

Piezoresponse Force Microscopy (PFM)

Piezoelectricity (from greek: *piezein*, for to press or squeeze) is a fundamental physical phenomenon where electric surface charges (or polarisation) build up upon application of pressure to a material. The inverse effect, i.e. the expansion of a material by applying an electric field, is also known, experimentally verified by the brothers Curie in 1880ies [1]. Both effects are found for a broad variety of materials from ceramics (e.g. LiNbO₃) to bones or teeth to polymers like polyvinylidene fluoride and their co-polymers. Their sensitivity to pressure or the excitation of ultrasound by an AC voltage makes them attractive materials for applications from pressure gauges to hydrophones or actuators and many others.

A special class of materials among the piezoelectrics are the so called ferroelectric materials which possess a permanent dipol moment and spontaneous polarisation which can be permanently switched upon application of a temporal electrical field. This switching between two different states ("1" and "0") makes them potential candidates for next-generation non-volatile memory devices or switchable field effect transistors (FerroFETs) [2]. Similar to ferromagnetic materials, ferroelectrics consist of complex domain structures which diminish in a

solid-solid phase transition above a characteristic Curie-temperature. The switching and stability of these domains determines the overall optical, mechanical and electrical properties of these materials. Especially for data storage and micro-electromechanical devices, where micro- to nano-scopic properties come into play, detailed knowledge of the domain structures and switching behaviour with nanometer resolution becomes important.

Until the late eighties high resolution imaging of ferroelectric domain switching was restricted to electron microscopy in transmission or reflection mode, selective chemical etching or decoration and orientation of liquid crystals on the surface of ferroelectrics. However, in 1992 Dransfeld and co-workers [3] invented a new and versatile method for manipulating ferroelectric domains by simply applying voltage pulses to a conductive tip of a scanning force microscope: The birth of the Piezoresponse Force Microscope (PFM).

Principle of PFM

Ferroelectric domains respond to an electrical field with a characteristic deformation (strain) in a characteristic magnitude and sign. In PFM a AC voltage is applied to a conductive tip acting as a movable top electrode coupled to the ferroelectric (piezoelectric) surface via a nanomechanical contact as illustrated in Fig. 1. In the simplest case the vertical (z-direction) surface strain is recorded by measuring the amplitude and phase of the periodic z-response of the material transferred to the cantilever beam (zPFM signal) by the lock-in technique.

The magnitude of the amplitude is a quantitative measure for the local piezoelectric constant (d_{33}) and the phase carries the information of the domain orientation (parallel or anti-parallel). In case that there are domains with a lateral (in-plane) orientation present a shear movement is induced by the electric field. Similar to dynamic friction force microscopy this shear is transferred in torsion of the cantilever and can thus be recorded simultaneously to the zPFM as an xPFM signal. Combining both signals gives a map of the local 2D domain orientation and geometry.

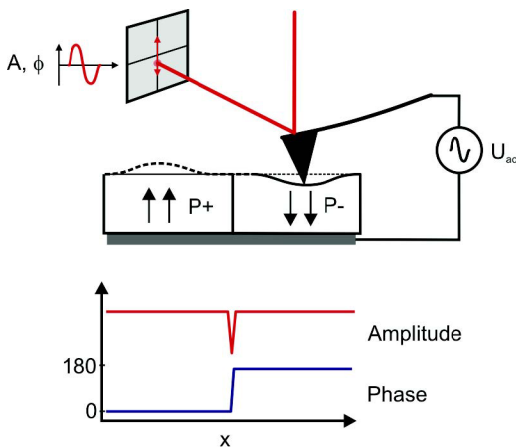


Fig. 1: Principle setup of PFM: A AC voltage is applied between tip and sample, whereas the piezoelectric domains expands or contracts regarding to the bias-sign and the orientation of the domain orientation which gives an in-phase response for $P+$ and out-of-phase response for $P-$ domains relative to the modulated bias. The amplitude response is independent from the direction of domain polarization, if there size and depth is the same.

Beyond just imaging: Hysteresis loops and switching studies

In contrast to many other microscopies, PFM is also a spectroscopic tool for the kinetics of nanoscale domain switching. If voltage pulses higher than the characteristic coercive voltage (electrical field strength) are applied to the conductive tip, the spontaneous polarisation underneath the tip can be switched. Imaging the formed new domains in size and distribution provides direct information about local coercive field strength for nucleation of new domains and the velocity domain walls move. Moreover, if a triangular voltage or a pulse train with a triangular envelope is applied, the piezoresponse reveals a characteristic hysteresis loop similar to the well known switching in ferromagnetics. The shape and/or shift of the hysteresis loop contains important information about e.g. frozen dipole layers or the degradation of the switchable polarisation.

Instrumentation

The following examples were recorded using the JPK NanoWizard® II AFM extended by a digital look-in amplifier (7280 DSP, Signal Recovery) which is software controlled by the AFM using the scripting capabilities of the JPK control software.

Vertical PFM (zPFM) in Lithium Niobate

Beside its well established nonlinear optical properties, lithium niobate (LiNbO3) is a ferroelectric material. In the ferroelectric phase only two domain orientations appear: parallel or anti-parallel (180 deg rotated) to the crystallographic z-axis, separated by domain boundaries. Periodically poled lithium niobate (PPLN) can be easily fabricated by applying a strong electric field (kV) to a thin, z-cut crystal (perpendicular to the z-axis of the crystal) using micro-structured electrodes as shown in figure 2a.

Figure 2b displays a height image (left) and the corresponding piezoresponse (zPFM, middle) amplitude and phase image (right) of the z-surface of the PLLN ($V_{ac} = 2\text{ V}$, $f = 25\text{ kHz}$, far below the contact resonance). Whereas the surface topography of the crystal reveals no features, anti-parallel domains are clearly resolved in the zPFM amplitude- and phase-images. The zPFM phase indicates the change in domain orientation from parallel to anti-parallel by a jump in phase of 180°. However the zPFM amplitude remains constant for both types of domains which is a proof for a homogenous poling process of the single crystal. Only domain boundaries are visible in the zPFM amplitude image due to the change in polarisation

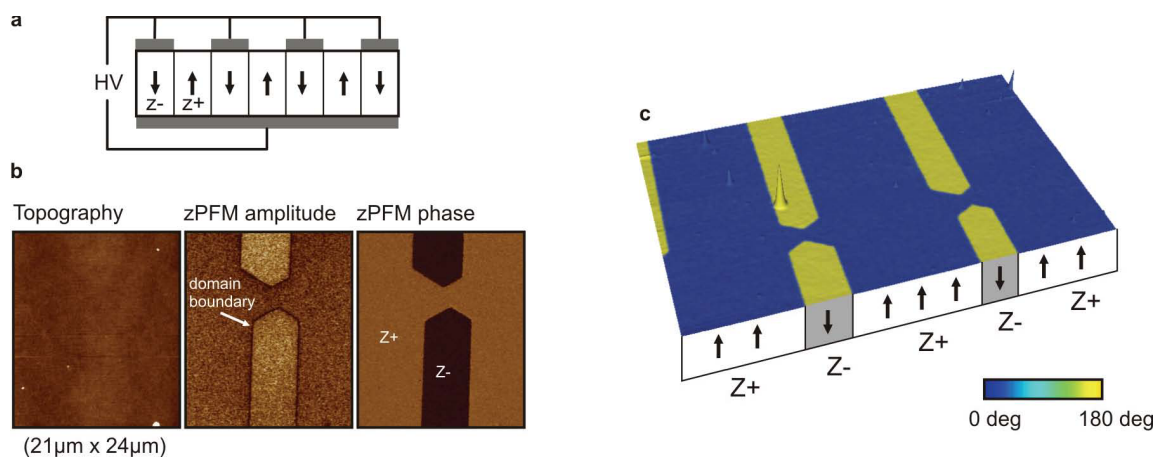


Fig. 2: Periodically poled LiNbO3 single crystal can be fabricated starting from initially z+ poled state as sketched in (a). Topography, piezo-response zPFM-amplitude and -phase images of the crystals z-plane in vertical direction (zPFM) are shown in (b). The anti-parallel polarization of the crystal can be directly stated from the zPFM phase image (180 deg phase shift) as shown in (c) were the 3D topography is textured by the zPFM phase image (scan size: 66 µm x 43 µm).

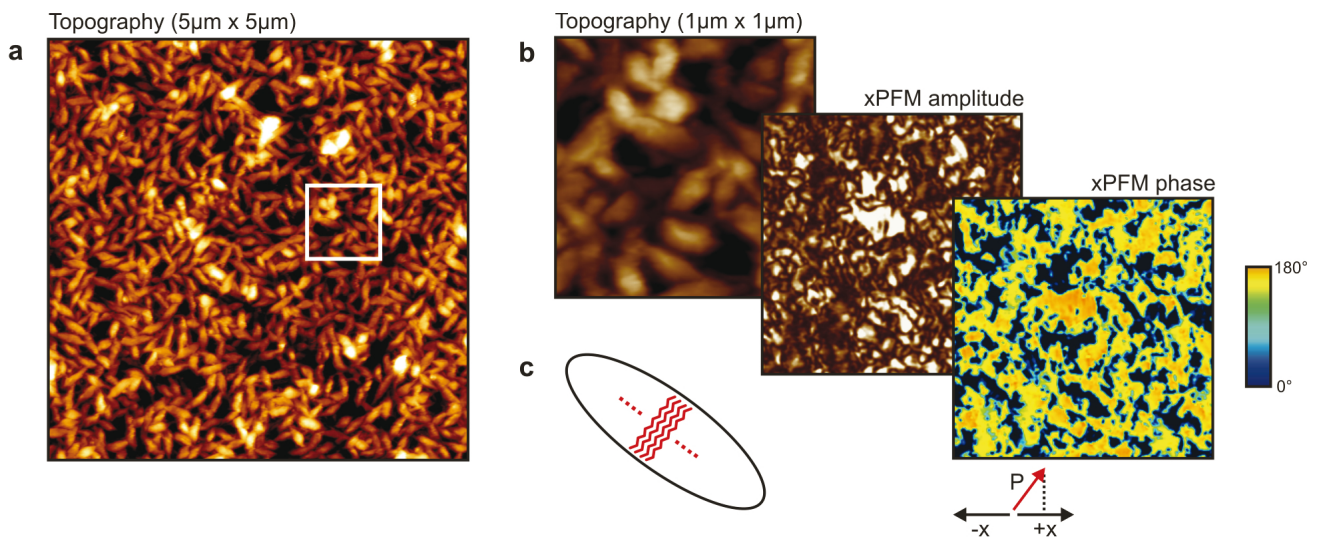


Fig. 3: Overview topography image of a thin, ferroelectric polymer film of P(VDF-TrFE) on gold, annealed at 120°C (sample courtesy of M. Geuss, Adolphe Merkle Institute Fribourg, Switzerland) in which the polymer is crystallized in lenticular shaped lamellae. The xPFM amplitude and -phase image of the lateral piezo-response (scan size: 1.0 µm x 1.0 µm) are shown (b). Domain boundaries visible in the xPFM amplitude image can be correlated with the in-plane polarization of the domains displayed in the xPFM phase. The orientation of molecules in the lamellae is shown in (c).

phase in case of a z- polarized domain. Figure 2c shows the overlay of the zPFM phase information to the, three dimensional sample topography on a larger scale.

Lateral PFM (xPFM) on Ferroelectric Polymer Films

Ferroelectric copolymer poly(vinylidene fluoride-co-trifluoroethylene), P(VDF-TrFE), is a widely investigated piezoelectric material used for pressure gauges [4] and recently for organic FerroFETs and non-volatile organic memory cells [5]. Thin films of this polymer can be prepared by spin-coating from solution. Such films show a significant polarisation switching using a bias of the order of several volts which is compatible with modern microelectronic devices. High polarisation values, the absence of size effects and, more important, a compatibility with many organic and biological materials are also beneficial for molecular electronics and biology due to a possibility of polarisation-driven assembly [6]. Figure 3a shows the topography of an thin film of P(VDF-TrFE) spin-coated from 2-butanone solution after annealing for 2h at 139°C (sample courtesy of M. Geuss, Adolphe Merkle Institute Fribourg, Switzerland). After the annealing

step the polymer film shows a characteristic, lamellar structure with lenticular shaped crystalline structure with a size of approx 280 nm (long axis of the lamellae) in which the individual polymer chains are oriented mainly perpendicular to the long axis of the lamellae as sketched in figure 3c.

Geuss et al. [7] showed that almost no vertical polarisation component is observed for such thin films. However, the lateral piezoresponse reveals complex domain shapes separated by domain walls (dark lines, xPFM amplitude) as shown in Fig 2 c.

PFM Spectroscopy and Hysteresis

While imaging pristine domains as they emerge after cooling the polymer below the Curie temperature provides insight in the statistical process of domain growth during the phase transition but no information about the switching behaviour under an electric field. Fig.4 a shows a representative zPFM phase hysteresis loop recorded while applying a triangular pulse train. The nearly rectangular and symmetric shape indicates the high crystallinity of the polymer lamellae and coercitive voltages around ±5 V, which are well within the range of industrial applications of

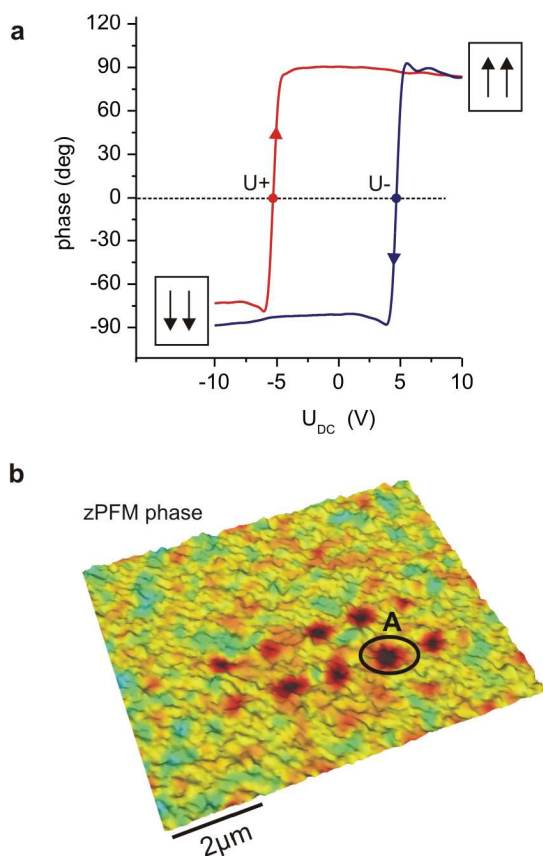


Fig. 4: Hysteresis of zPFM phase at location **A** (indicated in Fig. 4 b) while cycling the DC part of the applied bias between -10V to +10V (sample: P(VDF-TrFE) on gold, thickness: 120nm) (a). The necessary switching voltage U_+ and U_- can be directly obtained. The newly formed domains are clearly visible in the zPFM phase-image (b).

data storage. After performing a series of hysteresis loops at different locations the zPFM phase was recorded (Fig. 4 b) showing new poled domains in the size of about 500 nm. This idea can be expanded to a systematic mapping of loops providing e.g. information about the energy distribution of nucleation centers for domains with a high resolution in the sub 100 nm scale [8]

Conclusions

Scanning probe microscopy has been verified as a powerful tool for probing piezo-responsive structures and their functionality. Beside basic sample topography, detailed information about domain size, 3D polarisation and the switching behaviour kinetics can be easily obtained in parallel which allows a widespread quantitative characterisation of such materials. With the JPK NanoWizard® II as a high resolution and versatile SPM base in combination with the powerful scripting capabilities of the JPK's AFM software, PFM can be integrated in the setup ranging from simple PFM imaging to even more sophisticated switching-hysteresis studies with a minimum of auxiliary equipment.

Acknowledgement

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