Template-based fluoroethylene-n-propylene piezoelectrets with tubular channels for transducer applications

JOURNAL OF APPLIED PHYSICS, v.106, n.1, 2009
http://producao.usp.br/handle/BDPI/14668

Downloaded from: Biblioteca Digital da Produção Intelectual - BDPI, Universidade de São Paulo
Template-based fluoroethylene-propylene piezoelectrets with tubular channels for transducer applications

Ruy Alberto Pisani Altafim, Xunlin Qiu, Werner Wirges, Reimund Gerhard, Ruy Alberto Corrêa Altafim et al.

Citation: J. Appl. Phys. 106, 014106 (2009); doi: 10.1063/1.3159039
View online: http://dx.doi.org/10.1063/1.3159039
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v106/i1
Published by the American Institute of Physics.

Related Articles
Polarization switching at the nanoscale in ferroelectric copolymer thin films

Tunable temperature dependence of electrocaloric effect in ferroelectric relaxor poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene terpolymer

Beneficial and detrimental fatigue effects of dielectric barrier discharges on the piezoelectricity of polypropylene ferroelectrets
J. Appl. Phys. 110, 024108 (2011)

Energy harvesting by nonlinear capacitance variation for a relaxor ferroelectric poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) terpolymer
Appl. Phys. Lett. 98, 222901 (2011)

Photocrosslinking of ferroelectric polymers and its application in three-dimensional memory arrays
Appl. Phys. Lett. 98, 183302 (2011)

Additional information on J. Appl. Phys.
Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors

ADVERTISEMENT

Explore AIP’s new open-access journal
• Article-level metrics now available
• Join the conversation! Rate & comment on articles

Submit Now
Template-based fluoroethylene-propylene piezoelectrets with tubular channels for transducer applications

Ruy Alberto Pisani Altafim,1,a) Xunlin Qiu,1,b) Werner Wirges,1 Reimund Gerhard,1,c) Ruy Alberto Corrêa Altafim,2 Heitor Cory Basso,2 Werner Jenninger,3 and Joachim Wagner2
1Applied Condensed-Matter Physics, Institute of Physics and Astronomy, University of Potsdam, Karl-Liebknecht-Strasse 24–25, 14476 Potsdam-Golm, Germany
2Department of Electrical Engineering, Sào Carlos School of Engineering, University of São Paulo, Av. Trabalhador São-Carlense 400, 13566-590 São Carlos, SP, Brazil
3Bayer MaterialScience AG, 51368 Leverkusen, Germany

(Received 8 May 2009; accepted 1 June 2009; published online 9 July 2009)

We describe the concept, the fabrication, and the most relevant properties of a piezoelectric-polymer system: Two fluoroethylene-propylene (FEP) films with good electret properties are laminated around a specifically designed and prepared polytetrafluoroethylene (PTFE) template at 300 °C. After removing the PTFE template, a two-layer FEP film with open tubular channels is obtained. For electric charging, the two-layer FEP system is subjected to a high electric field. The resulting dielectric barrier discharges inside the tubular channels yield a ferroelectret with high piezoelectricity. \(d_{33}\) coefficients of up to 160 pC/N have already been achieved on the ferroelectret films. After charging at suitable elevated temperatures, the piezoelectricity is stable at temperatures of at least 130 °C. Advantages of the transducer films include ease of fabrication at laboratory or industrial scales, a wide range of possible geometrical and processing parameters, straightforward control of the uniformity of the polymer system, flexibility, and versatility of the soft ferroelectrets, and a large potential for device applications e.g., in the areas of biomedicine, communications, production engineering, sensor systems, environmental monitoring, etc. © 2009 American Institute of Physics. [DOI: 10.1063/1.3159039]

I. INTRODUCTION

Soft piezoelectric transducer films have a large range of existing and potential applications. In particular, they are useful, e.g., in ultrasonic sensors or in dynamic-pressure transducers for biomedical devices, in microphones, microphone arrays, curved or flat loudspeakers, and headphones for electroacoustical systems, in transmitters and receivers for ultrasonic ranging and inspection, in electromechanical sensors for production engineering and process control, etc. Therefore, several routes have been proposed and demonstrated toward soft piezoelectric materials and devices: Polymers with molecular dipoles such as polyvinylidene fluoride and some of its copolymers, ceramic-polymer nano- and microcomposites, e.g., from lead-titanate particles and epoxy resin, charge-polymer electrets such as polytetrafluoroethylene (PTFE) and some of its copolymers, etc. Over the past decade, ferroelectrets1,2 emerged as an additional class of soft transducer films that may be “engineered” by processing or combining suitable materials.

Polymer-based transducers such as electret-condenser microphones or piezoelectric-polymer loudspeakers are usually assembled from several mechanical and electrical components including the active polymer film. In contrast to this use of active “materials in a device,” ferroelectrets1,2 may be considered as films with “devices in a material.” In cellular-foam ferroelectrets,3–5 micrometer-scale voids with electrically charged internal surfaces work as tiny electret transducers. All together, the large number of such active transducerlike voids yield surprisingly high piezoelectric coefficients. Depending on the material and the charging conditions, piezoelectric \(d_{33}\) coefficients of up to 1400 pC/N have been reported.6 Alternatively, the individual voids with internal charges of both polarities may be viewed as micrometer-scale dipoles whose dipole moments vary significantly under mechanical or electrical stresses. Since the relations between the mechanical and electrical input and output quantities are essentially linear, ferroelectrets show primary piezoelectricity.

Cellular-foam ferroelectrets have the disadvantage that their cellular voids always have a rather wide and not so well-controlled size and shape distribution so that only some of the voids are optimal for charging and for transducer operation.7,8 In addition, most of the piezoelectric sensitivity is already lost between 60 and 70 °C in polypropylene (PP) ferroelectrets.9 Consequently, cellular-foam ferroelectrets with higher thermal stability have been developed from polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) by means of physical foaming with supercritical carbon dioxide.10,11 The polyester ferroelectrets exhibit slightly higher thermal and long-term stabilities that are, however, still not sufficient for many practical applications.

Mainly for these two reasons (wide and not well-
controlled size and shape distribution of the cellular voids, as well as insufficient thermal stability in readily foambable polymers), alternative approaches with thermoformed and relatively large voids between fluoropolymer-electret films or with laser-perforated holes in the central layer of a three-layer fluoropolymer sandwich have been suggested more recently. These systems are, however, still difficult to charge optimally and do not lend themselves easily to large-scale production with good reproducibility. Here, we present an approach that avoids these shortcomings and that can serve as a material platform for several types of piezoelectric or even multifunctional ferroelectret films. In order to achieve good thermal stability of the ferroelectret properties, only fluoropolymers with proven stability of the electret properties for both charge polarities were used in the present film systems. The FEP-film ferroelectret systems have well-controlled homogeneous tubular channels due to the template-based fabrication process.

II. SAMPLE PREPARATION

For sample fabrication in the laboratory, a lamination apparatus (model L-280, Assane®, Brazil) was fitted with a suitable temperature controller (MT-511R, Full Gauge, Germany) so that lamination temperatures up to 300 °C can be attained. The laboratory template consisted of a 100 μm thick Teflon PTFE film with an area of 30×40 mm² and with parallel rectangular openings (area 1.5×30 mm²) cut into the PTFE films by means of computer-controlled laser ablation. The PTFE separations between adjacent openings also had a width of 1.5 mm. Before lamination, the PTFE template was inserted between two Teflon FEP films with a thickness of 50 μm each. The three-layer fluoropolymer-film sandwich was fed to the lamination apparatus which had been preheated to 300 °C. The chosen lamination temperature is substantially higher than the melting temperature of FEP (about 260 °C), but still well below the melting point of PTFE at 327 °C.

After cooling down under ambient conditions in the laboratory, the two FEP layers are permanently fused to each other through the openings of the PTFE template. Because of the antiadhesive properties of fluoropolymers, the PTFE template can be easily removed after cutting it open at one end. The resulting FEP-film system contains well-defined tubular channels as shown in Fig. 1. Part (a) schematically illustrates the laboratory fabrication process, while an optical micrograph of a typical sample is shown in part (b). Obviously, it is possible to generate uniform channels with a large range of widths, heights, and lengths, as well as arbitrary channel patterns with the present technique. For industrial fabrication, the PTFE templates may be replaced by fixed templates with nonadhesive surfaces around which continuously moving polymer films are laminated in a roll-to-roll process. The laboratory samples were metallized on both sides with circular aluminum electrodes with a diameter of 16 mm and a thickness of 40 nm each.

III. EXPERIMENTS AND RESULTS

A. Charging and the resulting piezoelectricity

In order to charge the FEP foams by means of internal dielectric barrier discharges across the tubular channels, a dc voltage was applied to the electrodes for 10 s by means of a high-voltage supply (Trek model 610D).

The resulting piezoelectric $d_{33}$ coefficient of tubular-channel FEP ferroelectrets as a function of the charging voltage is plotted in Fig. 2. The $d_{33}$ coefficients were determined by means of dynamic mechanical excitation with a sinusoidal force with an amplitude of 1 N and a frequency of 2 Hz (Brüel & Kjaer model 4810 shaker), superimposed with a static bias force of 3 N. The resulting electric response of the sample was amplified by means of a Brüel & Kjaer model 2635 amplifier and recorded with an oscilloscope. From the applied force and the resulting electrical signal the respective $d_{33}$ coefficients were calculated. The voltage dependence of the piezoelectric coefficient in the tubular-channel polymer-film systems clearly shows a threshold behavior similar to

![FIG. 1. (Color online) (a) Schematic of the laboratory fabrication process. The ferroelectret system consists of two FEP films that are laminated around a well-designed PTFE template at 300 °C. After lamination, the stack is cooled down to room temperature. (b) Optical micrograph of a typical ferroelectret system with tubular channels. Both the cross section at the end of the film and the film surface are visible.](image1)

![FIG. 2. Piezoelectric $d_{33}$ coefficient of tubular-channel FEP ferroelectrets as a function of the charging voltage. The line that connects the data points has been drawn as a guide for the eyes only.](image2)
that found previously on cellular PP ferroelectrets.\textsuperscript{15} For the present samples, the piezoelectric $d_{33}$ coefficient remains nearly zero for charging voltages below 1.3 kV. Thereafter, $d_{33}$ increases strongly with charging voltage and finally reaches a saturation value of about 160 pC/N at a charging voltage of about 2.7 kV.

Paschen breakdown in the gas has been suggested as the essential mechanism for the internal charging of the voids inside ferroelectrets.\textsuperscript{4,7,16} According to Townsend’s model, the critical breakdown field of common gases in a uniform electric field is a function of gas pressure $p$ and electrode spacing $d$ (which in our case is equal to the internal void height),\textsuperscript{17}

$$E_c = \frac{A_p}{B + \ln(pd)},$$

(1)

where the constant $B$ is given by

$$B = \ln\left(\frac{C}{\ln(1 + 1/\gamma)}\right).$$

(2)

For air, $A=273.8$ V m$^{-1}$ Pa$^{-1}$ and $C=11$ m$^{-1}$ Pa$^{-1}$ are experimentally determined constants, and $\gamma=0.01$ is the so-called second ionization coefficient. Paschen breakdown must take place inside the voids (i.e., within the tubular channels for the present case), in order to initiate microplasma discharges. For an externally applied voltage $V$, the electric field in the tubular channels $E_c$ is given by

$$V = E_c\left(\frac{d_p}{e} + d_s\right),$$

(3)

where $d_p=100$ $\mu$m is the accumulated thickness of the FEP layers, $d_s=100$ $\mu$m is the internal void height, and $e_p=2.1$ is the dielectric permittivity of the solid FEP film. From Eq. (1), the breakdown electric field for a $d$ of 100 $\mu$m (internal height of the tubular channels between the FEP films) at atmospheric pressure is found to be approximately 8.7 MV/m. Equation (3) yields a corresponding threshold voltage of about 1280 V for the present film system, in very good agreement with the threshold voltage seen in Fig. 2.

The electrical breakdown process inside the tubular channels represents a dielectric barrier discharge (DBD).\textsuperscript{18} It is known that DBDs in cellular PP ferroelectrets are accompanied by light emission that can be recorded with a digital camera. The characteristics of the light emission may also be used to investigate the DBDs in more detail.\textsuperscript{17} Figure 3 shows the spatially resolved light emission from an FEP ferroelectret with tubular channels recorded by means of a PC-controlled electron-multiplying charge-coupled-device camera (EMCCD) (iXon, Andor Technology). For such an investigation, samples are metallized on both sides with semitransparent Au electrodes having a diameter of 16 mm and a thickness of 20 nm each. In order to block any light originating from corona discharges at the electrode edges, the sample is covered by a mask with a circular hole of 8.5 mm diameter. A positively biased sinusoidal voltage $V = \frac{1}{2} V_{pp}[1+\sin(\omega t)]$ with a peak-to-peak amplitude $V_{pp}$ of 3.5 kV and a frequency of 100 Hz is applied to the sample. According to the widely accepted model of the piezoelectricity in cellular polymer ferroelectrets, charges of opposite sign are trapped at the top and bottom surfaces of the voids during charging by means of DBDs.

A schematic model of the charge distribution in a tubular-channel FEP ferroelectret is shown in Fig. 4. The charged tubular channels, which carry positive charges on one of their inner large surfaces (here on the top surface) and negative charges on the other (here on the bottom surface), can be considered as macroscopic dipoles. The change in the channel height upon mechanical stress leads to a corresponding change of the dipole length and thus also the dipole moment, which results in a change of the induced charges on the electrodes.

Dielectric resonance spectra\textsuperscript{19} (DRS) of cellular FEP ferroelectrets with four different channel heights are depicted in Fig. 5. The thickness resonances of the tubular channels are found at frequencies between 20 and 50 kHz. As expected, higher resonance frequencies are observed for thinner ferroelectret systems. The real part of the capacitance of a three-layer FEP ferroelectret well below the resonance frequency can be modeled as parallel arrangement of a three-layer capacitance (FEP-channel-FEP) and one-layer FEP capacitance (cf. Fig. 4). If it is assumed that the areas of the tubular channels and of the laminated zones between the channels are equal (cf. Figs. 1 and 3), the capacitances of FEP ferroelectrets with a circular electrode and with channel heights of 25, 50, 70, and 100 $\mu$m are calculated to be 31.0, 27.9, 26.3, and 24.8 pF, respectively, in reasonable agreement with the $C'$ values found in Fig. 5 at frequencies well below the respective resonance frequency. Figure 5 also illustrates that the resonance frequency of the ferroelectret systems can be adjusted by controlling the height of the tubular channels via
PTFE templates of suitable thickness. A detailed analysis of the DRS results is under way and will be published elsewhere.

Optimization of the piezoelectric properties and, in particular, of the piezoelectric thickness coefficient and the resonance frequency is thus possible through adjustments of the geometrical parameters of the tubular-channel fluoropolymer-film ferroelectret system, such as the overall thickness of the materials system and the dimensions and the patterns of the tubular channels in it, and through control of the space-charge levels on the internal top and bottom surfaces of the tubular channels. To this end, polymer layers of the required thickness and PTFE templates of suitable geometry have to be employed together with adequate charging voltages and times.

**B. Thermal stability of the piezoelectricity**

A typical example for the thermal stability of the piezoelectricity in the tubular-channel FEP-film ferroelectrets is shown in Fig. 6. A sample was charged at room temperature (RT) under 3 kV for 10 s, and the initial $d_{33}$ coefficient was determined at RT. Then the sample was stored in an oven at a preset elevated temperature for 1 h. Subsequently, the sample’s $d_{33}$ coefficient was measured again at RT. Figure 6 (solid squares) indicates a slight decay of $d_{33}$ after a 1 h storage at 80 °C. Storage at 100 °C leads to a significant decay of $d_{33}$. Thus the thermal stability of the piezoelectricity of tubular-channel FEP ferroelectrets charged at RT is roughly comparable to that of cellular PEN ferroelectrets. Since the macroscopic dipoles (charged voids or channels) rely on the simultaneous existence of equal amounts of positive and negative charges (trapped on the top and bottom surfaces, respectively), the thermal stability of the piezoelectricity of FEP ferroelectrets is limited by the inferior thermal stability of positive charges on FEP, rather than by the superior thermal stability of the negative charges.

It is well known that charging at elevated temperatures is an effective way to improve the thermal stability of positive charges in FEP. The decay of the $d_{33}$ coefficient in a sample charged at 140 °C is also shown in Fig. 6 (solid circles). The sample was stored at 140 °C for 30 min and was then charged with 3 kV for 10 min at the same temperature. After charging, the sample was cooled down to RT under ambient conditions in the laboratory within 20 min still under the charging voltage, and the decay of its $d_{33}$ coefficient was determined in the same way as detailed above. Obviously, the thermal stability of the piezoelectric $d_{33}$ coefficient of the sample that had been charged at 140 °C is much better than that of the one charged at RT. Only a slight decay of about 15% is observed after annealing at 130 °C. Therefore, the piezoelectricity of properly charged FEP ferroelectrets is much better than that of PP ferroelectrets whose piezoelectricity decays already quite significantly at 60 °C.

**IV. CONCLUSION**

Tubular-channel FEP-film ferroelectret systems have been fabricated by laminating two FEP films around a PTFE template at 300 °C, followed by removal of the PTFE template from the laminated stacks. A piezoelectric $d_{33}$ coefficient of up to 160 pC/N has been obtained. The piezoelectricity of tubular-channel FEP ferroelectrets charged at elevated temperature is thermally stable at temperatures of at least 130 °C. Advantages of the material system include its simplicity, its suitability for small-scale laboratory and large-scale industrial fabrication, and its well-controlled geometry that can be adjusted over a wide range of channel sizes and patterns according to the requirements of the respective device applications. Since the transducer function has been built into the material system, transducer elements or arrays can be cut from a roll of the ferroelectret polymer film and only need to be connected to a suitable amplifier.

**ACKNOWLEDGMENTS**

The present work has been partly supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazil, by the German Academic Exchange Service (Deutscher Akademischer Austauschdienst, DAAD) and by the University of Potsdam, Germany. The second author (X.Q.) thanks the Deutsche Forschungsgemeinschaft (DFG)
for providing a Research Fellowship (Reference No. QI 65/1-1) to him.