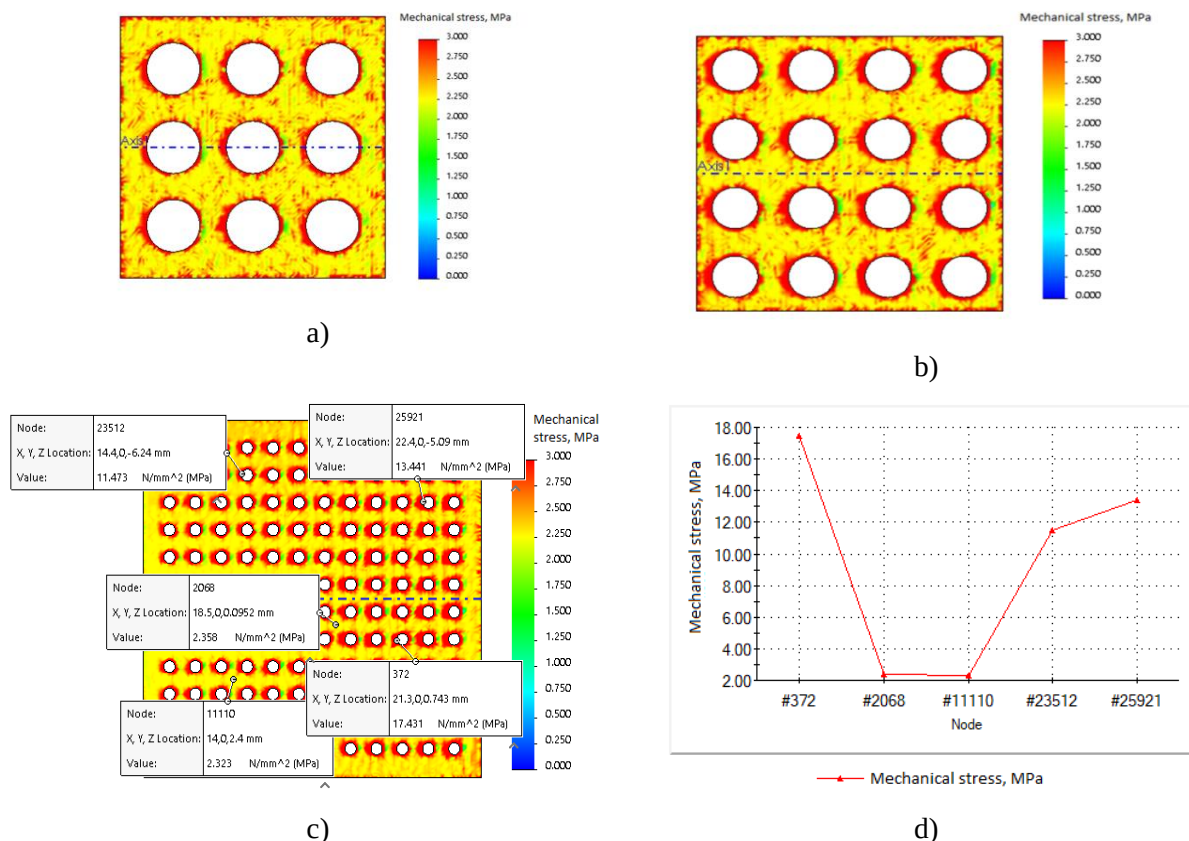


Fig. 3. PEG with an active area of the piezoelectric film 196.73 mm²: a) having 9 vias with diameter of 2 mm; b) having 12 vias with diameter 1.5 mm; c) having 144 vias with diameter 0.5 mm and mechanical load at the selected points; d) distribution of the stress in the different points around and inside the concentrators

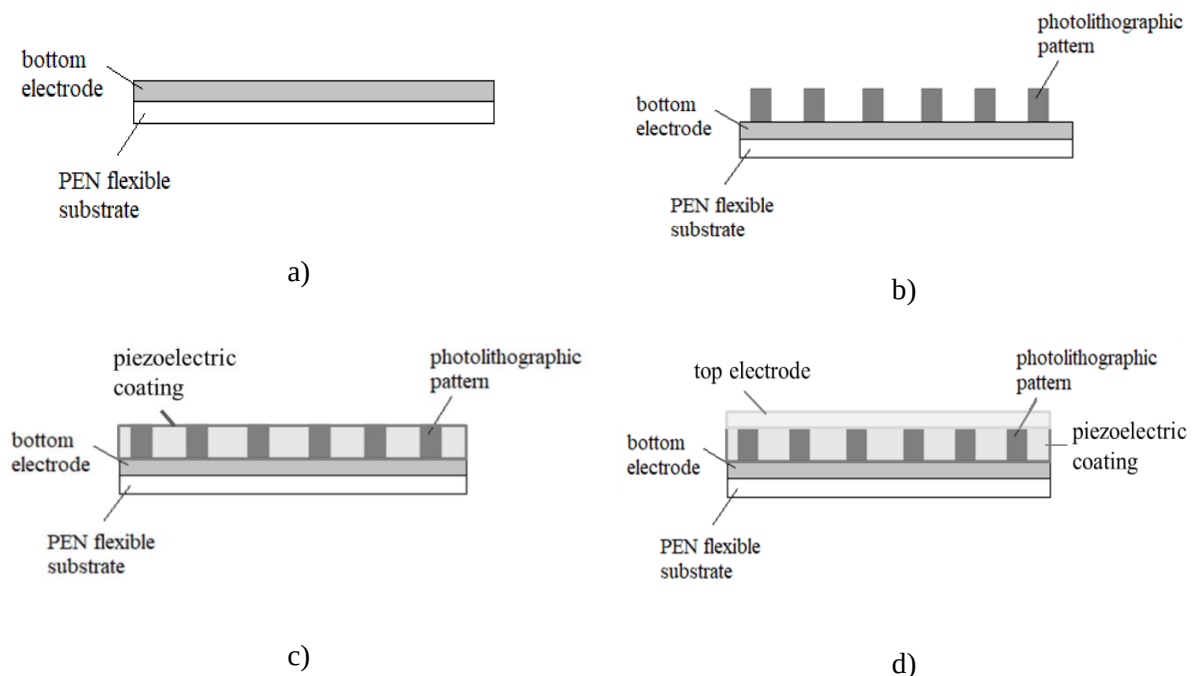
The total number of vias should be in balance with the total remained active piezoelectric area, in order to achieve a reasonable ratio of mechanical load versus generated voltage. To estimate the optimal ratio, simulations of piezoelectric generators, having a total active area of 15 mm x 15 mm

and vias with diameters in the range $\Phi 2\text{-}\Phi 0.2$ mm were made and the strain distribution was visualized by using color diagrams (Fig. 3).

The color diagram indicated the stress concentration in the red zones, as compared with the less loaded zones, colored in yellow. It could be seen that the strongest stress was induced with the structure from Fig. 3c – the largest number and the smallest vias at one and same active area of the piezoelectric film. Although the software is not able to determine the exact area of the red and yellow zones, the mechanical stress in the different nodes can be visualized.

2.2. Technology flow and device fabrication

The fabrication process flow chart for PEG is shown in Fig. 4. For fabrication of the PEG samples, polyethylene naphthalate (PEN) flexible substrates with size 20 mm x 20 mm were cut and clean with detergent solution in a supersonic bath for 180s. Gold film with thickness of 100 nm was DC sputtered from 2-inch target (Goodfellow, 99.995) at 30 mA per 4 min in Emitech K550X installation for producing the bottom electrode. Aluminum film with thickness 200 nm was thermally evaporated from wire (Kurt Lesker, 99.998) at base pressure 10^{-5} Torr (Fig. 4a). The piezoelectric material was barium-strontium titanate (BST) and BST film was RF sputtered without additional oxidation at sputtering pressure of 1.5×10^{-2} Torr and specific plasma power of 125 W/cm^2 . The resulting film thickness was 340 nm, measured by a profilometer. Top electrodes were grown under the same conditions like the bottom ones. For making the design of PEG with stress concentrators lift-off process was used. For this purpose, positive photoresist ma-P 1240 (MicroChem) was spin-coated on the bottom electrodes at 1500 rpm per 30 s and approximately $0.7 \mu\text{m}$ film thickness was achieved. The photoresist was exposed through photomasks, containing the same images like the structures proposed after simulation (Fig. 4b). On the shaped micro-columns the piezoelectric and top electrode films are deposited (Fig. 4c and 4d). Afterward, the samples were dipped in acetone, stripping selectively the photoresist, taking away the materials on its top side, causing remaining of vias (holes) that serve as stress concentrators (Fig. 4e). Photo of the bendable PEG sample is shown in Fig. 4f.



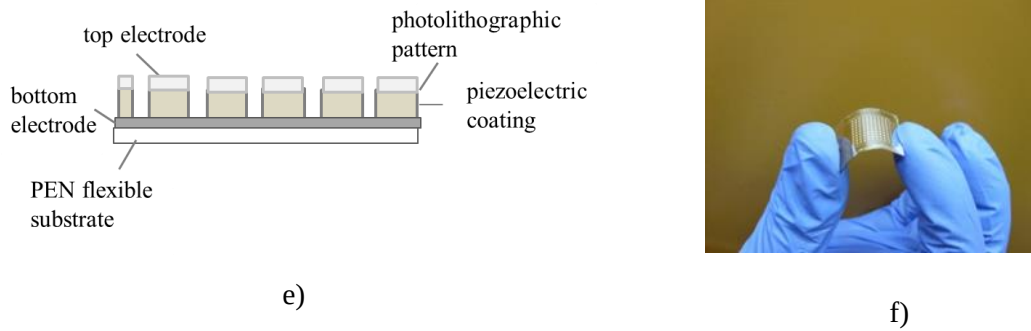


Fig. 4. Technology flow and step-by-step fabrication of the flexible piezoelectric generator with round shaped stress concentrators

2.3. Device measurements and characterization

For stimulation of piezoelectric charges, specially designed laboratory made stand was used to apply vibrations with defined intensity and frequency. Measurements of the average piezoelectric voltage in the dynamic mode were conducted with digital oscilloscope DQ2042CN. The capacity of the thin film devices was measured at bias 0.1V and a standard frequency of 1kHz with LCR meter Gwinstek 819. Current through the device was measured with precise picoammeter Keithley 6485 for estimation of the electrical contact type (Ohmic or Schottky) by using low noise instrumental amplifier for noises compression. Surface morphology of the piezoelectric films was imaged by scanning electron microscope Philips SEM 515.

3. RESULTS AND DISCUSSION

Results from SEM analysis at a magnification of 40 000 showed uniform distribution of the piezoelectric particles on the flexible substrate. The image was taken in the intermediate zone of the surface between photoresist columns (Fig. 5a). After the lift-off process and concentration formations, the piezoelectric film around them remained continuous, although its roughness increased as can be seen from the grains formed near the vias (Fig. 5b). This is a precondition for good contact properties with the top electrode film, although distortions in the signal are expected due to the point contact in the zones with irregularities.

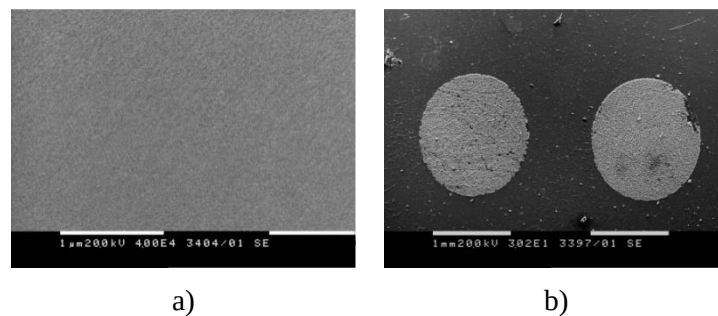


Fig. 5. a) SEM morphology of the BST surface in the zone between photoresist columns;
b) concentrators after lift-off of the photoresist

The data presented in Table 1 are for the bulk resistance and capacitance, contact capacitance and dielectric losses before lifting-off the photoresist and correspond to the physical design according to the simulation in Fig. 3a. The measurements were made before electromechanical stimulation for a PEN/Au/ BaSrTiO₃/Al device.

$U_{bias}=100\text{ mV}$	50 Hz	1kHz	50kHz	100kHz
$C_{cont}, \text{ pF}$	37	8.66	3.28	2.59
$R, \text{ k}\Omega$	914	900	886	317.5
$C_{bulk}, \text{ pF}$	217	187	127.84	2.7
$tg\delta$	0.010	0.0037	0.015	0.03

Table 1. Electrical parameters of flexible PEG without concentrators and before electromechanical stimulation

The behavior of the structure is favorable in the low to medium frequency range, after which the reactive resistance decreased and the useful capacity was similar in value with the junction (interface) contact capacity. The dielectric losses were tripled, probably due to the impossibility of the dipoles to follow the rapid changes of the electrical field due to insufficient mobility at this frequency. They also experience resistance to the medium and heat losses also occur. Here the resistance R represents the bulk resistivity of the layer, considering the space charge effects due to the accumulative distribution of charges near the poles, so it is also frequency dependent.

At the start of the stand engine rotation, the generated piezoelectric signal was periodic, consisting of short pulses with superimposed high peak disturbances (Fig. 6a). After the transition process (4 minutes later) a stable periodic signal with a clearly defined sinusoidal shape and negligible non-linear distortions were established (Fig. 6b). The average value of the piezoelectric voltage was 600 mV and is expected to increase after the perforation of the piezoelectric film.

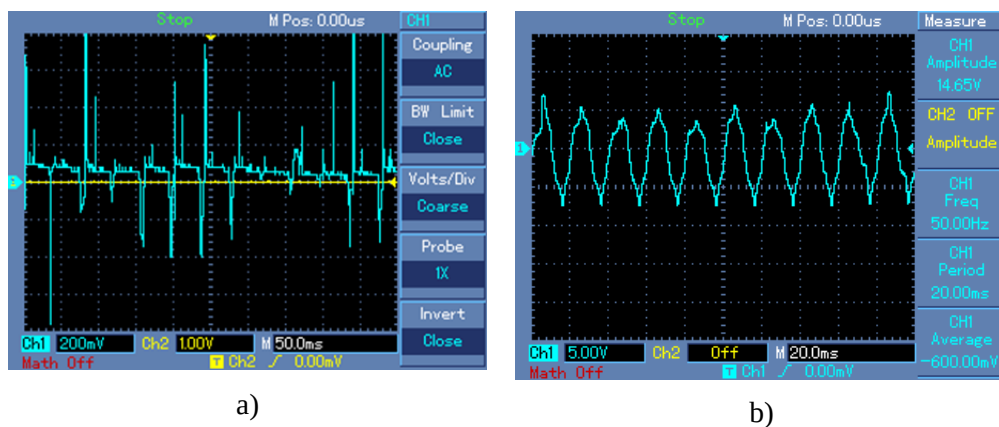


Fig. 6. Oscillograms of the generated piezoelectric voltage from PEG without concentrators:
a) immediately after switching; b) after transition time of 4 minutes

The device can stand continuous bending without failure, but after an hour of bending with frequency up to 52 Hz (187 000 bends), the electrical parameters were changed as was shown in Table 2. The useful capacity was reduced in the whole frequency range by average 7%. The stability of the contact deteriorated, as indicated by the interfacial capacity variation of 18%. The resistance of the sample abruptly drops from kilohm to ohm values with the mean of a partial physical breakdown of the nanofilms and initial process of short circuit. Although these conditions are extreme for the real potential application of the device (power from human body motion), they are indicative for the weakest parts of the device, needed improvement – namely the interface piezoelectric film/electrode.

$U_{bias}=100\text{ mV}$	50 Hz	1kHz	50kHz	100kHz
C_{cont}, pF	6.75	2.253	2.48	1.91
R, Ω	48	36.3	47.7	68.9
C, pF	200.47	55.9	252.89	187.19
$tg\delta$	0.064	0.0289	0.046	0.021

Table 2. Electrical parameters of flexible PEG without concentrators and after electromechanical stimulation

For estimating the effect of the concentrators' presence, the generated piezoelectric voltage was measured after photoresist lift-off and the oscillogram is shown in Fig. 7. As could be seen the voltage increased with 77.16 mV because the stress increased due to piezoelectric film perforation. The generated signal is 11.3% stronger, in accordance with the expectations. The non-linear distortions were estimated to be ~1.6 % due to the irregularities in the BST film after treatment of the sample in acetone for photoresist removing. Nevertheless, suitable electric filtration could be applied for effective removing of the excessive peaks [12].

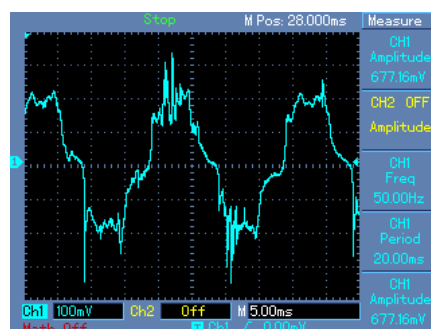


Fig. 7. Piezoelectric voltage generated from flexible PEG after formation of concentrators with size Φ 2 mm

After applying cyclic electrodynamic loading for a longer time it was found that the working range of the frequency is narrowed and unwanted changes in contact and bulk parameters began to occur at 1 kHz instead of 50 kHz. Although dielectric losses are still very low at 1 kHz, the useful capacitance of the structure was found to be comparable with the contact parasitic capacity, from which the further structural changes revealed at 50 kHz and 100 kHz.

$U_{bias}=100\text{ mV}$	50 Hz	1kHz	50kHz	100kHz
C_{cont}, pF	391.8	848	851.9	852.47
$R, \text{M}\Omega$	2.419	2.401	2.388	0.779
C, pF	591	850	851.89	852.43
$tg\delta$	0.0013	0.0010	0.00015	0.0228

Table 3. Electrical parameters of flexible PEG with concentrators and after electromechanical stimulation

After the physical realization of the design, according to the simulation presented in Fig. 3b (larger numbers of smaller concentrators), it was found worsening of the electrical behavior in term of 2.5 times lower voltage (average value of 249.48 mV), compared with the device having smaller number of large concentrators. A possible reason could be some damage of the top aluminum contact in the intermediate zones around the concentrators, which are overlapped for neighboring close situated vias. In contrast to the simulation conducted, predicting improved electromechanical stability and greater conversion efficiency, the real fabrication showed obstacles in keeping the continuity of the aluminum contact, which may be a reason for the exhibition of an opposite behavior (Fig. 8). The average voltage dropped down from 297 to 249 mV, varying with 16%.

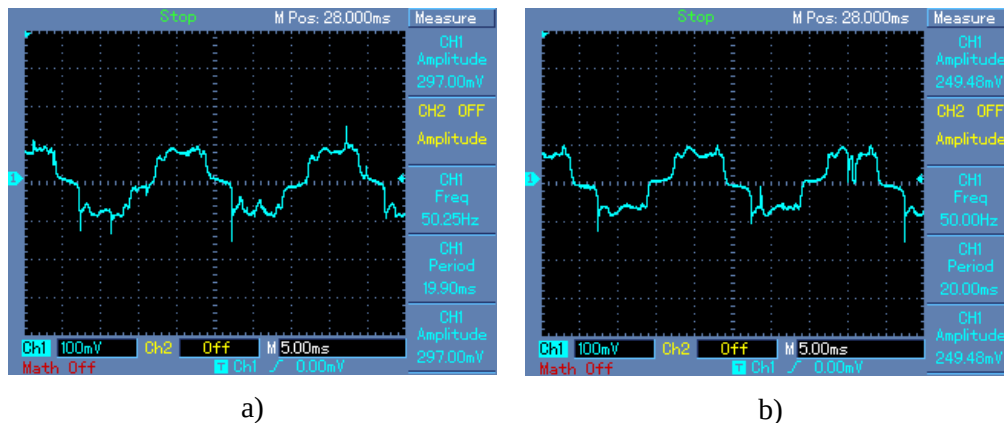


Fig. 8. Piezoelectric voltage generated from flexible PEG a) before formation of concentrators with size Φ 1.5 mm; b) after their formation

After activation, despite the available generations, the structure didn't work properly - its behavior is not typically capacitive, as the capacities (the useful and the contact's one) didn't appear as frequency dependent. It means that the element goes into an unknown at this stage working mode characterized with inverse electrical behavior. It is possible formation of space charge zone, resulting in the redistribution of the charges. Possible cause is due to a lifted-off aluminum top electrode that has poor adhesion to the piezoelectric layer for the case where areas with a tight fill of material are too close to each other. This is in contrast with the simulation in Fig. 3b, however, it cannot consider bulk electrical processes like charge redistribution together with mechanical wave distribution. As a result, the opposite behavior of the piezoelectric voltage decrease was detected. The measurements showed (Fig. 8) that the voltage decreased from 297 mV for a dense BST layer to 249.48 mV for BST layer with concentrators' size Φ 1.5 mm.

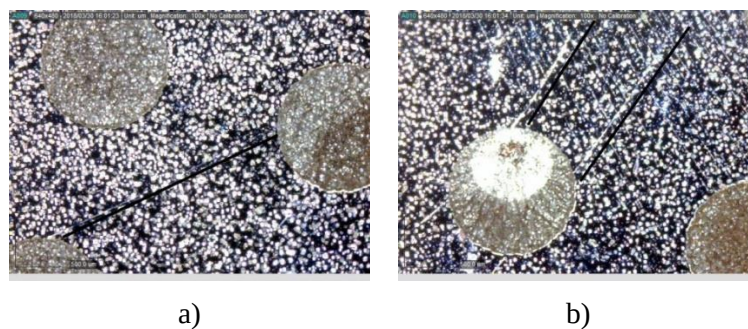


Fig. 9. Optical microscopy of PEG surface, showing cracking of the top electrode when lifted areas are closer than 1 mm to each other

Fig. 9 presents optical microscopy images of PEG surface, showing cracking of the top electrode when lifted areas are closer than 1 mm to each other. The microcracks are additionally marked with dark lines for better visibility. The shining bright spots represent aluminum particles irregularly distributed around the concentrators being affected by the lifting process.

The piezoelectric coefficient revealed across the two electrodes (gold-aluminum) for a structure with dense layers without concentrators was calculated to be 10.5 pC/N before and 11.28 pC/N (in the low-frequency area) after concentrators' formation. This polarization developed at a 340nm thickness of the generating layer. For comparison, scientists have tried to boost the polarization of barium titanate by introducing calcium (BaCaTiO_3) instead of strontium, but the report announced utilization of piezoelectric layer with a greater thickness of 1 mm and achieved only 8 pC/N [13]. In addition to the stronger piezoelectric effect, the proposed in the present article structures exhibited dielectric losses 0.003-0.03 before and 0.05-0.021 after the photoresist lift-off versus 0.1-0.5 in [13], which is approximately 10 times lower. Another group has made concentrators only on the electrodes - the lower (golden again) and the upper (platinum). 400 mV is their best result achieved for 300 nm barium titanate [14]. They claim 78 pC/N has been achieved, which at first glance looks good (apparently because of a higher capacity that is not given however and it is unknown how much it is and how it is measured), but at the end obviously this energy is not used.

4. CONCLUSIONS

It was found that the proposed flexible piezoelectric energy harvesting device exhibits optimized performance in term of piezoelectric coefficient due to the novel design, containing round shaped stress concentrators in the piezoelectric films. Based on the measured piezoelectric voltages and capacities for all combinations of concentrators versus high-density piezoelectric layer, it can be concluded that this construction approach and proposed technology flow are applicable to any kind of flexible piezoelectric harvesting device, independently on the concretely used piezoelectric film.

Future work will be related to improving the conditions for top electrode forming, in order to avoid its partial destruction from the acetone. A possible solution is coverage with conductive polymer PEDOT:PSS as a sandwich with Al intermediate film. Due to its elasticity and low solubility in acetone, it is expected that such layer would prevent aluminum not only from the influence of the acetone, but also would keep it unaffected by the mechanical loading for a longer time.

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