743. Intelligent piezoelectric polymers PVDF-PZT for biosensing applications

S. Ponelytė[1], A. Guobienė[2], J. Puišo[3], A. Palevičius[4], I.Prosyčevas[5]
[1]Kaunas University of Technology, Department of Physics, Studentų 50, 50244 Kaunas
International Studies Center, A. Mickevičiaus 37, 44244 Kaunas, Lithuania
[2]Kaunas University of Technology, Department of Physics, Studentų 50, 50244 Kaunas
Institute of Materials Science, Savanorių 271, 50131 Kaunas
International Studies Center, A. Mickevičiaus 37, 44244 Kaunas, Lithuania
[3]Kaunas University of Technology, Department of Physics, Studentų 50, 50244 Kaunas, Lithuania
[4]Kaunas University of Technology, A. Mickevičiaus 37, 44244 Kaunas, Lithuania
[5]Kaunas University of Technology, Institute of Materials Science
Savanorių 271, 50131 Kaunas, Lithuania
E-mail: [1]*sigita.ponelyte@ktu.stud.lt*, [2]*asta.guobiene@ktu.lt*, [3]*judita.puiso@ktu.lt*, [4]*arvydas.palevicius@ktu.lt*, [5]*igoris.prosycevas@ktu.lt*

(Received 15 September 2011; accepted 14 February 2012)

Abstract. Nowadays a growing number of biosensing systems in micro- and nanoscale rely in expensive and bulky equipment that must capable accurately to resolve the angle or wavelength of optical interrogation. The costs, size, sensitivity, properties and etc which are required to assemble these biosensing tools, may limit the portability of such systems, and may restrict their usefulness in sensing applications outside of a controlled environment. This research covers creation and investigations of new piezoelectric materials based on PVDF and PZT with unique properties, i.e. synthesis, piezoelectric thin film formation, imprint of microperiodic structures, analysis of surface morphology by Atomic Force Microscopy, and analysis of diffraction efficiencies using laser diffractometer. These developments of new piezoelectric films have made it possible to understand the strengthening and deformation mechanisms in micro- and nanoscales together by bringing new insights in biosensing applications.

Keywords: PVDF, PZT, PMMA, piezoelectricity, atomic force microscope, laser diffractometer.

Introduction

With the recent technological developments of piezoelectric materials employed in microelectromechanical systems (MEMS), portable electronics and biologically adaptive sensors have yielded several specialized embedded platforms capable of sensing, computing and communication with advantages such as small size, light-weight, short response time, ease of implementation, low costs, high accuracy, high reliability and etc.

Nowadays, piezoelectric materials play an important role in biosensing applications [1, 2]. These advances are promoting the use of certain new classes of materials - piezoelectric and piezoceramic materials, such as Poly (vinylidene) Fluoride (PVDF) and Lead Zirconate Titanate (PZT), which have unique and unusual properties, not found in other materials. These mainly include sensing and actuating (self-power) capabilities which can be used to monitor the static and dynamic behavior of structures and systems. PVDF has been widely used in engineering applications due to its favorable chemical and mechanical properties [3-7], high piezoelectric coefficient, good flexibility and biocompatibility [8-10]. PZT films are of great interest for microsystems applications where direct coating onto microelectronic substrates and high electromechanical performance are required [11]. There are numerous references in recent literature describing the potential biomedical applications for new/emerging piezoelectric polymers: large displacement actuators for catheter navigation, artificial muscle structures, artificial sphincter cuffs, and many more. Although these materials and applications represent an exciting field of study, piezoelectric PVDF and PZT are by far the most widely deployed polymers in the market today and are therefore the focus of these investigations.

This research covers the development of new piezoelectric thin films with unique combination of properties and controlled and/or predicable behavior, in terms of principles of adaptiveness, properties, structure design and characterization with an emphasis on their applications. Synthesis and use of different piezoelectric and organic polymers allowed the preparation of combined materials having specified combination of properties. It is highly desirable to partten PVDF-based thin films with feature size down to micro- or nanometer scale allowing to probe piezoelectricity and to extend biosensing application fields. In this case, the miscibility of piezoelectric polymers PVDF and PZT with organic polymer Poly(methyl methacrylate) (PMMA) gave the morphological stabilization of formed PVDF-based thin film layers. Further investigations were done by embossing microperiodic structures on these layers and analyzing surface morphology at the nanoscale and optical properties.

These developments of new piezoelectric films have made it possible to understand the strengthening and deformation mechanisms in micro- and nanoscale together by bringing new insights in biosensing applications.

Materials and synthesis

Piezoelectric polymers – 5% PVDF (average M_W = 34 000) and barium titanium oxide $BaTiO_3$ (or PZT) were taken in suitable and definite compositional ratios and mixed with appropriate amount of 5% PMMA (average M_W = 15 000).

Thin films formation

PMMA and piezoelectric PVDF-based polymer thin films were produced on the glass substrates, pretreated in O_2 plasma, from coating polymer blend by spin–coating technique. Layers were spin–coated with “DYNAPERT PRECIMA” centrifuge. The spin speed was above 1800 rpm and spinning time was 15 s. Afterwards, thin films were dried in an oven (80^{o}C) for 10 min. UV source (Hibridas Exposure Unit MA4, power 1200 W, wavelength 254 nm, exposure time from 1 to 4 min) was used for UV irradiation.

Fabrication of microperiodic structures

Using low–cost and high–throughput replication technology – a hot embossing process [12], microperiodic structures were imprinted on formed thin film layers. This methond has therefore been considered as an innovative method for mass production of gratings for micro-devices.

A glass substrate with formed thin film is placed together with a master grating (see Table 1.) in the metallic mandrel between plates, tightened and putted in the furnace of 120^{o}C for 15 min. Well-defined microperiodic structures were obtained.

Table 1. Properties of master grating

Grating periodicity	Depth	700±5	nm
	Periodicity	4±0.01	μm
Grating dimensions	Length	2	mm
	Width	16	mm
Grating lines	Parallel to the short edge		

Hot embossing procedure in polymers was analyzed in previous science researches [12].

Analythical techniques

Atomic Force Microscopy (AFM) is one of most popular methods used for in situ measuremens of topography, force-distance curves and friction forces of surfaces. In this case, the morphology and elastic properties of formed thin films and microperiodic structures were investigated by Atomic Force Microscope NT – 206. V type non–contact silicon cantilever NSC11/15 probe (constant force 3 N/m, resonant frequency 60 kHz) was used.

For measurements of diffraction efficiency of microperiodic structures in all peaks for different incident angles, a laser diffractometer was used. In this device a photodiode is used for recording intensity and angle of diffracted light in all maxima (0, ±1, ±2, and etc.). That depends on the period of diffraction grating. Red He–Ne laser of wavelength 632.8nm incident to grating was used.

Vibrations were measured with a laser vibrometer (Polytec Fiber Interferometer OFV 512). The ADC provides a solution for measuring and recording voltage signals onto PC. PicoScope is a program, which enables to use the Pico Technology range of analog to digital converters to provide the function of a storage oscilloscope, a spectrum analyser and a digital meter.

Results

PVDF and PZT polymers have been studied extensively, mainly in relation to piezoelectric properties. Much attention has been paid to problems such as miscibility of the amorphous phase, crystallization of PVDF and PZT in various phases, and there molecular origin of interactions. Synthesizing with polymer PMMA is an original way to force PVDF and PZT to crystallize into piezoelectric phases, which are thermodynamically unstable in pure materials.

Analysis of piezoelectric thin films

In this research after formation of thin films, surface morphology and elastic behavior of each sample were analyzed by AFM. If the adhesion forces, measured with increasing external loads, remain constant, it can be concluded that the contact is elastic and that no material transfer occurred at these loads. Adhesion influences the degree of deformation of the roughness at the contact and is dominated by the attractive portion of the interacting forces between the surface atoms of the contacts. In AFM surface view of formed PVDF thin film (Fig. 1, a) there are observed small islands, i.e. crystalline structures, with surface roughness of 33.2 nm. Adhesive force required to approach the surface with a probe was extremely high - 13978 nN (Fig. 1, b). Obtained polymer PMMA surface roughness was very smooth – 1.4 nm (Fig. 1, c). Adhesive force required to approach the surface with a probe was 414 nN (Fig. 1, d).

Further investigations were perfomed by forming PVDF-based piezoelectric thin films and analyzing the influene on surface morphology and elastic behavior when modifying PVDF with PMMA, PVDF with PZT and PVDF with PVDF and PMMA, respectively.

Significant improvements were obtained modyfing piezoelectric polymer PVDF with organic polymer PMMA (Fig. 2 a and b), i.e. smooth surface with roughness 51.1 nm and adhesive force, required to approach the surface with a probe was only175 nN. Accordingly, the presence of marginal amounts of surface contamination considerably reduces the adhesion of modified piezoelectric surface. Extremely high adhesion force was required for PVDF/PZT thin film – 14353 nN (Fig. 2, d). Small irregularities (with average depth of 160 nm and width of 338 nm) were observed on surface of PVDF/PZT with surface roughness of 34 nm (Fig. 2, c). Thus, introducing PMMA in PVDF/PZT reduces adhesion force to 2413 nN (Fig. 2, f) compared to PVDF/PZT, but six times rougher surface with roughness of 200 nm (Fig. 2, e). So, here the breakfree distance was used as a measure of the adhesion force between the tip and the surface of polymer. The distance was measured from the point that the tip feels a repulsive force to the point where the tip breaks away from the polymer surface. And the importance of adhesion is undisputable in many phenomena even beyond tribology, like coating performance, self cleaning surfaces, wetability, and micro/nanotechnology. But for tribology the understanding of adhesion is of fundamental importance, because it is one of the basic mechanisms of friction and also influences the deformation of thin film when microperiodic structures must be imprinted.

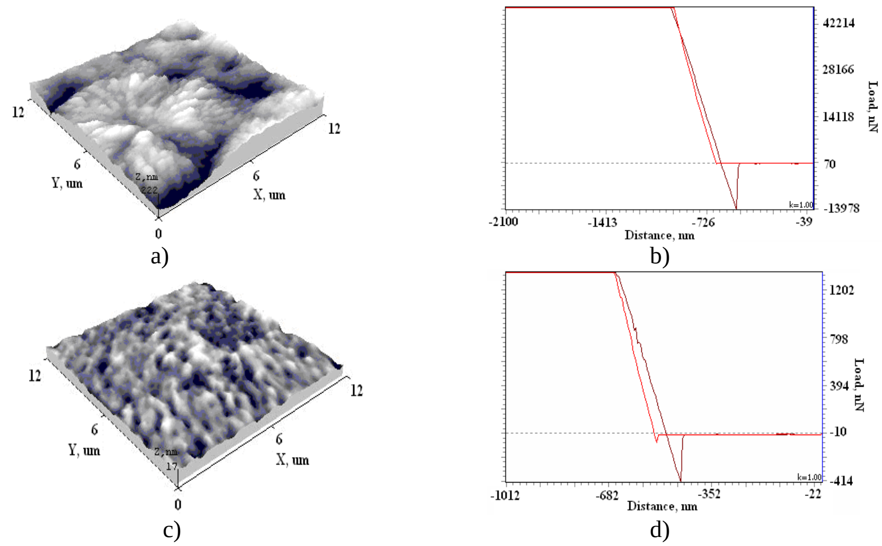

Fig. 1. a) 3D view of PVDF, b) Load – Distance diagram of PVDF, c) 3D view of PMMA and d) Load – Distance diagram of PMMA

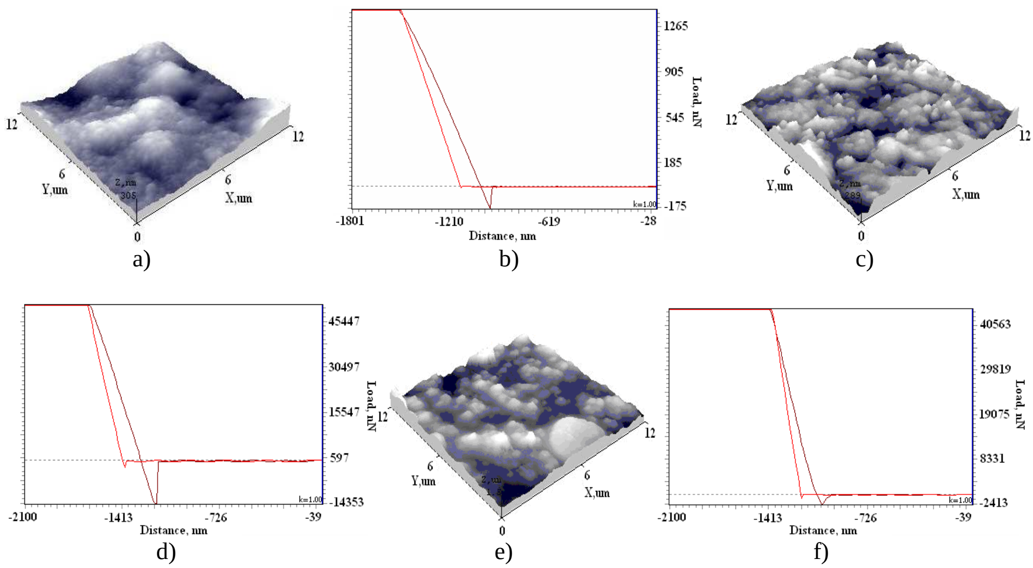

Fig. 2. a) 3D view PVDF/PMMA, b) Load – Distance diagram of PVDF/PMMA, c) 3D view of PVDF/PZT, d) Load – Distance diagram of PVDF/PZT, e) 3D view PVDF/PZT/PMMA and f) Load – Distance diagram of PVDF/PZT/PMMA

As results imply, PMMA here acts as material improving thermo–plasticity of PVDF-based piezoelectric thin films. This is essential when imprinting microperiodic structures on these piezoelectric thin films, i.e. as further investigations showed – grating parameters and optical properties are highly dependent on the incorporated polymer PMMA.

Analysis of microperiodic structures

Well-defined microperiodic structures – gratings, are essential part of biosensing systems used in micro-devices. Diffraction-based biosensors operate at a fixed wavelength and detection angle; they exploit the variation of diffraction efficiency that occurs due to the bonding of a chemical or biological species on a diffraction grating. The diffraction efficiency, taken as the ratio of input power and output power for a selected diffraction order, is a ratio of beam powers, and is thus unaffected by fluctuations or decay in the power of the probe laser. A uniform change in the height of both the grating lines and the height of the grating channels would result in no change in diffraction efficiency. Moreover, the limited surface area available for biochemical attachment on the gratings ultimately limits the device performance.

Using hot embossing process, microperiodic structures were imprinted on five different thin films – PVDF, PMMA, PVDF/PMMA, PVDF/PZT and PVDF/PZT/PMMA (Fig. 3).

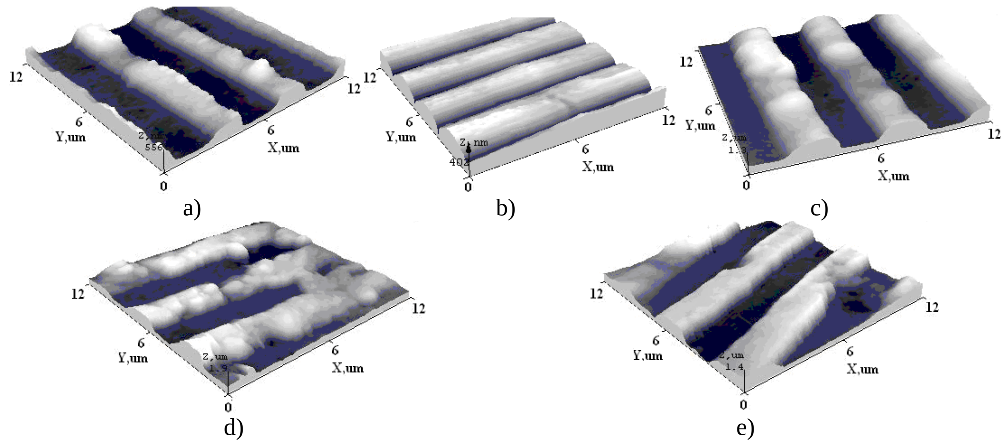

Fig. 3. Microperiodic structures imprinted on a) PVDF, b) PMMA, c) PVDF/PMMA, d) PVDF/PZT, e) PVDF/PZT/PMMA thin films

As AFM measurements showed, grating imprinted on PVDF thin film had parameters of average width of 2.1 µm and average depth of 0.55 µm (Fig. 3, a). As for PMMA grating, the average grating depth was 0.34 µm and width was 4 µm (Fig. 3, b). Microperiodic structure of PVDF/PMMA had properties of average grating depth of 0.71 µm and width 4.1 µm (Fig. 3, c). Imprinting gratings on PVDF/PZT (Fig. 3, d) and PVDF/PZT/PMMA (Fig. 3, e) thin films led to narrow and irregular forms of gratings with average depth of 0.71 µm and width of 2.8 µm for PVDF/PZT, and with average depth of 0.78 µm and width of 3.4 µm for PVDF/PZT/PMMA, respectively.

For measurements of diffraction efficiency in all peaks of different incident angles a laser diffractometer was used. Distribution of diffraction effectiveness was observed in 0, ±1 and ±2 order maximums. Using red laser light, characteristics of efficiencies, versus wavelength of diffraction grating, have been registered. Classical ruled gratings usually peak with very high efficiency at a certain angle and become rapidly less efficient as deviated from that angle.

As diffraction efficiency measurements show, for a grating imprinted on PVDF, most of diffraction energy was concentrated on zero order (~ 72 %). Mixing PVDF with PMMA leads to decrese of diffraction efficiency in zero order and increase in first orders of its maximum, i.e. most of the diffracted energy were concentrated on zero (~ 40 %) and first orders (~ 27 %). For grating imprinted on PVDF/PZT/PMMA, diffracted energy was concentrated simillarly in its zero order (~ 12 %) and first orders of its maximum (~ 10 %).

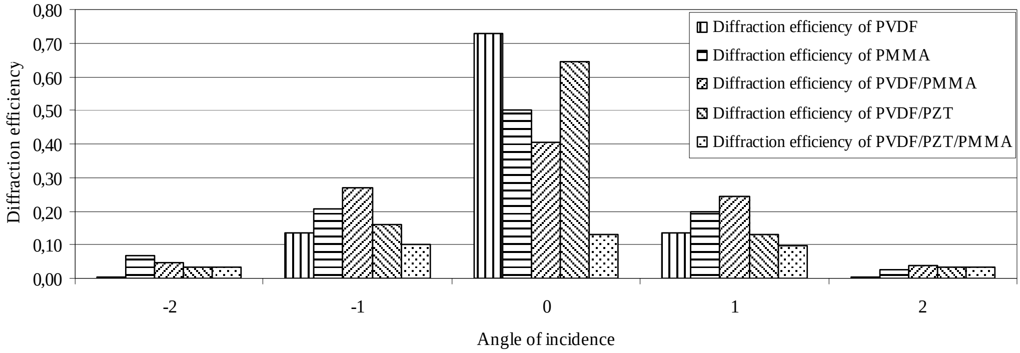

Fig. 4. Diffraction efficiencies of gratings imprinted on investigated thin film layers

Since diffraction efficiencies in 0 and ±1 orders of its maximum are of most importance, it may be concluded, that microperiodic structure imprinted into PVDF/PMMA, because of good parameters and form similar to master grating, leads to very good diffraction efficiency results, i.e. diffracted energy mainly concentrated in its zero and first orders of its maximum.

Piezoelectric effect of intelligent piezoeletric polymers

Piezoelectric materials are a class of materials which can be polarized, in addition to an electric field, also by application of a mechanical stress. It is well known that the potential applications of PVDF mainly come from the piezoelectricity and ferroelectricity of its polar phase [13]. Self-organizing ferroelectric nanomesas and nanowells were reported in Langmuir-Blodgett PVDF films annealed above the ferroelectric phase transition temperature [14-16]. Based on previous researches [17], piezoelectric polymers were mixed with organic polymer PMMA to form oriented grains distributed in the plane of the film that exhibits piezoelectric effects (Fig. 5). Likewise, piezoelectric films with random grain orientation were polarized by an electric field.

In this case, the piezoelectric effect was examined registering the voltage spike by picoampermeter. Tapping of each piezoelectric thin film with force of 0.85 N generates a voltage spike. Tapping pure PVDF, thin film generates around 50 mV, and PVDF/PZT film generates around 62 mV. A generated voltage decrease when PMMA is introduced in thin films, i.e. PVDF/PMMA generates around 29 mV and PVDF/PZT/ PMMA – around 32 mV. So, what is obvious, that the peak values depend on the force applied, the sample thickness, and even the boundary conditions of the sample.

Conclusions

Varying concentration of materials used to form intelligent polymeric layers with piezoelectric properties, it is possible to control sensitivity and morphology of these thin films in nanometer level.

Diffraction efficiency results imply that diffracted energy of piezoelectric polymers was mainly concentrated in its zero and first orders of its maximum.

Piezoelectric effect is dependent on the force applied, the sample thickness, and even the boundary conditions of the sample.

Nano and micromehanical biosensors are devices that measure physical quantities by utilizing variations in the physical properties of specifically fabricated microstructures that originate from biological interactions. So, advances in intelligent materials creation and technologies have facilitated the development of biosensors in MEMS and NEMS with many advantages, such as greatly reduces size,improved tribological properties, high sensitivity, increased minimum detectable sensitivity, greater realibility and etc.

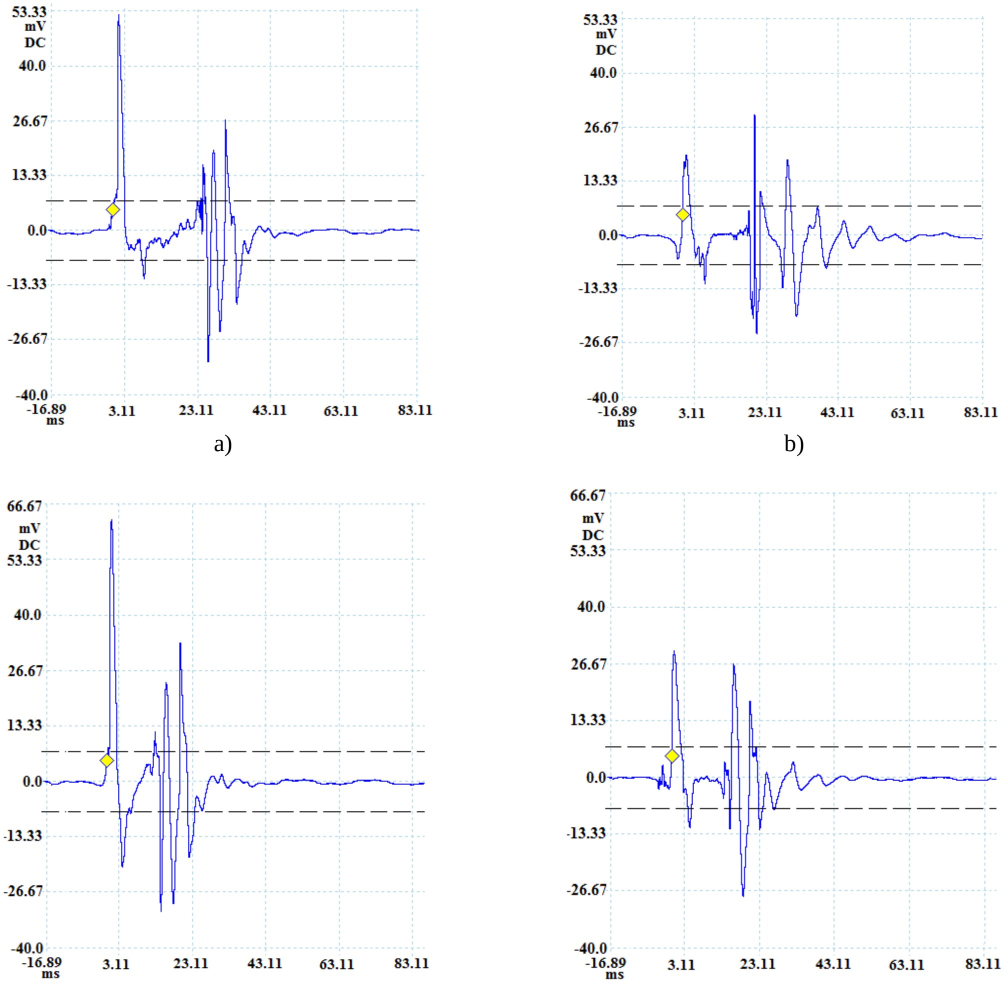

Fig. 5. Registered voltage spikes of a) PVDF, b) PVDF/PMMA, c) PVDF/PZT and d) PVDF/PZT/PMMA

Acknowledgements

This research was funded by a Grant (No. MIP-058/2011) from the Research Council of Lithuania and by the Lithuanian State Studies foundation.

References

[1] **Madou M.** In Fundamentals of Microfabrication. CRC Press: Boca Raton, FL, 1997.
[2] **Kovacs G.** In Micromachined Transducers Sourcebook; McGraw-Hill: New York, 1998.
[3] **Crane G. R., Comparini A. A.** Transducer applications of piezoelectric polymers. IEEE Trans. on Ind. Appl., 1977, p. 380-382.

[4] **Murayama N., Obara H.** In Piezoelectric Polymers and Their Applications; Tokyo, Japan, 1983, p. 3-6.

[5] **Seo I.** Piezoelectric polymers and their applications. J. Jpn. Soc. Precis. Eng. 55, 1989, p. 1374-1347

[6] **Xiao D. Q, Lang S. B.** Measurement applications based on pyroelectric properties of ferroelectric polymers. IEEE Trans.on Electr. Insul. 24, 1989, p. 503-516.

[7] **Chen Q. X., Payne P. A.** Industrial applications of piezoelectric polymer transducers. Meas. Sci. Technol. 6, 995, p. 249-267.

[8] **Aoshima R., Kanda Y., Takada A., Yamashita A.** Sulfonated poly (vinylidene fluoride) as a biomaterial: Immobilization of urokinase and biocompatibility. J. Biomed. Mater. Res. 16, 1982, p. 289-299.

[9] **Sons I.** Polyvinylidene fluoride (PVDF) as a biomaterial. From polymeric raw material to monofilament vascular suture. J. Biomed. Mater. Res. 29, 1995, p. 152-153.

[10] **Bouaidat S., Winther-Jensen B., Christensen S.F., Jonsmann J.** Plasma-polymerized coatings for bio-MEMS applications. Sens. Actuat. A, Phys. 110, 2004, p. 390-394.

[11] **Gebhardt S., Seffner L., Schlenkrich F., Schönecker A.** PZT thick films for sensor and actuator applications, Journal of the European Ceramic Society, Vol. 27 (13-15), 2007, P. 4177-4180

[12] **Guobiene A.** Formation and analysis of periodic structures in polymer materials. Doctoral dissertation, Kaunas: Technologija, 2005, p.86.

[13] **Kepler G., Anderson R. A.** Ferroelectric polymers. Advances in Physics, 41 (1), 1992, p. 1-57.

[14] **Bai M. J., Ducharme S.** Ferroelectric nanomesa formation from polymer Langmuir–Blodgett films. Appl. Phys. Lett. 85, 2004, p. 3528-3530.

[15] **Bai M. J., Poulsen M., Ducharme S. J.** Effects of annealing conditions on ferroelectric nanomesa self-assembly. Phys. Condens. Matter 18, 2006, p. 7383.

[16] **Li J. Y., Luo Y., Bai M. J., Ducharme S.** Nanomesa and Nanowell Formation in Langmuir Boldgett Polyvinylidene Fluoride Trifluoroethelyne Copolymer Films .Appl. Phys. Let., 87, 2005, p. 213116.

[17] **Lei Zhang L., Ducharme S., Li J.** Microimprinting and ferroelectric properties of poly (vinylidene fluoride-trifluoroethylene) copolymer films. App. Phys. Let., 91, 2006, p. 172906.