New Journal of Physics
The open access journal at the forefront of physics

Deutsche Physikalische Gesellschaft DPG IOP Institute of Physics

Aligning in-plane polarization multiplies piezoresponse in P(VDF-TrFE) films on graphite

To cite this article: Robert Roth *et al* 2018 *New J. Phys.* **20** 103044

New Journal of Physics
The open access journal at the forefront of physics

Deutsche Physikalische Gesellschaft DPG
IOP Institute of Physics
Published in partnership with: Deutsche Physikalische Gesellschaft and the Institute of Physics

OPEN ACCESS

RECEIVED
8 August 2018

REVISED
10 October 2018

ACCEPTED FOR PUBLICATION
16 October 2018

PUBLISHED
31 October 2018

PAPER

Aligning in-plane polarization multiplies piezoresponse in P(VDF-TrFE) films on graphite

Robert Roth[1], **Martin Koch**[1], **Jakob Schaab**[2], **Martin Lilienblum**[2], **Frank Syrowatka**[3], **Tino Band**[1], **Thomas Thurn-Albrecht**[1] and **Kathrin Dörr**[1]

[1] Institute of Physics, Martin Luther University Halle-Wittenberg, Von-Danckelmann-Platz 3, D-06099 Halle, Germany
[2] Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland
[3] Interdisciplinary Center of Materials Science, Martin Luther University Halle-Wittenberg, Heinrich-Damerow-Straße 3, D-06099 Halle, Germany

E-mail: robert.roth@physik.uni-halle.de

Keywords: ferroelectric polymers, domains, piezoresponse force microscopy, piezoelectricity, mechanical force

Supplementary material for this article is available online

Abstract

Ferroelectric polymers are promising as piezoelectric sensors and devices for data storage, energy harvesting and fast energy storage. However, efficient electric polarization as well as piezoelectric and dielectric responses of as-deposited films are often much lower than expected in a crystalline model, because the local orientations of electric dipoles show substantial disorder. Here we introduce an approach for in-plane alignment of the polarization based on applying soft mechanical pressure with a force microscopy tip. Micron-sized ferroelectric domains with well-defined in-plane and out-of-plane polarization orientation and low surface roughness have been written in poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) films on graphite. Inside such domains, the piezoelectric response is more than four times that of the untreated film. The achieved polarization alignment can advance the performance of many devices, since it reduces the cancellation of local responses to electric fields or mechanical strains resulting from polarization disorder.

1. Introduction

Ferroelectric polymers are attractive candidates for functional layers in electronic devices like non-volatile memories [1–6], piezoelectric and magnetoelectric sensors [7, 8], energy harvesters [9, 10], and capacitor-based energy storage devices [11]. They offer substantial magnitudes of piezoelectricity, dielectric permittivity, ferroelectric polarization and low leakage currents combined with mechanical flexibility, optical transparence, and inexpensive near-room-temperature processing. As a major challenge for applications, the piezoelectric and dielectric responses of as-deposited films are often much lower than expected in a crystalline model [12]. This is due to the fact that the crystalline lamellae in polymer films are usually not aligned. Additionally, they are surrounded by amorphous regions [13]. Misalignment of electric dipoles/local ferroelectric polarization results in partial compensation of the averaged response to an electric field. In order to enhance the parallel alignment of electric dipoles, two approaches may be followed: (i) three-dimensional alignment of crystalline lamellae and (ii) poling of the polarization in non-aligned lamellae like in a polycrystalline ferroelectric ceramic. The first approach includes attempts to achieve epitaxial growth on a crystalline substrate. Advances have been made for the often applied ferroelectric polymers like poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) in recent years [1, 14, 15], but fully oriented epitaxial growth of films thicker than few nm is not yet achieved. Some applied substrates like, e.g., graphite possess high symmetry resulting in several allowed epitaxial orientations of the polymer film [1, 16]. Alternatively, crystallographic alignment induced by mechanical action of a force microscopy tip in similarity to a nanoscopic drawing process has been suggested [17]. The second approach of orienting local polarizations through a poling procedure works readily for vertical electric poling in thin films. Additionally, in-plane electrodes could be used to apply an electric field for aligning the in-plane component of polarization. However, such electrodes are often an obstacle for designing devices. (For instance, they cover a significant part of the film surface with a conducting material.) We report on an alternative method to achieve the in-plane alignment of polarization which is based on mechanical pressure of a force microscopy tip. Large ferroelectric domains containing many crystalline lamellae have been written with well-defined in-plane and out-of-plane polarization orientation in the applied scanning range of a force microscope. The in-plane polarization orientation can be deliberately chosen by the scan direction. Subsequent electrical switching maintains the uniform polarization orientation in the 'written' area if the vertical electric field is appropriately chosen. The poling of the ferroelectric polarization with in-plane and out-of-plane components results in strong enhancement of the piezoresponse up to more than the four-fold value of the as-grown film. These findings bear strong potential to advance device applications, since many key parameters of performance are weakened as a consequence of misaligned local polarization.

2. Experimental section

2.1. Materials preparation

We fabricated a 2 wt% solution of P(VDF-TrFE) granules (70/30 mol%, Piezotech) in 2-Butanon (Carl Roth) which was spin-coated at 3000 rpm for 60 s onto a highly ordered pyrolytic graphite (HOPG) substrate. The spin-coated film was subsequently annealed at 180 °C for 30 min in vacuum and then quenched on a large metal plate to room temperature. The film thickness of about 65 nm has been measured using a profilometer (Ambios-XP 1, Cenimat) on films prepared in the same way on silicon wafer substrates. Local checks have been done at trenches introduced down to the substrate with a force microscopy tip.

2.2. X-ray diffraction

Thin film x-ray scattering was performed on a SAXSLAB RETRO-F setup equipped with a microfocus source and an ASTIX multilayer optics from Axo, Dresden, Germany. The setup contains a movable DECTRIS Pilatus R 300 K detector in a vacuum housing. A sample-detector distance of 92 mm was used, giving access in θ-2θ-geometry to a maximum scattering vector q_z of about 20 nm^{-1} in vertical direction.

2.3. Atomic force microscopy (AFM) of surface topography

After fabrication, the surface topography was imaged in a Multimode 8 (Bruker) AFM operating in repulsive tapping mode with NSG30 tips (NT-MDT, tip radius ~6 nm, force constant ~40 N m^{-1}).

2.4. Mechanical tip scanning

A force in the range of 170–300 nN has been applied with a Pt/Ir-coated AFM-tip (HQ:CSC17-Pt, MikroMasch, tip radius ~35 nm, force constant ~0.2 N m^{-1}) in contact mode to the polymer film in both an MFP-3D (Asylum Research) and a NTEGRA Aura (NT-MDT) force microscope. Mechanical scanning was performed with scan line distances of ~6–9 nm in an electrically poled area with the slow scan direction parallel to the cantilever orientation and scanning speed of ~2.5 μm s^{-1}. The force was adjusted by the cantilever deflection signal multiplied by inverse optical lever sensitivity and the cantilever spring constant. Lever sensitivity was obtained by measuring force distance curves. The spring constant was determined by measuring the thermal noise of cantilever at resonance frequency and calculating the spring constant using the equipartition theorem of a simple harmonic oscillator.

2.5. Piezoresponse force microscopy (PFM)

PFM images were taken in an Asylum Research MFP-3D microscope measuring with dual ac resonance tracking (DART) mode [18]. Pt/Ir coated HQ:CSC17 tips (MikroMasch) with a loading force of 8–15 nN have been used to avoid surface damage. An AC tip bias of 1.5 V was applied with drive frequencies near the contact resonance to image the vertical and lateral PFM signals. To measure both lateral orientations, the sample region of interest was imaged in two different sample orientations rotated by 90°. The vertical piezoresponse was calibrated by multiplying the lock-in amplifier measured amplitude on photodiode with inverse optical cantilever sensitivity. Torsional inverse optical lever sensitivity was estimated by measuring and linearly fitting the lateral photodetector signal while vibrating the sample by 2 nm in-plane and perpendicular to the cantilever axis. *Off-resonant* PFM measurements have been carried out in a NTEGRA Aura AFM system (NT-MDT) using same tips (HQ:CSC17-Pt, MikroMasch) with a loading force of ~40 nN and a PFM frequency of 17.365 kHz with 1.5–2.5 V AC bias. Due to low PFM signals, the lock-in X and Y outputs were measured and the system inherent background [26] was subtracted before calculating the PFM amplitude and phase images.

2.6. Electrostatic force microscopy (EFM)

EFM and related PFM images have been taken with a NTEGRA Prima system using external lock-in amplifiers (SR830 DSP, Stanford Research systems). PFM images have been recorded with PtIr coated CSG30 tips (NT-MDT, force constant ~0.6 N m^{-1}, loading force 35–50 nN) at drive frequency of 56.14 kHz applying an AC bias of 2.5 V. EFM was performed as non-contact single-pass technique by oscillating the cantilever (ANSCM-PT, AppNano, force constant 6 N m^{-1}, resonance frequency ~60 kHz) in tapping mode at its resonance frequency and simultaneously applying an AC bias of 1 V with frequency of 17.587 KHz to the tip. Signals corresponding to fixed charges were recorded by analyzing the deflection (DFL) signal at the AC frequency with Lock-In amplifiers.

3. Results and discussion

The microstructure of the films has been evaluated based on AFM height and phase images, see figures 1(b)–(d) for a 65 nm thick P(VDF-TrFE) film. P(VDF-TrFE) is one of the best characterized and most applied ferroelectric polymers [9, 12, 17, 20–24, 19]. Ferroelectric polarization is perpendicular to the polymer chain axis and can be switched between six directions of a hexagon (figure 1(a)), thereby inducing a slight orthorhombic distortion. In the orthorhombic unit cell, the chain axes lie along the *c* direction. The polarization is oriented along the *b* direction according to [12] (figure 1(a)). Kim *et al* reported on an epitaxial orientation of P(VDF-TrFE) on graphene where the polymer film has a (100) out-of-plane orientation [1]. The (100) orientation is sketched in figure 1(a), left panel; we note that graphene and the graphite substrate applied in our work have identical surface lattices. The epitaxial in-plane orientation of the lamellae, with chain axes along the $10\bar{1}0$ direction of graphene, is lost in films with a thickness beyond few nm [1]. In agreement with that, our film shows some lamellae with preferred orientations resulting from epitaxy on the HOPG substrate (directions marked by yellow lines in figure 1(b)), but most lamellae are not well aligned to the hexagonal substrate lattice. In this film, crystalline lamellae have an average thickness of 28.7 nm and a long period, denoting the average distance between two parallel lamellae, of 46.8 nm. Hence, the averaged width of the amorphous regions between lamellae is 18.1 nm. Height profiles (figure 1(d), lower panel) have a peak-to-valley distance of $\leqslant 7$ nm arising from the lamellar microstructure. Slightly stronger height fluctuations are present on a larger length scale of few microns (figure 1(d), upper panel). X-ray diffraction indicates a well-defined out-of-plane orientation of (100) or $(1\bar{1}0)$ (figure 1(f)); these two orientations differ only in the switchable polarization direction (figure 1(a)). The crystallographic out-of-plane orientation of P(VDF-TrFE) on graphite determines the possible orientations of the polarization with respect to the film normal as tilted by 30° or 90° (figure 1(a)). The in-plane polarization orientation depends on the local direction of the chain axes, since it is perpendicular to the *c* orientation. Thus, it is subject to the disorder of the in-plane lamellae orientations (figure 1(b)).

In this section, we introduce an approach to reorient the direction of the in-plane polarization using a force microscopy tip. PFM is a tool regularly utilized for investigations of nanoscale ferroelectric switching in P(VDF-TrFE) films [19, 25–28]. At first, the film has been electrically poled by applying a tip voltage of 10 V in an area of several μm^2. Afterwards, the grounded tip is scanned with a mechanical load of 180 ± 10 nN in four rectangular areas indicated in figure 2(a). Lines with a distance of about 6 nm have been written along the fast scan direction in back-and-forth mode. The slow scan direction and the cantilever orientation have been varied in the four areas as indicated in the figure. The cantilever is perpendicular to the fast scan direction, since we observed a reduction of mechanical damage of the film for this cantilever orientation. This 'mechanical scan' applied here resembles the 'mechanical annealing' suggested by Choi *et al* [17]. In contrast to that work, it introduces much less surface roughness (discussed below, figures 3(b), (c)) and does not result in the strong structural reconstruction reported in [17]. After the mechanical scan, the piezoresponse parallel to the slow scan direction is recorded with low tip force (of 30 nN). The phase image (figure 2(d)) reveals an efficient alignment of the in-plane polarization component along the slow scan direction in the rectangular areas. The in-plane polarization points into the slow scan direction. The amplitude image (figure 2(c)) shows considerable enhancement of the piezoresponse amplitude as result of the polarization alignment. The cantilever orientation had no impact on the polarization direction, but it influences the roughness after the mechanical scan (figure 2(b)). Smoother surfaces are obtained when the cantilever is dragged backwards; this configuration is used for further work. Hence, the orientation of the in-plane polarization can be switched to a uniform direction by the mechanical scan. This process can be repeated to set the polarization into a different direction at the same position. Note that a featureless phase image means no domains with opposite polarization orientation are detectable within the resolution limit of the measurement which is ~40 nm due to tip size. No reorientation of crystalline lamellae needs to be involved as is discussed in detail below; the effect of the mechanical scan may resemble the poling of a polycrystalline ferroelectric as sketched in figure 2(e). We further note that no

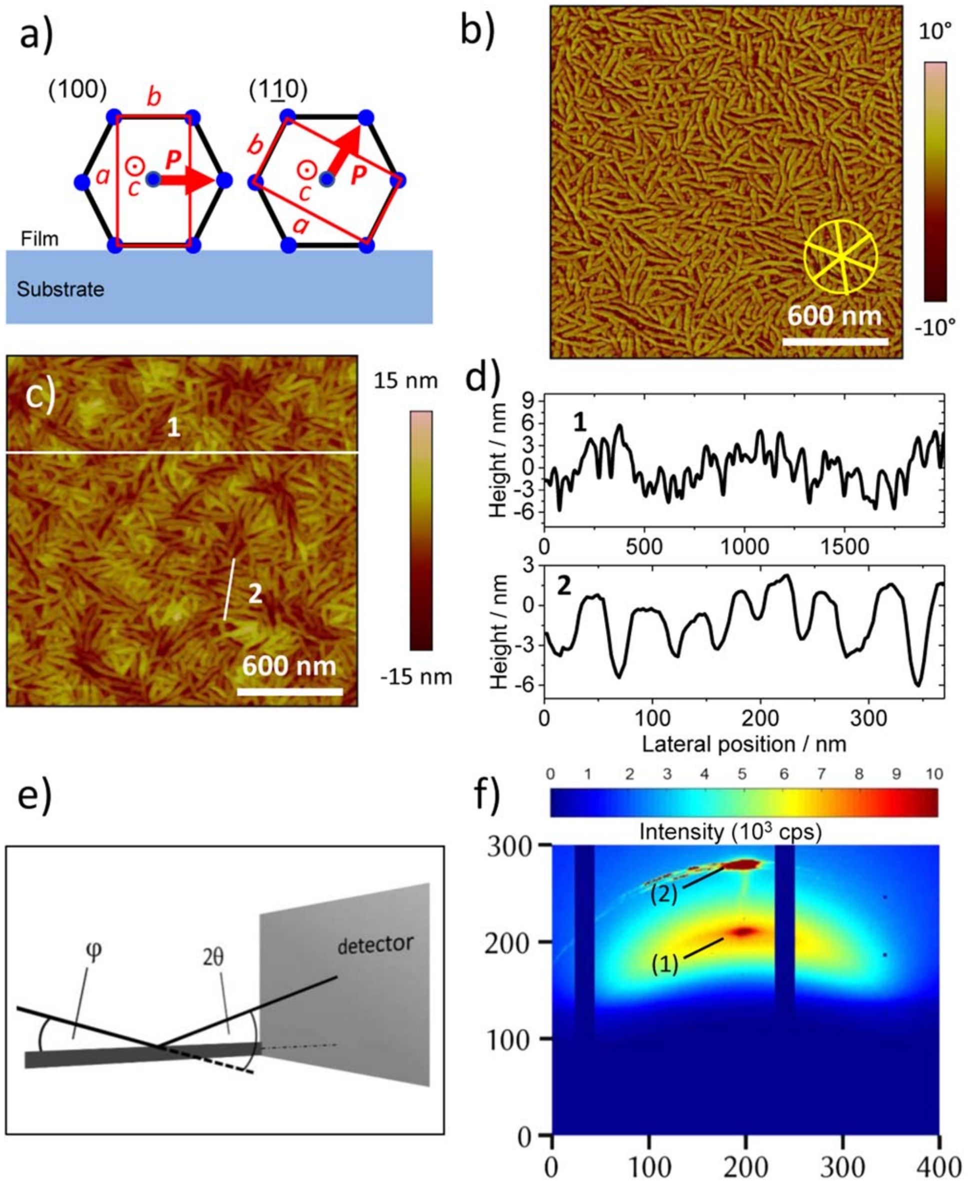

Figure 1. Microstructure and crystallographic structure of P(VDF-TrFE) on graphite. (a) (100) and $(1\bar{1}0)$ orientations of the orthorhombic unit cell with the polarization vector along the crystallographic *b* axis. Polymer chain axes lie along the *c* axis. Polarization switches by multiples of 60°, reorienting the orthorhombic cell. Atomic force microscopy phase (b) and height (c) images of a 65 nm film. Yellow lines in (b) mark preferred orientations of crystalline lamellae along the hexagonal directions of the substrate. (d) Height profiles recorded along white lines in (c). (e) Schematic XRD setup for measuring the out-of-plane orientation of P(VDF-TrFE). (f) 2D real-space scattering pattern showing oriented growth on graphite substrate. Peak (1) corresponds to the (110)/(200) Bragg reflections of the polymer, peak (2) to the (0001) reflection of graphite. For the incidence angle $\varphi \sim 10°$, the Bragg condition for the (110)/(200) film reflections is fulfilled. The width of peak (1) in azimuthal direction (FWHM $\approx 5°$) reflects the orientation distribution of P(VDF-TrFE) crystalline lamellae.

systematic impact of the substrate orientation has been found on the efficiency of the mechanical scan, when the slow scan direction is rotated in steps of 10° between 0° and 60° (not shown).

After identifying this approach as a tool to align the in-plane polarization in a deliberately selected direction, we investigated the writing and electrical switching of micron-sized ferroelectric domains and the resulting increase of the piezoelectric response. The domain writing procedure consists of three steps: (i) electrical poling by scanning a biased force microscopy tip with low mechanical force (~10 nN, blue area in figure 3(a)), (ii) mechanical scanning with grounded tip and tip force of 300 nN (red area in figure 3(a)), and electrical switching with low tip force (~10 nN, green inner areas in figure 3(a)). After electrical poling with 10 V, the vertical piezoresponse (VPFM) amplitude is strongly enhanced (figure 3(d)), indicating vertical alignment of electrical dipoles. The true enhancement of all piezoresponses has been measured in *off-resonant* mode as reported in the supplement, available online at stacks.iop.org/NJP/20/103044/mmedia. In the present case, the VPFM amplitude is about doubled (figure S1). In the electrically poled area, a mechanical scan has been applied using a

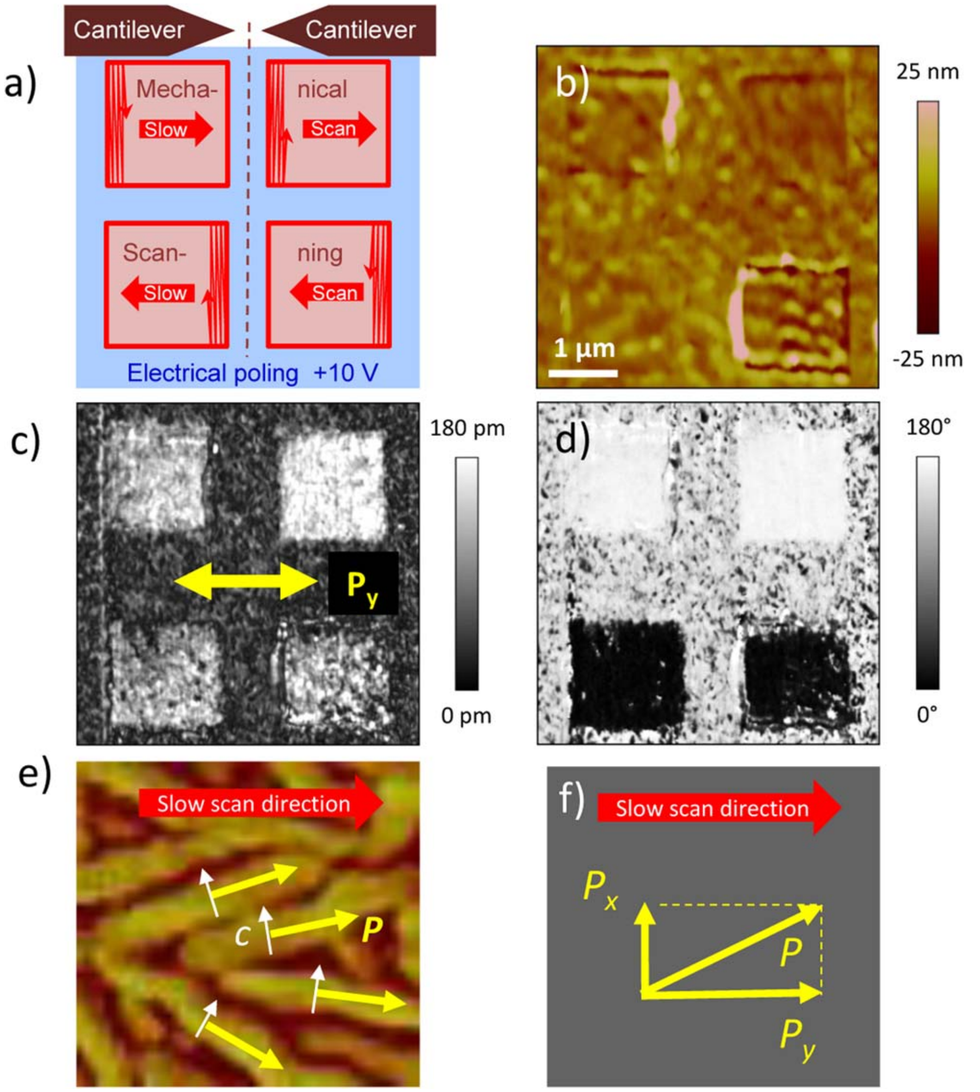

Figure 2. Aligning in-plane polarization. (a) Four areas scanned with tip force of 180 ± 10 nN and no electrical bias in different slow scan directions (red arrows) and cantilever orientations (as indicated). (b) Topography image revealing resulting surface changes. In-plane piezoresponse amplitude (c) and phase (d) images show that the slow scan direction defines the direction of in-plane polarization, resulting in an enhanced amplitude. (e) Schematic image of local polarization orientation after the mechanical scan. Lamellae are assumed to keep their original crystallographic orientation. (f) Orientation of in-plane components P_x and P_y with respect to the slow scan direction.

tip force of 300 nN on a tip with nominal radius of 35 nm. AFM topography images of the scanned area (figures 3(b), (c)) reveal a moderate increase of surface roughness which is largest at the edges of the area. The rms roughness increases from 2.5 nm (as prepared) to 3.5 nm (after mechanical scan, without edges); peak-to-valley distances are marginally larger than in the surrounding (figure 3(c)). Repeated mechanical scans in different sample positions and with different tip radii showed that there is an optimum of the mechanical deformation: if trenches are too deep, the piezoresponse amplitude is suppressed and phase images show more inhomogeneity. Best results have been obtained for surface deformations like those in figure 3(c). The piezoelectric response of the written domain has been probed with both in-plane components (P_x, P_y) and the out-of-plane component (P_z) by measuring the vertical and two orthogonal lateral PFM signals parallel (P_y) and perpendicular (P_x) to the mechanical slow scan direction. First, we discuss the domain area without further electrical switching (red in figure 3(a)). The polarization is inclined at an angle of $\alpha = 30^\circ$ to the film normal (figure 1(a)), because full in-plane orientation of the polarization can be excluded based on the presence of strong vertical piezoresponse. The vertical polarization component P_z is only slightly disturbed after the mechanical scan, as is visible in the PFM amplitude (figure 3(d)) and the related phase (figure 3(g)) images. The P_y amplitude image (figure 3(e)) shows a strongly enlarged signal in the mechanically scanned area. *Off-resonant* measurements demonstrate more than four times larger lateral piezoresponse in this area (supplement, figure S2). Further, the amplitude image suggests low inhomogeneity (figure 3(e)). The corresponding featureless phase image (figure 3(h)) even indicates uniform orientation of the lateral polarization component P_y within the resolution limit of the measurement. On the other

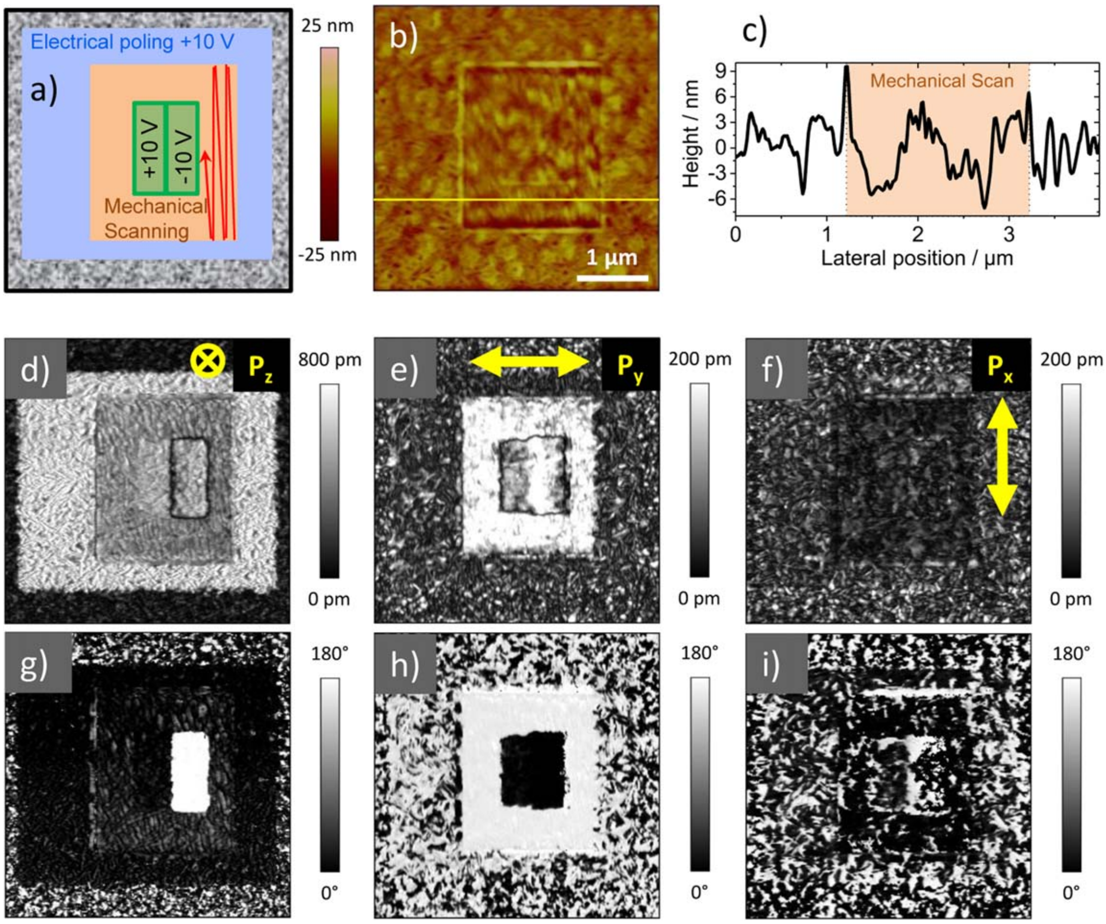

Figure 3. Ferroelectric domain writing in P(VDF-TrFE) on graphite. (a) Scheme of the writing procedure: step 1—electrical poling with 10 V (blue area), step 2—mechanical scan with grounded tip and tip force of 300 nN (red area, red scan lines), step 3—electrical switching with ±10 V (green area). (b) Topography image after mechanical scan. (c) Line scan along the yellow line in (b). (d)–(f) Amplitude and (g)–(i) phase images of piezoelectric responses parallel to P_z (vertical), P_y (in-plane, along mechanical slow scan direction) and P_x (along mechanical fast scan direction). PFM measured in resonance mode.

hand, the polarization component P_x along the back-and-forth fast scan direction (vertical red lines in figure 3(a)) is small, the PFM amplitude is very low (figure 3(f)). The phase image (figure 3(i)) indicates mixed orientations of this polarization component; probably, the back-and-forth movement suppresses preferred orientation of the P_x component. Hence, a high degree of polarization alignment has been obtained in the written domain. Larger areas could be written depending on the instrumental scanning range. To our knowledge, it was not possible previously to write well-defined domains of this size in P(VDF-TrFE) films or another ferroelectric polymer film.

Subsequently, electrical switching of the written large domain has been probed. The tip has been scanned with a bias of either +10 V or −10 V and low tip pressure (~10 nN) in rectangular areas marked green in figure 3(a). These are the inner parts of figures 3(d)–(i). P_z has been reversed by negative bias in the right half of the green area (figure 3(g)), while positive poling has been reinforced in the left half. Interestingly, P_y has been reversed in both parts of the green area (figure 3(h)). This is in contrast to the effect of the vertical electric field during poling the blue initial area (figure 3(a)) where no influence on the in-plane polarization is found. Sharma *et al* reported on 180° switching driven by larger tip fields, while a smaller field resulted in pure P_z reversal [19]. This agrees with our result when a gradually rising tip voltage is applied (supplement, figure S4): at −10 V, 90% of the electrically biased area undergoes 180° switching, in agreement with the observation of 180° switching in the negatively biased green area, while 75% of the electrically biased area undergoes 120° switching at −7 V (figure S4). The purely lateral switching (P_y reversal) observed in the positively biased green area is reproduced in the gradual-voltage-rise study (figure S4), but the origin of this 60° in-plane switching process is unclear at present. Both, the slow scan direction and the electric tip trailing field [29–31] in the gradual-voltage-rise study are oriented along the *x*-axis and, thus, are unlikely as origin of the P_y reversal.

The magnitudes of the vertical and the lateral piezoresponse are larger by a factor of more than two and four, respectively, inside the written domains of figure 3 (supplement, figures S1, S2), in comparison with the surrounding as-grown film. Here we argue that the piezoresponse amplitude truly reflects the degree of parallel

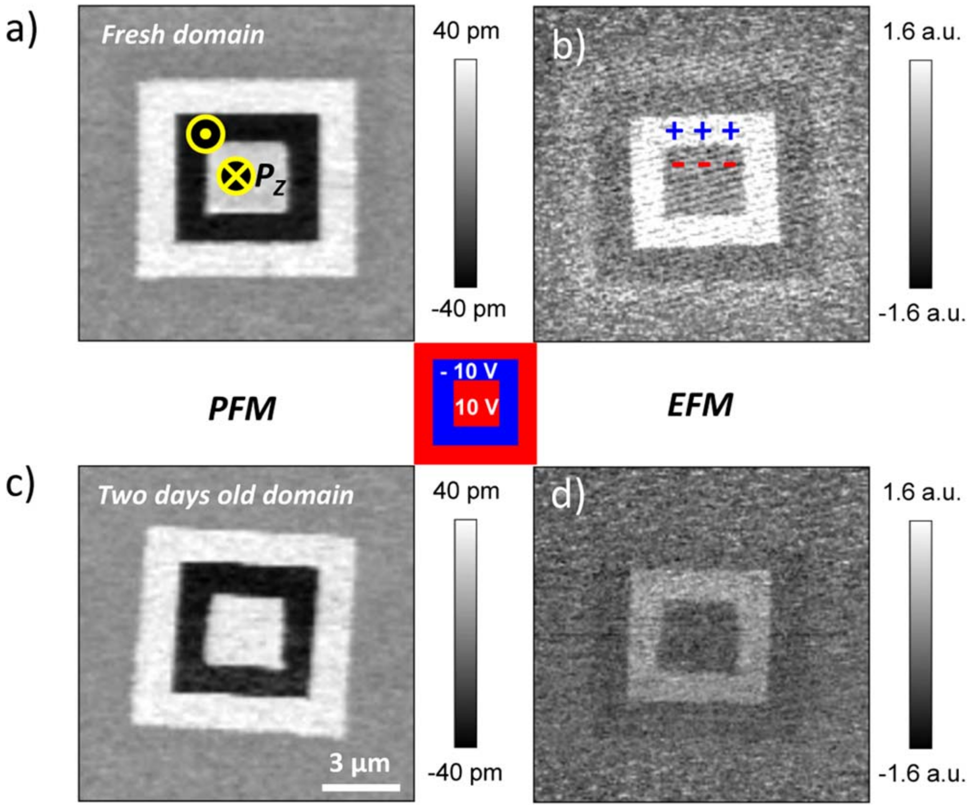

Figure 4. Vertical piezoresponse and electrostatic force microscopy (EFM) images of fresh and aged electrically written domains. PFM (a) and EFM (b) images of a fresh domain pattern written with tip bias of ±10 V. Vertical polarization direction (P_z) and sign of the surface charge as indicated. (c), (d) show the same for a two day old domain. Piezoresponse measured in off-resonant mode and plotted as amplitude multiplied by cosine of phase.

alignment of the electric dipoles in the film and rule out a significant contribution caused by charge injection (below). The force microscopy tip with nominal radius of 35 nm electrically contacts an area of about 3800 nm^2. In a 65 nm thick P(VDF-TrFE) crystallite, there would be ~2000 dipoles per nm^2 between the tip and the conducting bottom electrode. Thus, the tip probes the averaged response of more than seven millions of dipoles. Since the piezoelectric effect changes sign when dipoles are reversed, deviations from parallel alignment lead to compensation effects and a reduction of the piezoresponse. However, before regarding the piezoresponse amplitude as a probe for dipole order, care is required to consider other possible sources of a larger measured piezoresponse. An injection of electrical charge into the surface of an insulator can cause apparent vertical piezoresponse in non-piezoelectric materials [32, 33]. (An oscillating electrostatic force arises between the AC biased tip and the charged surface.) This mechanism may contribute to the vertical piezoresponse in strongly insulating P(VDF-TrFE). Therefore, PFM and EFM images of electrically written domains have been used to characterize the role of charge injection from the tip into the P(VDF-TrFE) surface. EFM recorded at the excitation frequency is sensitive to the surface charge density. Figure 4 shows the vertical PFM response (as amplitude multiplied by cosine of phase) and respective EFM images of concentric domains poled alternatingly with ±10 V. One set of domains has been written immediately before imaging (figures 4(a), (b)), the other is two days old (figures 4(c), (d)). The PFM images of both domains appear identical. Domain boundaries have remained sharp within the resolution limit after two days. The related EFM images (figures 4(b), (d)) reveal the surface charge polarity in agreement with the expected bound polarization charge. (For instance, writing with positive tip resulted in negative surface charge, in contrast to the positive sign of injected charges.) The EFM image of the old domain shows weaker contrast reflecting the screening process of bound polarization charge. The younger domain has an additional margin of bright contrast beyond the written area. This is a typical feature of injected surface charges originating from the PFM imaging process itself or from the written domains. Thus, the EFM images reveal substantial changes in the surface charge distribution taking place within two days. These are not associated with any detectable change of the PFM amplitude, ruling out a significant contribution of injected charges to the PFM response. In fact, the domains shown in figure 3 showed excellent long-term stability: they remained apparently unchanged for more than 9 months (figure S3). These observations allow one to exclude a significant contribution of tip-injected charge to the measured piezoresponse.

4. Conclusions

The aligned in-plane polarization in P(VDF-TrFE) films on graphite is expected to be beneficial for devices relying on electrical or mechanical in-plane properties like piezoelectric strain transferred between layers, effective in-plane polarization, dielectric permittivity. This can be concluded from the fact that the alignment reduces the mutual cancellation of local responses to an external stimulus such as an electric field or elastic strain. As an example, magnetoelectric coupling in heterostuctures with ferroelectric and magnetic components exploits the elastic strain coupling in the film plane [8]. The electrically driven in-plane piezo-strain is four times larger and more homogeneous in our written domains than in the surrounding film. Additionally, complex patterns of in-plane polarization may be fabricated as required for device functionality. Regarding the feasibility of the approach for various device concepts, graphite or graphene electrodes can be transferred onto most types of substrates. In order to overcome the slow sequential writing of domains, multi-tip arrangements such as combs may be applicable.

A prerequisite for the latter, however, is a better fundamental understanding of the microscopic mechanism of the in-plane polarization alignment. Lateral polarization switching in ferroelectric oxide films has previously been achieved by scanning an electrically biased tip: the in-plane polarization in $BiFeO_3$ could be aligned along the slow scan direction using the so-called tip trailing field [29–31]. This effect is also observed in our films for larger tip voltages (beyond 10 V, not shown). Drawbacks are (i) an uncontrolled expansion of the switched domain beyond the defined area due to the large stray field of the tip and (ii) the impossibility to manipulate vertical and lateral polarization components individually. During our mechanical scan, the tip is grounded. Nevertheless, there may be a built-in electric field at the tip-film Schottky junction which is, however, not larger than the tip field at bias voltage of 1–2 V. Scans with low mechanical force (~10 nN) and tip voltages between 0 and 30 V revealed no in-plane polarization switching up to 10 V in our film. Hence, any electric field of the tip can be ruled out as the origin of in-plane polarization alignment. Alternatively, the mechanical pressure under the scanning tip creates strain and strain gradients. The ordering effect of the mechanical scan sets in at a minimum tip force and has an optimum range of tip force in order to achieve aligned in-plane polarization. Hence, the mechanical effect of the tip is essential. A well-known mechanism of a strain-gradient-induced electric field is the flexoelectric effect [34]. P(VDF-TrFE) had been reported to show very large flexoelectricity [35]. The bulk flexoelectric coefficient has been corrected in subsequent work to ~190 nC m^{-1} [36], but a strong increase with decreasing film thickness was found [37]. A recent experiment by Chen *et al* demonstrated vertical polarization switching in a 30 nm thick P(VDF-TrFE) film induced by a tip pressing vertically down with a force as small as 64 nN [38]. The authors of [38] attributed their observations to the flexoelectric effect. However, it is not clear if flexoelectricity contributes to the achieved in-plane polarization alignment. Alternative mechanisms such as purely mechanical ferroelastic switching could be involved.

Finally, the possibility of tip-induced crystallographic alignment of lamellae is considered. Choi *et al* [17] investigated P(VDF-TrFE) films on Si substrates and discovered an enhancement of the piezoelectric response after a mechanical scan ('mechanical annealing') using tip forces of 600–1400 nN on similar tips like ours. Due to larger tip pressure, a more pronounced surface roughness resulted in that work. The authors argued that polymer lamellae structurally reconstruct in a way that chain axes align with the fast scan direction of the tip, similar to a drawing process. In our investigations, films are not reconstructed across their total thickness (supplement, figure S5). The crystallographic alignment suggested by Choi *et al* may be present in a surface layer which is clearly structurally modified. The deeper-lying range of the film in the mechanically scanned area shows as-grown lamellae orientations in scanning electron microscopy images (figure S5). Hence, crystallographic alignment is not the major source of the large domains with enhanced piezoresponse in our work. In spite of lacking crystallographic in-plane alignment, the enhancement of vertical and lateral piezoresponses is considerably larger in our study, indicating that there is further potential for improvement if crystallographic alignment of lamellae could be achieved. As another advantage of the present approach, the roughening of the film surface can be kept very low. We note that the improved piezoelectric performance is likely to result in part from using the graphite-electrode substrate, since a quite homogeneous microstructure of dense lamellae and a well-defined out-of-plane orientation have been obtained on graphite.

Acknowledgments

The authors gratefully acknowledge funding by Deutsche Forschungsgemeinschaft, SFB TRR 102 *Polymers under multiple constraints* (B3), SFB *762 Functionality of oxide interfaces* (A8) and the funding programme Open Access Publishing. JS acknowledges funding from the ETH Zurich and the SNF (proposal no. 200021-149192). ML was supported by the ETH Research Grant No. ETH-06 12-2. We thank E Soergel for an in-plane polarization test sample, G Catalan for discussions on ferroelastic switching and M Fischer for advice on x-ray diffraction measurements.

ORCID iDs

Robert Roth https://orcid.org/0000-0002-7352-2067

References

[1] Kim K L *et al* 2016 *Nano Lett.* **16** 334
[2] Wang X *et al* 2016 *Opt. Quantum Electron.* **48** 345
[3] Lee Y T *et al* 2015 *ACS Nano* **9** 10394
[4] Hu Z, Tian M, Nysten B and Jonas A M 2009 *Nat. Mater.* **8** 62
[5] Kang S J, Bae I, Shin Y J, Park Y J, Huh J, Park S-M, Kim H-C and Park C 2011 *Nano Lett.* **11** 138
[6] Liu Y, Weiss D N and Li J 2010 *ACS Nano* **4** 83
[7] Persano L, Dagdeviren C, Su Y, Zhang Y, Girardo S, Pisignano D, Huang Y and Rogers J A 2013 *Nat. Commun.* **4** 1633
[8] Jin J, Zhao F, Han K, Haque M A, Dong L and Wang Q 2014 *Adv. Funct. Mater.* **24** 1067
[9] Hu F, Cai Q, Liao F, Shao M W and Lee S T 2015 *Small* **11** 5611
[10] Chang C, Tran V H, Wang J, Fuh Y-K and Lin L 2010 *Nano Lett.* **10** 726
[11] Ranjan V, Nardelli M B and Bernholc J 2012 *Phys. Rev. Lett.* **108** 087802
[12] Bystrov V S, Paramonova E V, Bdikin I K, Bystrova A V, Pullar R C and Kholkin A L 2013 *J. Mol. Model* **19** 3591
[13] Strobl G 2007 *The Physics of Polymers* 2nd edn (Berlin: Springer)
[14] Park Y J, Kang S J, Shin Y, Kim R H, Bae I and Park C 2011 *Curr. Appl. Phys.* **11** e30
[15] Fu Z, Xia W, Chen W, Weng J, Zhang J, Zhang J, Jiang Y and Zhu G 2016 *Macromolecules* **49** 3818
[16] Löhmann A-K, Henze T and Thurn-Albrecht T 2014 *Proc. Natl Acad. Sci.* **111** 17368
[17] Choi Y Y *et al* 2015 *ACS Nano* **9** 1809
[18] Rodriguez B J, Callahan C, Kalinin S V and Proksch R 2007 *Nanotechnology* **18** 475504
[19] Sharma P, Wu D, Poddar S, Reece T J, Ducharme S and Gruverman A 2011 *J. Appl. Phys.* **110** 052010
[20] Lovinger A J 1983 *Science* **220** 1115
[21] Kassa H G, Cai R, Marrani A, Nysten B, Hu Z and Jonas A M 2013 *Macromolecules* **46** 8569
[22] Hu W, Wang Z, Du Y, Zhang X X and Wu T 2014 *ACS Appl. Mater. Interfaces* **6** 19057
[23] Pramod S and Gangineni R B 2014 *Phys. Procedia* **54** 101
[24] Shingne N, Geuss M, Hartmann-Azanza B, Steinhart M and Thurn-Albrecht T 2013 *Polymer* **54** 2737
[25] Kalinin S J, Morozovska A N, Chen L Q and Rodriguez B 2010 *Rep. Prog. Phys.* **73** 056502
[26] Soergel E 2011 *J. Phys. D: Appl. Phys.* **44** 464003
[27] Sharma P, Reece T J, Ducharme S and Gruverman A 2011 *Nano Lett.* **11** 1970
[28] Wu Y, Li X, Jonas A M and Hu Z 2015 *Phys. Rev. Lett.* **115** 267601
[29] Balke N, Choudhury S, Jesse S, Huijben M, Chu Y H, Baddorf A P, Chen L Q, Ramesh R and Kalinin S V 2009 *Nat. Nanotechnol.* **4** 868
[30] Bea H, Ziegler B, Bibes M, Barthélémy A and Paruch P 2011 *J. Phys.: Condens. Matter* **23** 142201
[31] Crassous A, Sluka T, Tagantsev A K and Setter N 2015 *Nat. Nanotechnol.* **10** 614
[32] Balke N, Maksymovych P, Jesse S, Herklotz A, Tselev A, Eom C-B, Kravchenko I I, Yu P and Kalinin S V 2015 *ACS Nano* **9** 6484
[33] Johann F, Hoffmann A and Soergel E 2010 *Phys. Rev.* B **81** 094109
[34] Zubko P, Catalan G and Tagantsev A K 2013 *Ann. Rev. Mater. Res.* **43** 387
[35] Baskara S, He X, Chen Q and Fu J Y 2011 *Appl. Phys. Lett.* **98** 242901
[36] Poddar S and Ducharme S 2013 *Appl. Phys. Lett.* **103** 202901
[37] Poddar S, Foreman K, Adenwalla S and Ducharme S 2016 *Appl. Phys. Lett.* **108** 12908
[38] Chen X, Tang X, Chen X-Z, Chen Y-L, Guo X, Ge H-X and Shen Q-D 2015 *Appl. Phys. Lett.* **106** 042903