Higher Order Ferroic Switching Induced by Scanning Force Microscopy

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We present the observation of ferroelastoelectric switching in a ferroelectric material. It is achieved in barium titanate thin film by simultaneously applying electric field and compressive stress with the tip of a scanning force microscope. For low compressive stresses, the presented measurements reveal classical ferroelectric domain reversal, i.e., the spontaneous polarization is aligned parallel to the applied electric field. However, for high compressive stresses the direction of polarization after switching is *antiparallel to the poling field,* demonstrating ferroelastoelectric switching.

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Ferroelectric polarization reversal phenomena have recently become again a topical issue. The research is driven both by specific features of switching effects in thin films [1,2] and by applications for thin film memories. Scanning force microscopy (SFM) is one of the essential methods used to obtain fundamental data on domains and switching in ferroelectric thin films. Customarily, it is operated in the piezoelectric contact mode. The locally applied electric field produces, via piezoelectricity, a small deformed region in which the sign of induced strain is determined by the sign of a piezoelectric coefficient which in turn is given by the local direction of spontaneous polarization $\mathbf{P}_S$. However, simultaneous application of field and stress involved in this mode of SFM can, as we show in this contribution, lead to new effects which are of importance and, when not taken into account, may lead to misinterpretation of observed effects.

Here we report the observation of $\mathbf{P}_S$ reversal due to the combined application of electric field and stress in a ferroelectric. This so-called ferroelastoelectric switching results, in our case, in the antiparallel alignment of the poling field and the spontaneous polarization, i.e., in the situation opposite to the one obtained without stress. This effect can be expected to significantly influence the performance of ferroelectric devices simultaneously exposed to electric field and stress and, in addition, has to be taken into account when interpreting domain and switching observations in thin films. Note that an (unintentional) stress is always present when a voltage is applied, due to the electrostatic interaction of the two electrodes. As will be shown, this Maxwell stress alone may be sufficient for ferroelastoelectric switching to occur. The reported effect therefore may set an upper limit to the voltage applied to ferroelectric devices.

In the basic classification [3,4], ferroics are classified as ferroelectrics (occurrence of $\mathbf{P}_S$), ferroelastics or ferrobielectrics (spontaneous strain $\boldsymbol{\epsilon}_S$ or new permittivity components $\boldsymbol{\kappa}$), ferroelastoelectrics (new components of piezoelectric tensor $\mathbf{d}$), and ferrobielastics (new components of elastic compliance $\mathbf{s}$). Two domain states [(1), (2)] differ in the Gibbs free energy G when electric field $\mathbf{E}$ and elastic stress $\boldsymbol{\sigma}$ are applied. This difference ΔG provides the driving force for ferroelectric, ferrobielectric, ferroelastic, ferroelastoelectric, and ferrobielastic switching:

$$\begin{aligned}\Delta G = {}& -(P_{Si}^{(2)} - P_{Si}^{(1)})E_i - \tfrac{1}{2}\kappa_0(\kappa_{ij}^{(2)} - \kappa_{ij}^{(1)})E_iE_j \\ & - (\epsilon_{Si}^{(2)} - \epsilon_{Si}^{(1)})\sigma_i - (d_{ij}^{(2)} - d_{ij}^{(1)})E_i\sigma_j \\ & - \tfrac{1}{2}(s_{ij}^{(2)} - s_{ij}^{(1)})\sigma_i\sigma_j\,. \end{aligned} \qquad (1)$$

While ferroelectricity and ferroelasticity have been repeatedly demonstrated in numerous materials by switching in applied electric fields or elastic stress, the attempts to prove the existence of higher order ferroics were accompanied with difficulties. Obviously, to demonstrate ferroelastoelectric properties requires the simultaneous application of both $\mathbf{E}$ and $\boldsymbol{\sigma}$. If the material is both ferroelectric and ferroelastic, it may not be easy to separate the phenomena involved in switching. This is why the prominent candidates to observe higher order switching are those ferroics in which pure ferroelectricity and ferroelasticity are forbidden by symmetry. One candidate for ferroelastoelectric switching was quartz; since its ferroic properties are specified by the symmetry change from the point group $G = 622$ to $F = 32$ and the two domain states (Dauphiné twins) differ in their piezoelectric as well as elastic tensorial properties. Pure ferrobielastic switching was realized in quartz crystal [3,5], and only later the lower order ferroelastoelectric effect was observed [6]. Up to now quartz seems to be the only material in which ferroelastoelectricity was proved experimentally. Attempts to observe the effect in two other candidates, $\mathrm{CsCuCl_3}$ (species $6/mmm$-622) and $\mathrm{NH_4Cl}$ ($m\bar{3}m$-$\bar{4}3m$), were unsuccessful [7,8].

Note that in these ferroics, as well as in quartz, ferroelastoelectric switching is the lowest order change of a ferroic state. However, if the experimental conditions are carefully defined, taking into account the signs of involved coefficients, ferroelastoelectric switching can be unambiguously recognized even in materials which are at the same time

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ferroelectric and ferroelastic. We now treat one particular case, barium titanate, and show that in this classical ferroelectric material ferroelastoelectric switching can be achieved. In its tetragonal phase, $BaTiO_3$ represents the species $m\bar{3}m$-$4mm$. There exist six domain states, and symmetry analysis shows that all terms in Eq. (1) can be active in switching phenomena induced by applied electric field and mechanical stress.

Let us restrict ourself to the simplified situation of a c-oriented film. Both electric field and mechanical stress are applied only locally. To do so the tip of an SFM is used as the top electrode while the conductive substrate of the film serves as the bottom electrode. The local stress is applied, within a small region under the tip, by pressing the tip to the surface with a controlled force F_0. The predominant components of electric field and stress will be normal to the film and therefore along the polar axis.

The sharp tip used as a top electrode results in field components nearly parallel to the film surface in a small volume around but not below the tip. There, the $-\mathbf{E} \cdot \mathbf{P}_S$ term in Eq. (1) would prefer 90° switching to align the spontaneous polarization parallel to the electric field. Such a process appears to be very improbable since these field components "rotate" around the tip and no particular 90° domain is preferred. However, four 90° wedge-shaped domains could be formed around the tip with their polarization vectors along the four a directions. As the field is nearly horizontal only very close to the tip the 90° domains would be small. These domains would be connected with a large domain wall energy since the geometry requires bent ferroelastic walls.

Similarly, there exist nonzero σ_{xx} and σ_{yy} components close to the tip. Again, even if this stress would tend to prefer local a domains due to the $-\boldsymbol{\epsilon}_S \cdot \boldsymbol{\sigma}$ term in Eq. (1), their formation appears improbable since mechanically noncompatible domain walls, connected with high local mechanical energy, would have to be formed.

The local application of field and stress as done by the SFM tip therefore favors local 180° switching. In Eq. (1) for the difference in Gibbs free energy the states (1) and (2) correspond to the antiparallel alignment of electric field and spontaneous polarization and to the parallel alignment. We obtain

$$\Delta G = -2P_S E_3 - 2d_{33} E_3 \sigma_3 \,. \tag{2}$$

In the following we assume the crystal to be in its stable state at any time. We do not consider the dynamics of the switching process itself or any hysteresis effect. Then, in the absence of stress, the application of an electric field E_3 tends to align the spontaneous polarization parallel to the field, as can be seen from the negative ΔG. In the presence of a compressive stress ($\sigma_3 < 0$), however, the second term opposes the first one if P_S is positive (d_{33} is positive by definition). This is the case in tetragonal barium titanate. For a compressive stress above

$$\sigma_C = -\frac{P_S}{d_{33}} \,, \tag{3}$$

the antiparallel alignment is favorable, as ΔG becomes positive. The "critical stress" as given by Eq. (3) is independent of the applied electric field E_3.

We performed measurements on thin barium titanate-films. They were grown by pulsed laser deposition by Siegert *et al.* at the Institute of Thin Film and Ion Technology (ISI) of the Research Center Jülich GmbH (Germany) [9]. The substrate is niobium doped strontium titanate. A commercial SFM (Explorer, Topometrix/Thermo Microscopes) was extended to measure the piezoelectric response. We used boron doped silicon cantilevers (Nanosensors) with a nominal spring constant of 39 N/m and a resonance frequency of approximately 300 kHz. The piezoelectric response was probed with an ac field of 20 kHz and 2 V amplitude.

We applied a single voltage pulse to the SFM tip simultaneously with a high mechanical force. The image [as shown in Fig. 1(a)] was then taken in the piezoresponse mode of SFM [10–12]. The bright ring-shaped domain corresponds to the parallel orientation of the spontaneous polarization and the poling field. The center, however, shows an inverted response (black spot) with the spontaneous polarization oriented antiparallel to the poling field. The surrounding area remains in the original unpoled (gray) state, very probably consisting of a large number of small antiparallel domains. The same results are obtained from Fig. 1(b), showing the piezoresponse along the horizontal line indicated in 1(a) by a dashed line.

In one of his previous studies, Gruverman *et al.* [Fig. 2(a) in [13]] observed a nearly identical picture. However, the domains were formed by a different procedure based on a purely ferroelectric switching process: a positive field pulse was followed by a shorter and weaker negative field pulse, applied at the same spot of a $Pb(Zr_x, Ti_{1-x})O_3$ (PZT) sample. Based on their experimental approach, the obtained domain pattern consisting of a black spot surrounded by a bright ring was undoubtedly interpreted as two concentric domains of opposite polarization. In the present experiment the same configuration is reached by simultaneous application of electric field and mechanical stress. The stress is applied by the tip only in the area in contact with the sample. The electric field, which is also present around this contact area, results in poling under no pressure in a ring around the contact area. This fact and comparison of the resulting domain configuration strongly support the interpretation based on the ferroelastoelectric switching.

We also measured the component of the spontaneous polarization parallel to the surface by piezoresponse SFM [14,15]. None was detectable. This implies that the polarization points either up or down.

For a systematic study, trains of voltage pulses have been applied simultaneously with defined forces F_0. The

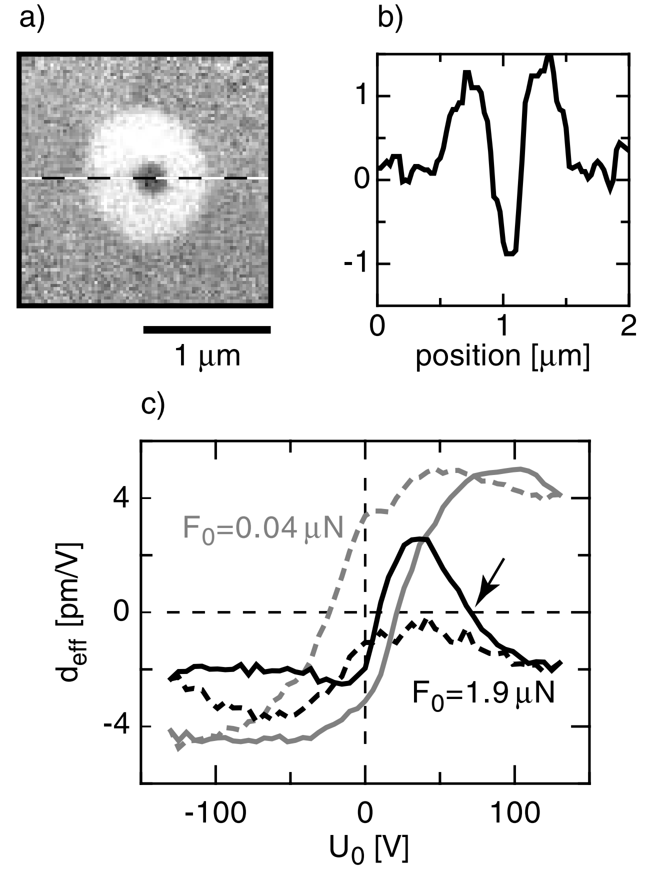

FIG. 1. (a) Domain pattern created by a single voltage pulse applied under high mechanical force, imaged by piezoresponse SFM. The dark center at the place the tip was positioned during poling corresponds to an antiparallel alignment of the spontaneous polarization and poling field. (b) Piezoresponse measured along the horizontal line indicated in (a). (c) Local hysteresis loops measured under an applied force $F_0 = 0.04$ and 1.9 μN on a 4-μ-m thick barium titanate thin film. The solid lines correspond to increasing voltage and the dashed lines correspond to decreasing voltage. The curves shown are averages of three loops of 100 voltage pulses of 1 s duration each. Under high mechanical load the response switches sign again (arrow), resulting in the domain pattern shown in (a).

magnitude of the pulses is varied while the duration and the force F_0 are constant. After each pulse the inverse piezoelectric response is measured by probing the surface deformation caused by a small ac voltage. The measured piezoelectric coefficient d_{eff} is plotted as a function of the voltage of the last applied pulse. This results in curves showing the remanent inverse piezoelectric response of the sample after poling [16–19]. As the sign of the measured d_{eff} corresponds to the direction of spontaneous polarization, successful switching can be detected.

For low applied forces F_0 the obtained loops show a saturation for high fields as seen in Fig. 1(c). At high forces, however, the loops show a different shape: the inverse piezoelectric response, and with it the spontaneous polarization below the tip, is oriented antiparallel to the formerly applied electric field at high voltages. This corresponds to the black spot seen in Fig. 1(a). Similar loops have been found in $Bi_4Ti_3O_{12}$ recently [19]. In PZT thin films a decrease in signal but no change in sign has been reported [18].

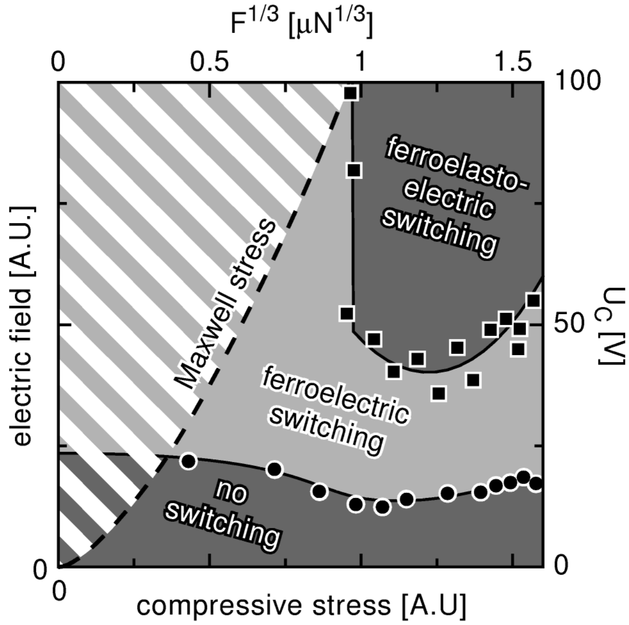

FIG. 2. Dependence of the coercive voltage (points) and the critical voltage U_C at which the piezoelectric response d_{eff} is maximal (squares) is shown as a function of the third root of the total force present during domain formation. These experimental points separate areas of different switching mechanisms. The applied electric field results in the indicated Maxwell stress. The dashed area to the left was not accessible during our experiments because we had no means to compensate for the Maxwell stress.

From the loops the "critical voltage" U_C, above which the polarization is aligned antiparallel to the field, can be deduced for different forces F_0. We defined U_C as the voltage above which the response decreases again. The decrease is interpreted as being due to the occurrence of a domain with opposite polarization.

The experimental results cannot be compared directly with Eqs. (2) or (3), since the critical stress and electric field are not known. However, the force F_0 and the voltage U_C are known.

The electric field is roughly proportional to the voltage U_C. For the stress the situation is more complicated, as the total force F applied by the tip is increased by the electrostatic attraction between the electrode and the tip (Maxwell force):

$$F = F_0 + \underbrace{\frac{1}{2}\frac{dC}{dz}U_c^2}_{\text{Maxwell force}} . \tag{4}$$

The change in capacitance dC/dz of the tip-sample system can be determined from tear-off experiments [17,18]. Assuming a Hertzian contact [20], the contact area A between tip and sample will vary as $F^{2/3}$. Thus the stress is proportional to $F/A \propto F^{1/3}$. Using Eq. (4) and the determined F_0 and U_C allows one to derive a quantity proportional to the total compressive stress.

In Fig. 2 the critical voltage is shown as a function of this quantity (squares). For low stresses we find $F^{1/3}$ and thus the critical stress to be independent of the critical voltage (and therefore electric field) as predicted by Eq. (3) (vertical line).

The total force required for an antiparallel alignment of the polarization is found to be 0.9 μN. In order to correspond to the theoretically found value of the critical stress given by Eq. (3) of about -3×10^9 N/m^2, the radius of the contact area would have to be 10 nm. The real contact radius for these forces is larger, about 50–100 nm. A better correspondence cannot be expected taking into account the crude simplifications for deducing Eq. (3), namely, the homogeneous electric field and homogeneous uniaxial stress. Also the geometry of the tip and its contact with the sample are strongly idealized.

An approximately parabolic dependence is obtained for high stresses (Fig. 2). A minimum is found at about 2 μN. The approach presented here is not able to explain such behavior. The inhomogeneous distribution of electric field and stress should be taken into account. It has to be mentioned that the resulting domain structure—bright ring with dark center—is stable for at least one month.

Let us consider the situation where initially a negatively poled domain is located below the tip. For small applied positive electric fields no switching is observed (left-hand side of Fig. 2); the spontaneous polarization remains antiparallel to the poling field. Ferroelectric switching is observed only for fields exceeding the coercive field, resulting in the parallel alignment of the spontaneous polarization and poling field. The coercive field can be defined as the field at which the piezoresponse in the loops shown in Fig. 1(c) vanishes for the first time on increasing voltage. These fields, shown as points in Fig. 2, are found more or less independent of the compressive stress. At even higher fields—as discussed above—ferroelastoelectric switching is found, resulting in an antiparallel alignment of the spontaneous polarization and poling field. Ferroelastoelectric switching was observed above the squares shown in Fig. 2.

Note that, due to the electrostatic attraction of the tip and the conductive substrate (counterelectrode), the indicated Maxwell stress is present during poling. This implies that for high fields no additional stress has to be applied to obtain ferroelastoelectric switching. If this interpretation is correct, then the generally expected ferroelectric switching is only obtained for a range of voltages for certain electrode configurations (large dC/dz). Below a lower limit no switching will take place, while above an upper limit again no change of the spontaneous polarization would be expected. As, in general, faster switching is obtained for higher voltages, this would also set a limit to the speed of ferroelectric devices.

We have reported ferroelastoelectric switching in a ferroic material, where lower order effects are allowed by symmetry. It must be stressed that the properties of barium titanate are adequate for the observation of ferroelastoelectric switching since the spontaneous polarization is positive for the positive piezoelectric coefficient d_{33}. This is the necessary condition for inducing the observed alignment of spontaneous polarization against applied field. A similar situation can be expected in other ferroelectric perovskites (lead titanate and potassium niobate in particular).

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