Optimizing dimensions of unipolar Teflon-FEP piezoelectrets with micro-system-technology

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Abstract. In this work we present a new micro-system-technology based production process for unipolar ferroelectrets. Theoretical analysis of the influence of the air-gap size on the electric field distribution as well as on the induced charge on the electrodes shows superior performance of unipolar piezoelectrets with small air-gaps. For the production of these small air-gaps we developed a new design using a photoresist thermoforming master, an integrated micro-heater and shadow masks for metallization. Unipolar piezoelectrets produced with this technology exhibit increased $d_{33}$-coefficients compared to designs in previous publications. These piezoelectrets are highly preferable for energy-harvesting applications, as they promise high electric power output.

1. Introduction
Piezoelectricity in polymers can generally originate from three sources: the molecular structure of the polymer, embedded piezoelectric materials or tailored, macroscopic ferroelectric domains [1]. The latter are usually air-voids inside the polymer, showing piezoelectric behavior after appropriate electric charging. These so-called piezo- or ferroelectrets have been conducted for energy-harvesting applications, as they show good mechanical stability and high piezoelectric $d_{33}$-coefficients resulting in high electric power output [2]. Especially piezoelectrets with air-voids fabricated from structured Fluoroethylenepropylene (FEP) are promising examples of this class, with $d_{33}$-coefficients above 1,000 pC/N [3]. While these piezoelectrets are typically based on a bipolar charge distribution on opposite surfaces of the voids, only few research focuses on unipolar piezoelectrets. This may be explained by a complex production process allowing only for large air-gaps and thus comparatively small $d_{33}$-coefficients [4]. However, it should be pointed out that unipolar piezoelectrets storing only negative charges are clearly superior if thermal stability and longevity [4] are an issue.

2. Theoretical considerations on optimal dimensions in unipolar piezoelectrets
The performance of piezoelectrets is predominantly defined by their piezoelectric $d_{33}$-coefficients. Equations for the calculation of the expected $d_{33}$-coefficient of piezoelectrets with artificial voids have already been derived for two-layer [5] as well as for multiple-layer designs [6]. Solutions of these equations are in good agreement with experimental findings, even if the real void geometry is mathematically simplified to parallel plates with an air-gap. However, these calculations rely on a bipolar charge distribution inside the voids. For calculating the $d_{33}$-coefficient of unipolar piezoelectrets, an adequate simplification of the geometry must be done, as shown in figure 1:
Here, evaluation of the electric field using Gauss' and Kirchhoff's law leads to a different electric field distribution and different values for the induced charge on the electrodes as compared to bipolar charge distribution [6]. The electric fields $E_1$ and $E_2$ are described as

$$E_{11} = \frac{d_2 \sigma_{\text{stor}}}{\varepsilon_0 (d_{11} + d_2 \varepsilon_r)} \quad E_2 = \frac{d_1 \sigma_{\text{stor}}}{\varepsilon_0 (d_{11} + d_2 \varepsilon_r)}. \quad (1)$$

Assuming that thickness changes only occur in the air-gap $d_2$, the change of induced charge is calculated as function of air-gap size, to

$$\frac{\partial \sigma_{\text{ind. top}}}{\partial d_2} = \frac{\varepsilon_r d_{11} \sigma_{\text{stor}}}{(d_{11} + d_2 \varepsilon_r)^2} \quad \frac{\partial \sigma_{\text{ind. bottom}}}{\partial d_2} = -\frac{\varepsilon_r d_{11} \sigma_{\text{stor}}}{(d_{11} + d_2 \varepsilon_r)^2}. \quad (2)$$

Combining these equations with a stress-strain relation, one derives a formula for the $d_{33}$-coefficient, which is independent of layer number or charge distribution type,

$$d_{33} = \frac{\sigma_{\text{stor}} \varepsilon_r}{\gamma (1 + \frac{d_2}{d_1}) \frac{d_1}{d_2} (1 + \varepsilon_r \frac{d_2}{d_1})^2}. \quad (3)$$

However, values used for the unipolar case differ from that for the bipolar case: the charge density can achieve twice the value of a bipolar piezoelectret and the thickness of the solid layer can be reduced to half its value. Assuming a similar build-height as well as identical values for Young's modulus, this yields a higher $d_{33}$-coefficient, particularly for small air-gaps. The induced charge (figure 2 a), calculated from the electric field, as well as the change in induced charge (figure 2 b) is compared for unipolar and bipolar piezoelectrets built from 12.7 μm FEP. While high performance of FEP-based piezoelectrets at small air-gaps has generally been predicted by van Seggern [7], our calculations show a superior performance of unipolar piezoelectrets with thin FEP-foils for small air-gaps below 50 μm.

**Figure 2.** a) Comparison of the induced charge on the electrodes between unipolar (orange) and bipolar (blue) piezoelectrets for different air-gaps. Total charge-density in both systems is 1mC/m².  
   b) Comparison of the change in the induced charge for the same systems.

### 3. Processing of unipolar piezoelectrets

A major challenge for the production of FEP-piezoelectrets is the lack of control over the dimensions in the micrometer-range, which is very difficult for conventional thermoforming molds [3] or laser-cut thermoforming substrates [4]. As stated above, especially these small dimensions show promising high $d_{33}$-coefficients. To achieve a reduction of dimensions with satisfying precision we developed a novel micro-system-based process for the production of thermoforming molds. We produced unipolar piezoelectrets in a thermoforming-process adapted from Zhang et al. [3], but using a thermoforming master created with a micro-system-technology-based approach. This allows to produce all dimensions inside the piezoelectret with micrometer-precision. With this technology we were further able to adjust the current design to optimize unipolar piezoelectrets.

Borofloat glass pieces (Schott, Germany) with dimensions of 34x34 mm² were used as substrate for the production of the thermoforming master. After dehydration of the substrate at 150 °C for 60 minutes,
the adhesion promoter TI Prime (MicroChemicals, Germany) was applied. In the next step, approx. 10 ml SU8-100 (MicroChem, USA) were applied on the substrate and spin coated at 3,000 rpm for 30 seconds. Subsequently, a softbake (SB) step at 65 °C for 30 minutes followed by 95 °C for 60 minutes was performed using a precision hotplate (Harry Gestigkeit, Germany). Heating and cooling was performed with a slope of approx. 3 °C/min. After cooling to room temperature, the SU8 was exposed with an intensity of 1,200 mJ/cm² using a Cloë UV-KUB 2 exposure system (Kloe, France). Following a resting phase of 20 minutes, a post exposure bake (PEB) with parameters identical to the softbake step was performed. Shortly after cooling down, the SU8 was developed for 4 minutes in mr-dev 600 developer (MicroChem, USA). In order to achieve steeper edges, the master was additionally developed for 1 minute in a separate beaker with fresh developer. The resulting SU8 height was determined with a Dektak XT (Bruker, USA) to around 65 μm. On the thermoforming masters aluminum micro-heaters were implemented, using a production process described elsewhere [8]. The thermoforming master was surface treated in an air-plasma (Diener, Germany) for 5 minutes to increase the adhesion of the micro-heater. Directly after the surface activation, we applied full-surface metallization with approx. 150 nm aluminium on the thermoforming master via a Nano 36 sputtering device (K. J. Lesker, UK). Subsequently, about 1.5 μm of the positive tone photoresist AZ MIR 701 (MicroChemicals) was spin coated at 3,000 rpm for 30 seconds on the metallized surface. After exposure and development, the necessary areas for the micro-heater remained masked. Then the remaining aluminium was etched using TechniEtch 80 (MicroChemicals), the remaining photoresist was removed with AZ 100 remover (MicroChemicals), and the sample was cleaned thoroughly.

In this work we produced thermoforming master for piezoelectrets with a void width of 1,000 μm, a space between voids of 500 μm and an approximate void-height of 65 μm. The implemented micro-heaters showed an average resistance of 115 Ohm. It should be noted, that the mentioned process is suitable for downsizing the width dimensions from centimeters to 5 μm and the height dimensions from 150 μm down to 5 μm, allowing for a broad spectrum of possible piezoelectret designs. A schematic of the production process for the thermoforming master with integrated micro-heater is depicted in figure 3.

Figure 3. Schematic of the most important processing steps of the thermoforming master.

Piezoelectrets consisting of voids with tubular shape in 12.7 μm thick FEP-50A-foils (Wortmann, UK) with a width of 1,000 μm, spacing of 500 μm and height of about 65 μm were created during a thermoforming process at 100 °C on the SU-8-thermoforming master. During structuring, a load of 100 kPa was applied for 5 minutes. Parallel to the thermoforming process, a second 12.7 μm FEP-foil was metallized with approx. 150 nm aluminium applying shadow mask technology to achieve a metal layer corresponding to the channels in the structured foil. Subsequently, both foils were stacked according to the schematic in figure 4. With a static load of 50 kPa on the stack, local fusion-bonding was performed, using the integrated micro-heater design for 30 seconds. After bonding, the front of the stack was metallized with approx. 150 nm copper.

Figure 4. Schematic of the production process of optimized unipolar piezoelectrets.
Finally, the piezoelectrets were charged by applying a 2 kV saw-tooth-voltage in the right polarity between the electrodes for 10 s. A schematic of the finished piezoelectret is depicted in figure 5 a) and a cross section micrograph of a single void in the produced piezoelectret in figure 5 b).

![Figure 5](image)

Figure 5. a) Schematic of the unipolar FEP-piezoelectret. b) Bright-field micrograph of a cross-section of a single void in a micro structured FEP-piezoelectret.

4. Characterization of unipolar piezoelectrets

Using a quasistatic approach, the produced piezoelectrets were characterized with respect to their piezoelectric properties. A load of 1.5 kPa was attached and removed for ten times on each piezoelectret. The generated charge was measured on a Spider 81B vibration-controller (Crystal Instruments, USA) with integrated charge amplifier. From these preliminary measurements piezoelectric coefficients have been determined between 500 and 1,850 pC/N. As these values stayed constant also for higher loads, we assume that the small weight totally compressed the samples. Compared to previously published results [4], the new design in combination with thinner FEP and minimized air-gaps resulted in a drastic increase of the $d_{33}$-coefficient. In addition, the durability of the fusion-bond is superior to glued structures.

5. Conclusion

Optimizing the production process of unipolar FEP-piezoelectrets allows for a noticeable increase of $d_{33}$-coefficients up to 1,850 pC/N for quasistatic measurements. Especially for applications demanding high thermal $d_{33}$-stability, this kind of piezoelectret is highly preferable. Future work will focus on miniaturizing width as well as the height of the artificial voids, for a further increase of the $d_{33}$-coefficient. Determination of the frequency response in dynamic measurements as well as calculations for the maximum value of the $d_{33}$-coefficient at distinct geometries are under evaluation. Optimizing the design of the integrated micro-heater will additionally reduce the thermal stress on the thermoformed FEP during fusion bonding.

This work was partially supported by Bayerisches Staatsministerium für Bildung und Kultus, Wissenschaft und Kunst in the frame of ZEWIS. We want to thank the German Academic Exchange Service (DAAD) for a travel grant.

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