Preferred deposition of phospholipids onto ferroelectric P(VDF-TrFE) films via polarization patterning

A Heredia, M Machado, I K Bdikin, J Gracio, S Yudin, V M Fridkin, I Delgadillo, a L Kholkin

► To cite this version:

A Heredia, M Machado, I K Bdikin, J Gracio, S Yudin, et al.. Preferred deposition of phospholipids onto ferroelectric P(VDF-TrFE) films via polarization patterning. Journal of Physics D: Applied Physics, 2010, 43 (33), pp.335301. 10.1088/0022-3727/43/33/335301 . hal-00569679

HAL Id: hal-00569679

<https://hal.science/hal-00569679>

Submitted on 25 Feb 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Preferred deposition of phospholipids onto ferroelectric P(VDF-TrFE) films via polarization patterning

A Heredia^{1*}, M Machado¹, I K Bdikin², J Gracio², S Yudin³, V M Fridkin³,
I Delgadillo⁴, A L Kholkin¹

¹ Department of Ceramics and Glass Engineering & CICECO, University of Aveiro,
3810-193 Aveiro, Portugal

² TEMA, University of Aveiro, 3810-193 Aveiro, Portugal

³ Institute of Crystallography, RAS, 933333 Moscow, Russia

⁴ Department of Chemistry & QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal

E-mail: alejandro.heredia@ua.pt

Abstract

Ferroelectric polarization can be used to assemble various organic and inorganic species and to create nanostructures with controlled properties. In this work, we used P(VDF-TrFE) ultrathin films deposited by Langmuir-Blodgett technique as templates for the assembly of various phospholipids that are the essential components of cell membranes. It was observed that 1,2-Di-O-hexadecyl-*sn*-glycero-3-phosphocoline phospholipids (DHPC) form self-assembled structures (molecular domains) on bare P(VDF-TrFE) surfaces. These were revealed by the formation of homogenous and stable rounded blobs with diameters in the range 0.5-3 μm . Further, ferroelectric polymer films were polarized by the application of various voltages via conducting tip using Piezoresponse Force Microscopy (PFM) setup and PFM images were obtained showing controlled polarization distribution. After this, phospholipid molecules were deposited from the solution. Conventional Atomic Force Microscopy (AFM) experiments were then performed to assess the selectivity of the deposition process. It was observed that the deposition process is very sensitive to the concentration of the solution. The selective deposition was observed mainly at the polarization boundaries where the selectivity reached a maximum value of about 20-40%. In this way, the controlled assembly of organic molecules on the polymer surfaces could be achieved. In addition, the PFM tips could be functionalized by the phospholipids and switchable lines of the DHPC molecules on the P(VDF-TrFE) surface were then visualized by PFM.

Keywords: Self-assembly, P(VDF-TrFE), ferroelectric polarization, Piezoresponse Force Microscopy

1. Introduction

Ferroelectrics are the broad class of materials with switchable polarization that can persist for a long time without an applied electric field [1]. Along with numerous memory and electromechanical applications [2], ferroelectric polarization can also be used to assemble various organic and inorganic species on the surface, due to either specific change of the surface potential associated with the polarization switching, or due to the change of the chemical reactivity on the modified surface [3]. This process, called ferroelectric or polarization lithography, has been used in the past for the deposition of various metals on the surface of ferroelectric perovskites (BaTiO_3 or PbTiO_3) via photochemical process (photoreduction or photooxidation) [4,5]. In this way, it was possible to produce nanoscale patterns of different metals using prepolarized inorganic templates and create useful nanostructures [6]. The polarization can be switched by using contact electrode imprinting, an electron beam or the conducting tip of the Atomic Force Microscope (AFM) [6]. In the latter case, the polarization imaging can be conveniently done using Piezoresponse Force Microscopy (PFM) [7, 8] that allows one not only to control, but also to manipulate, the polarization at the nanoscale. However, the inorganic ferroelectric oxides are not compatible with the organic and bioorganic molecules that are currently of great interest for nanotechnology and biomedical applications. Therefore, there is an urgent need for the development of organic materials as templates having sufficiently high and patternable polarization to be used for ferroelectric lithography. For this purpose, we chose a well-known ferroelectric copolymer, poly(vinylidene fluoride-co-trifluoroethylene) or P(VDF-TrFE) (structure shown in Fig. 1a), that is among the most studied in the literature because of its potential biocompatibility and outstanding ferroelectric, pyroelectric and piezoelectric properties [9]. Another advantage is that this copolymer can be conveniently deposited by the Langmuir–Blodgett (LB) method to produce films with thicknesses from one to several molecular layers, very small roughness, and switchable polarization of the order of $10 \mu\text{C}/\text{cm}^2$ [10]. Equally important is that the polarization can be switched with a few volts, i.e., it is fully compatible with modern microelectronics [11].

In this work, we used 1,2-Di-O-hexadecyl-*sn*-glycero-3-phosphocoline (DHPC) phospholipids, extensively described in the literature [12]. As with many other biomolecules, they are amphipathic, consisting of a phosphate group and a fatty acid tail (Fig. 1b). Therefore, they have both polar and non polar units and thus can be selectively deposited via polarization lithography. As already described in the literature, they are compatible with

P(VDF-TrFE) via non-covalent bonding between phosphate and fluorine groups [13]. The biological importance of this type of lipid is that the alkylphosphocholines are cell membrane formers and, in some cases, DHCP behaves as a class of antitumour agent acting to induce apoptosis in several kinds of tumor cells [14]. The structural and physical-chemical properties of the lipids define their behavior in the self-assembly process, as was shown via the deposition of phospholipids on solid supports [15]. Lipids are frequently used as surfactants in various devices for biomedical detection (where microarrays are now common elements for diagnosis of diseases [16]), and P(VDF-TrFE) could be also potentially used for this purpose.

2. Experimental details

Ferroelectric P(VDF-TrFE) films with a copolymer content of 30% were deposited by means of the Langmuir-Blodgett transfer method. The films were transferred onto Al-coated Si substrates from an acetone-copolymer solution with a concentration of 0.01 wt%. From the macroscopic electrical measurements we confirmed the high quality of the films (remanent polarization of $\sim 10 \mu\text{C}/\text{cm}^2$ and coercive field $\sim 1.5 \text{ MV}/\text{cm}$). The thickness of the films was about 60 nm, i.e., corresponded to about 100 layers.

High purity chloroform was used to prepare the solutions of 1,2-Di-O-hexadecyl-*sn*-glycero-3-phosphocholine (0.5, 1.0, 1.5, 2.0, 3.3, and 5.0 mg/mL) (Sigma, CAS Number: 36314-473). The phospholipids were initially spread with a micropipette on the prepolarized or bare P(VDF-TrFE) surfaces. After the PFM poling was performed by the tip, the organic solution was deposited and left for drying and assembly by evaporation at room temperature. No chemical treatment of the surface was performed. Another method used was a dip coating with a withdrawal speed of about 5 mm/min. Manipulation of the lipids was also done directly by the AFM tip. Layers or lines were deposited on poled or bare P(VDF-TrFE) substrates by scanning the surface in contact mode with the tip previously functionalized with phospholipids (just attached by prior scanning on the lipid surface). The method is similar to that used by the authors of Ref. 17.

Topography and piezoresponse imaging were performed by the AFM-PFM method using a commercial Atomic Force Microscope (Ntegra Prima, NT-MDT, Russia) equipped with a function generator (FG120, Yokogawa, USA) and lock-in amplifier (SR-830, Stanford Research, USA). Standard doped (n^+) Si cantilevers (resistivity 0.01–0.02 Ω and tip apex radius of less than 10 nm) were used (spring constant of $k=0.1\text{--}10 \text{ N}/\text{m}$, Nanosensors, Germany). PFM scans were performed by applying an ac voltage of 5 V and a frequency $f = 50 \text{ kHz}$. As is standard in PFM measurements, signals were acquired in the form $A\cos\theta$,

where A is the amplitude of the piezoelectric displacement and θ is the phase shift between the applied and PFM signals. Therefore, antiparallel domains exhibit different contrasts of opposite polarities. Dark areas (“negative” domains) are due to polarization oriented towards the substrate ($\theta = 180^\circ$), and bright contrast (“positive” domains) correspond to areas with polarization terminated at the film surface ($\theta = 0^\circ$). In this work, the local values of the effective piezoelectric coefficients were not determined, and all data are plotted in arbitrary units and referred to the output signal of the lock-in amplifier.

2. Results and discussion

Figures 2a and 2b show a change in the topography image when the smooth P(VDF-TrFE) template film is covered with the phospholipids. Self-assembly is noticeable after the phospholipid deposition at the concentration of 1.2 mg/ml. Uniform blobs with diameters of 0.2-3 μm and heights between 20 and 40 nm are observed on the surface. The size distribution of the molecular domains demonstrates additional maximum B (in Fig. 2c) due to self-assembly, however, blobs with smaller diameters are abundant on the surface. The assembly of DCHP is apparently driven by intermolecular bonding, although a weak interaction with the P(VDF-TrFE) substrate is decisive for the nucleation of the observed domains. The formation process of lipid domains is currently unclear, although the molecular geometry, free energy reduction, and interaction of fatty tails with polymer surface are all important for their formation and stability. This study is beyond the scope of the current report and will be published elsewhere.

It is clear that the polarization domains and associated stray electric fields from the P(VDF-TrFE) surface should significantly affect the assembly of phospholipids via electrostatic interaction [4]. Similar effects were indeed observed after the surface chemical treatment before LB molecule deposition [3]. Likewise, the lipid layers are affected by the electric fields associated with the illumination with polarized light in which lipid molecular domains form at different scales [18]. In this work, we used electrical poling to reverse polarization locally and thus to promote selective deposition of DCHP polar molecules. Figure 3 compares the topographies of the prepoled template (polarization pattern created in the ferroelectric polymer is shown in the inset to Fig. 1a) after the application of the phospholipid solutions with different concentrations using the method described above. For all lipid concentrations (0.8-3.3 mg/mL), the surface topography is not influenced by the phospholipid molecular assembly, although the roughness increases as compared to bare P(VDF-TrFE). No sign of the polarization-induced assembly was seen even after long poling

times and high voltages. This indicates that the thickness of the deposited layers was too big, so that it masked the selective deposition due to polarization patterning. Therefore, we used the dip coating technique to drain the excess liquid and to decrease the thickness of the deposited layers. In this case, the thickness of DCHP was no more than 100 nm, as estimated by AFM scratching tests. The results are shown in Fig. 4 for different concentrations of the solution. At small concentrations of the phospholipid solution (Fig. 4a), no polarization assembly is obtained. Upon increasing concentration of the solution (Fig. 4b and 4c) we observed an apparent roughness increase accompanied with the appearance of assembly features due to the existence of prepolarized regions (black dotted lines in Fig. 4). The maximum effect was observed for the solution with the concentration of 1.5 mg/ml where the apparent stripes of the deposited materials are clearly seen on the topography image (Fig. 4c). These results suggest that the assembly is mainly driven by the polarization boundaries, as the maximum height of the deposited phospholipids corresponds to the polarization domain edge (Fig. 5a). It thus can be stated that the polarization-driven assembly is governed by the polarization interfaces, suggesting that it is not the stray electric field itself, but its *gradient*, that is responsible for the selective deposition. If the concentration of the lipid solution is 1.5 mg/mL or more the height difference in the lipid/P(VDF-TrFE) surface due to polarization assembly exceeds 20 nm. This corresponds to a selectivity (relative thickness variation) of more than 20 %. We suggest that the molecules are attracted to the polarization lines (shown in the inset to Fig. 4a) as $-\text{PO}_4^{3-}$ polar heads or $-\text{NH}_3^+$ groups, and might feel the gradients of the stray electrical field as is schematically shown in Fig. 5b. Phospholipids possess a dipole moment (characterized by the value p) due to the charge distribution in the polar head. The attraction of the dipoles existing in the lipid solution due to the polarization of the P(VDF-TrFE) surface seems to be based on the dielectrophoresis effect (DEP) [19]. In a classical dielectrophoresis, stray electric field induces a dipole moment which, in the presence of a field gradient, experiences a force towards either the high-field *intensity* region (positive DEP) or the low-field *intensity* region (negative DEP). In our case, these dipole moments do already exist, thus increasing the potential of DEP for scaling down and using it for the manipulation with nanosized objects such as DNA, proteins, nanotubes, nanoparticles, and, potentially, with individual molecules in aqueous solutions (as in our case with phospholipids). When placed in an electric field (E), equal but opposite forces arise on each side of the dipole creating a torque $\tau = p \times E$. In a homogeneous electric field ($\text{grad } E = 0$) the dipole molecules do not move, because the total force acting on the molecule is zero ($F_g \sim p \text{ grad } E$). Apparently, the maximum gradient of electrical field and F_g exists near the

polarization boundaries and thus can explain the observed effect (Fig. 5b). All in all, we believe that our results can be interpreted as follows: local poling of the P(VDF-TrFE) surfaces creates polarized areas on the surface that are associated with both polarization and screening charges that partly compensate each other. Partially or completely screened surfaces produce localized stray electric fields that can attract both dipolar and neutral particles in the solution. Chloroform solution used for the phospholipid deposition is not conductive, and is non polar with a sufficiently low dielectric constant. As such, the electric field is easily transferred to the molecules in the solution, and thus promotes preferred deposition of the phospholipids along written polarization lines, as clearly seen on the topography images in Fig. 5a and 5b.

To evaluate the switching process of both bare P(VDF-TrFE) films and those covered with phospholipid layers, piezoresponse hysteresis loops were acquired locally when the PFM tip was stopped near the selected location and the voltage pulses of both polarities were sequentially applied between the tip and the bottom electrode (Fig. 6) [7]. The loops are characteristic of a local switching process, where the contrast change is due to the integrated piezoresponse of nascent domain and background (unswitched) polarization [20]. The analysis of the hysteresis loops allows one to evaluate the dipole moment of the deposited phospholipid layer by the vertical offset of the loops based on the full switching polarization in P(VDF-TrFE) [21]. As the relative piezoelectric offset (defined as $\Delta d_{33}^{\text{eff}}/d_{33}^{\text{eff}}$, see Fig. 6) is about 0.35, it translates to a polarization offset (i.e., the value of non-switchable part of polarization of the composite film) of about $3 \mu\text{C}/\text{cm}^2$. This polarization is due to the fixed (aligned) dipole moment of phospholipid layer attached to the P(VDF-TrFE) surface. Further, we can roughly estimate the polarization value in phospholipids, using a molecular volume of 2 nm^3 and a $-\text{PO}_4^{3-}$ to $-\text{NH}_3^+$ distance of about 0.5 nm, that gives the corresponding dipole moment of ~ 24 Debye. This results in a polarization estimation of $\sim 4 \mu\text{C}/\text{cm}^2$, being close to the experimental value. The discrepancy may come from the experimental conditions. In our case, there could be a coupling with environmental water molecules and corresponding changes in the molecular density that may decrease the polarization. On the other hand, the small horizontal offset (i.e., internal bias field) can be explained by the existence of a depolarizing field compensated by the field produced by the space charges at both P(VDF-TrFE)-phospholipid and phospholipid-air interfaces [22]. The shape of the loop also suggests that the lipid layer is not switchable, and only transfers the applied electric field from the tip to the ferroelectric. This is also confirmed by the comparison of the polarization patterns produced by tip in contact with bare P(VDF-TrFE) surfaces and those created on the P(VDF-

TrFE)-phospholipid layers (Fig. 7). The domains were distinguished from the surrounding area by the strong dark contrast due to reverse polarization. It is seen that the domain size on bare P(VDF-TrFE) is approximately linear at high voltages, and strongly sub-linear (more precisely, two slopes in the linear dependence) in covered films, while the difference in domain sizes is about 2-4 times depending on the applied voltage (Fig. 7b). This means that the switching mechanism is significantly altered in P(VDF-TrFE) coated with the lipid layer (Fig. 7b). These dependences can be explained as follows: in bare P(VDF-TrFE) films the equilibrium domain size is determined by the minimum of the depolarization, domain wall and interaction energy, and gives a linear dependence of the diameter of created domain vs. applied voltage [23]. The change of the slope of the linear dependence in a coated film may be explained by the two stages of the electric field propagation across tip-lipid and lipid-P(VDF-TrFE) interfaces, and injection of the charge carriers accompanied with the corresponding field distortion. The size of the created domain is relatively small in bare films and, in general, satisfies the well known equations [23, 24]. When the film is covered with the lipid layer, the tip operates in the media with a sufficiently high dielectric permittivity, and the separation between the tip and the ferroelectric surface is significantly increased. This leads to an increase in the size of the created domain due to a less localized electric field and decrease of the depolarization energy. The rigorous calculation of the effect of the lipid on the shape of the domain is outside the scope of this paper and will be presented elsewhere. It is believed that these measurements can be used for the determination of the dielectric constant and its anisotropy in lipids if their thickness is known. It should be noted that the small local coercive fields measured at the nanoscale (Fig. 6) suggest easier nucleation and switching of P(VDF-TrFE)- phospholipid bilayer, this fact being unexplained so far.

Further, we performed PFM experiments on P(VDF-TrFE) to have a patterned phospholipid region (white dotted line, Fig. 8a). Black contrast in Fig. 8b signifies the polarization head terminated at the lipid layer. The black polarization lines (polarization with +50 V) can be seen through the lipid layer (Fig. 8b). Then the PFM tip was placed on the location marked with the black point (Fig. 8d) and -50 V was applied for 10 s. It is clearly seen that the switching occurs only in the areas covered by phospholipids following the polarization lines written in the previous experiment (white lines shown in Fig 8d). No change of the polarization was observed beyond this line. This once again confirms preferred deposition of the lipids (though not seen on the topography, Fig. 8c) along the polarization lines, allowing the formation of complicated domain patterns. Further experiments are needed to fully explain and quantify this behavior.

3. Conclusions

In this work, we developed a method for the preferred deposition of phospholipids on the prepatterned ferroelectric surface of P(VDF-TrFE) films. It is shown that this process is governed by the gradient of the stray electric field emanated from ferroelectric domains written by the PFM tip. This gives us a quite high selectivity of up to 20-40% and obvious advantages of being controllable by the electric field rather than by chemical reactions. Complex polarization patterns can be created by using the localized penetration of the electric field inside the lipid layer. The important parameters of the lipids can be obtained including their dipole moment and, in principle, dielectric permittivity. Easier switching of polarization in P(VDF-TrFE) in conjunction with the phospholipids is observed and might be useful for the study of the dynamics of ferroelectric domains in organic materials. The PFM is proved to be a very promising method for untangling the electromechanical behavior in many organic, hybrid (organic-inorganic) and inorganic structures at different scales and hierarchies.

Acknowledgements

This work was supported by the FCT project PTDC/CTM/73010/2006 (Portugal).

Figure Captions

Fig. 1. Schematics of poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] (a) and 1,2- Di-O-hexadecyl-*sn*-glicero-3-phosphocoline (DHPC) phospholipid (b) molecules.

Fig. 2. Topography of bare P(VDF-TrFE) film (a), self-assembled phospholipids on P(VDF-TrFE) surface (b) and grain size distribution (c) of bare P(VDF-TrFE) (A) and of self-assembled phospholipid molecular domains (B) on P(VDF-TrFE).

Fig. 3. Topography images of P(VDF-TrFE) after the application of a drop of the phospholipid solution. The surface blobs increase in size depending on the concentration of the solution. (a) – 0.8 mg/mL, (b) – 1.6 mg/mL, (c) – 3.3 mg/mL. Inset to (a) shows initial polarization patterns on P(VDF-TrFE) written with + 30 V and -30 V.

Fig. 4. Topography images of P(VDF-TrFE) surface after the application of the phospholipidic solution of different concentrations (a, b, c) during 10 s. (Concentrations of the solutions are labeled on the images). Inset to (a) shows initial polarization patterns on P(VDF-TrFE) written with + 50 V and -50 V. Red line in (c) denotes PFM signal cross-section shown in Fig. 5a.

Fig. 5. (a) Topography cross-section along the poled area before (dotted line) and after (solid line) the application of the phospholipid solution. (b) Schematic of the electric field distribution inside the lipid solution due to the poled P(VDF-TrFE) area.

Fig. 6. Hysteresis curves of the local piezoresponse coefficient d_{33}^{eff} measured as a function of the bias voltage U_{dc} in bare P(VDF-TrFE) film and in phospholipid/P(VDF-TrFE) composites. Vertical offset of the hysteresis Δd_{33}^{eff} is a measure of the nonswitchable polarization due to the presence of lipid layer.

Fig. 7. Comparison of artificial ferroelectric domains created with different voltages (10 s poling time) in bare P(VDF-TrFE) (a) and in phospholipid/ P(VDF-TrFE) composites (b). (c) Comparison of the domain sizes as a function of poling voltage in both cases.

Fig. 8. Topography (a) and PFM image (b) of the preferred deposition of phospholipids on P(VDF-TrFE) surface. Dotted line illustrates local deposition of lipids by the tip. (c) Cross-sections of the PFM signal (top) and topography (bottom) images of (a) and (b). (d) PFM image after poling of the patterned lipid lines (white area).

References

- [1] Lines M E and Glass A M 1979 *Principles and Applications of Ferroelectrics and Related Materials*. (Oxford: Oxford) p 248
- [2] Scott J F 2000 *Ferroelectric Memories* (Berlin-Heidelberg: Springer-Verlag)
- [3] Hirtz M, Fuchs H and Chi L, 2008 *J. Phys. Chem. B* **112** 824
- [4] Li D and Bonnell D A 2007 *Scanning Probe Microscopy Electrical and Electromechanical Phenomena at the Nanoscale*, ed S Kalinin and A Gruverman (New York: Springer) pp 906-928
- [5] Habicht S, Nemanich R J and Gruverman A 2008 *Nanotechnology* **19** 495303
- [6] Li D B and Bonnell D A 2008 *Ceram Int* **34** 157
- [7] Kholkin A L, Kalinin S V, Roelofs A and Gruverman, A 2006 *Scanning Probe Microscopy: Electrical and Electromechanical Phenomena at the Nanoscale*, Vol. 1, ed S V Kalinin and A Gruverman. (Berlin: Springer) pp 173–214
- [8] Kalinin S V, Setter N and Kholkin A L 2009 *MRS Bull* **34** 9
- [9] Lovinger A J 1983 *Science* **220** 1115
- [10] Bune A, Ducharme S, Fridkin V M, Blinov L, Palto S, Petukhova N and Yudin S 1995 *Appl. Phys. Lett.* **67** 3975; Bune A V, Fridkin V M, Ducharme S, Blinov L M, Palto S P, Sorokin A V, Yudin S G and Zlatkin A 1998 *Nature* **391** 874
- [11] Ducharme S, Fridkin V M, Bune A V, Palto, S P, Blinov L M, Petukhova N N and Yudin S G, 2000 *Phys. Rev. Lett.* **84** 175
- [12] Berg J, Tymoczko J L and Stryer L 2002 *Biochemistry* (New York,:W. H. Freeman & Co Ltd) p 603
- [13] Taguet A, Ameduri B and Boutevin B 2005 *Crosslinking in Materials Science* ed. Abe A, Albertsson A-C, Dusek K, de Jeu W H, Kausch H-H, Kobayashi S, Lee K-S, Leibler L, Long T E, Manners I, Möller M, Nuyken O, Terentjev EM, Voit B, Wegner G, Wiesner U and Vicent M J (Heidelberg: Springer) pp 127-211
- [14] Wieder T, Orfanos C E and Geilen C C 1998 *J. Biol. Chem.* **273** 11025
- [15] Hyun K K, Kwangmeyung K and Youngro B 2005 *Biomaterials* **26** 3435
- [16] Kanter, J L, Narayana S, Ho P P, Catz I, Warren K G, Sobel R A, Steinman L and Robinson W H 2005 *Nat. Med.* **12** 138
- [17] Tavares G D, de Oliveira M C, Vilela J M C and Andrade M S, 2005 *Microsc. Microanal.* **11**, supp 3 44.
- [18] Bernchou U, Brewer J, Midtiby H S, Ipsen J H, Bagatolli L A and Simonsen A C 2009 *J. Am. Chem. Soc.* **131** 14130-1
- [19] Pohl H A 1951 *J. Appl. Phys.* **22** 869
- [20] Kalinin S V, Gruverman A and Bonnell D A 2004 *Appl. Phys. Lett.* **85** 795; Wu A, Vilarinho P M, Shvartsman V V, Suchaneck G and Kholkin A L 2005 *Nanotechnology* **16** 2587
- [21] Bystrov V S, Bdikin I K, Kiselev D A, Yudin S, Fridkin V M and Kholkin A L 2007 *J. Phys. D: Appl. Phys.* **40** 4571
- [22] Gruverman A, Rodriguez B J, Nemanich R J and Kingon A I, 2002 *J. Appl. Phys.* **92** 2734
- [23] Molotskii M 2005 *J Appl. Phys.* **97** 014109 ; Pertsev N, Petraru A, Bdikin I, Kiselev D and Kholkin A L 2008 *Nanotechnology* **19** 375703
- [24] Molotskii M 2003 *J. Appl. Phys* **93** 6234

Fig. 1. Schematics of poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] (a) and 1,2-Di-O-hexadecyl-*sn*-glycero-3-phosphocoline (DHPC) phospholipid (b) molecules.

Fig. 2. Topography of bare P(VDF-TrFE) film (a), self-assembled phospholipids on P(VDF-TrFE) surface (b) and grain size distribution (c) of bare P(VDF-TrFE) (A) and of self-assembled phospholipid molecular domains (B) on P(VDF-TrFE).

Fig. 3. Topography images of P(VDF-TrFE) after the application of a drop of the phospholipid solution. The surface blobs increase in size depending on the concentration of the solution. (a) – 0.8 mg/mL, (b) – 1.6 mg/mL, (c) – 3.3 mg/mL. Inset to (a) shows initial polarization patterns on P(VDF-TrFE) written with + 30 V and -30 V.

Fig. 4. Topography images of P(VDF-TrFE) surface after the application of the phospholipidic solution of different concentrations (a, b, c) during 10 s. (Concentrations of the solutions are labeled on the images). Inset to (a) shows initial polarization patterns on P(VDF-TrFE) written with + 50 V and -50 V. Red line in (c) denotes PFM signal cross-section shown in Fig. 5a.

Fig. 5. (a) Topography cross-section along the poled area before (dotted line) and after (solid line) the application of the phospholipid solution. (b) Schematic of the electric field distribution inside the lipid solution due to the poled P(VDF-TrFE) area.

Fig. 6. Hysteresis curves of the local piezoresponse coefficient d_{33}^{eff} measured as a function of the bias voltage U_{dc} in bare P(VDF-TrFE) film and in phospholipid/P(VDF-TrFE) composites. Vertical offset of the hysteresis $\Delta d_{33}^{\text{eff}}$ is a measure of the nonswitchable polarization due to the presence of lipid layer.

Fig. 7. Comparison of artificial ferroelectric domains created with different voltages (10 s poling time) in bare P(VDF-TrFE) (a) and in phospholipid/ P(VDF-TrFE) composites (b). (c) Comparison of the domain sizes as a function of poling voltage in both cases.

Fig. 8. Topography (a) and PFM image (b) of the preferred deposition of phospholipids on P(VDF-TrFE) surface. Dotted line illustrates local deposition of lipids by the tip. (c) Cross- sections of the PFM signal (top) and topography (bottom) images of (a) and (b). (d) PFM image after poling of the patterned lipid lines (white area).