4. Piezoresponse-SFM for local electromechanical probing of ferroelectric thin films

The aim of this chapter is to analyze the possibilities of using the method of piezoresponse SFM not only to image the domain structure, as it was used up to now, but also to locally characterize the ferroelectric properties with a resolution of several nanometers. This expansion consists in describing some techniques that may be used to obtain *quantitative* information on the physical quantities involved in piezoelectric probing.

First of all, it is very important to establish the origin of the demodulated signals, especially the first harmonic component. With other words, it is important to know whether and how it is possible to probe the true electromechanical properties of ferroelectric samples. The next section ascertains that the first harmonic signal in the experiments presented in this work reflects the sample surface movements and not the electrostatic interaction between the tip and the electric field at the sample surface.

4.1 Analysis of the first harmonic signal in voltage modulated SFM

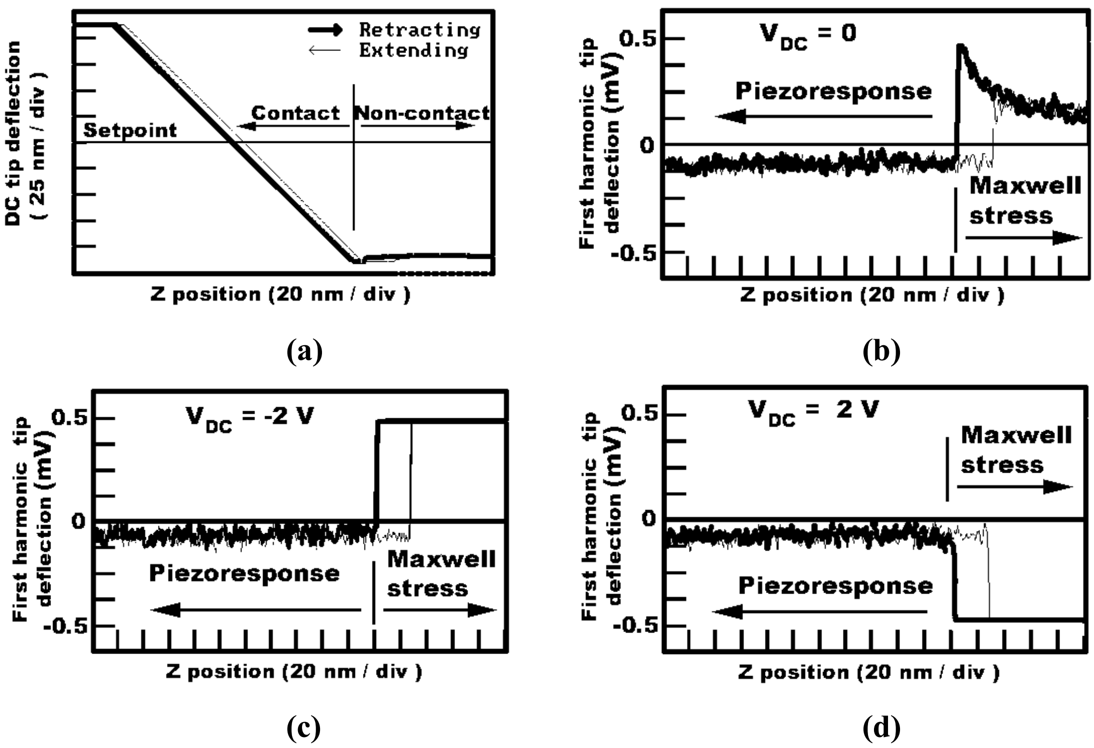
As has been shown in the sections 3.2.3 and 3.2.4, there are two types of forces governing the tip movement above the ferroelectric sample [85,48], namely the repulsive contact force and the electrostatic force.

The piezoelectric displacements of the sample surface are given in Eq. 12 (Sect. 3.2.3) and the first harmonic of the Maxwell stress force in Eq. 20 (Sect. 3.2.4). Both of these forces act simultaneously on the tip when operated in contact mode, therefore the first harmonic of the tip deflection is the superposition of their effects. Whether the tip movement is governed by the electrostatic interaction or by the surface displacements can be determined from the phase of the first harmonic, as it will be shown in the following.

The AC voltage was always applied to the SFM tip so that the phase shifts correspond to those calculated previously. To assure a proper ground of all the equipment in the setup, the DC voltages were applied to the bottom electrode (exactly as shown in Figure 10, Sect. 3.3), and not to the tip. However, the position of the DC source does not change the phase signal measured. For a region (ferroelectric domain) with polarization oriented downward (top-to-bottom) and an AC voltage applied to the tip, during the positive half-periods (electric field in the film directed downward, thus parallel to the polarization), the piezoelectric deformation is an extension, and the surface will move upward. Therefore, the piezoelectric signal is *in phase* with the applied AC voltage. At the same time, the first harmonic of the Maxwell stress (see F_ω in Eq. 20, Sect. 3.2.4, with α always positive) and the AC voltage are *out of phase*.

The above considerations lead to the conclusion that if the electrostatic interaction causes the cantilever deflection, *the tip does not follow the vertical displacements of the sample surface*, but oscillates out of phase with the induced piezoelectric deformations! Whether the tip vibrates in phase (therefore in permanent contact) with the ferroelectric surface or oscillates out of phase depends on the balance of the contact and electrostatic forces. The experiments presented in this work were performed using stiff cantilevers with high spring constants of $k = 40\ N/m$, which imply contact forces in the range from $2\ \mu N$ up to $10\,\mu N$. The Maxwell stress force F_ω estimated from Eq. 20 using $S = \pi\,(20\,nm)^2$, $t = 200\,nm$, $h = 1\,nm$, $\varepsilon_f = 200\,\varepsilon_0$, $\varepsilon_i = 2\,\varepsilon_0$, $V_{AC} = 2\,V$ and $P = 20\,\mu C/cm^2$ is found to be $0.12\,\mu N$, and therefore is about ten times smaller than the usual repulsive contact force.

The above estimation, however, needs to be validated experimentally. To demonstrate that in this work the first harmonic signal reflects the piezoelectric effect, the following experiment was performed: The SFM tip was positioned above a certain region of the sample surface, showing an in-phase oscillation of the first harmonic deflection with respect to the AC voltage applied. Therefore the polarization of the respective region was oriented downward. For practical reasons, the phase offset was always set to 180°, so that the piezoresponse signal from positive domains is positive. Above this point, the SFM tip was then scanned in the z-direction, using the force curve measurement procedure of the SFM controller. The DC deflection and the first harmonic component of the cantilever deflection were recorded at three values of the bias voltage: $V_{DC} = 0$, $V_{DC} = 2V$ and $V_{DC} = -2V$. The local coercive field of the ferroelectric sample probed in this experiment was $V_{coer} = 8V$, therefore the bias did not switch the ferroelectric domain ($V_{AC} = 2V$). The results are shown in Figure 14 as deflection versus z-scanner position plots.



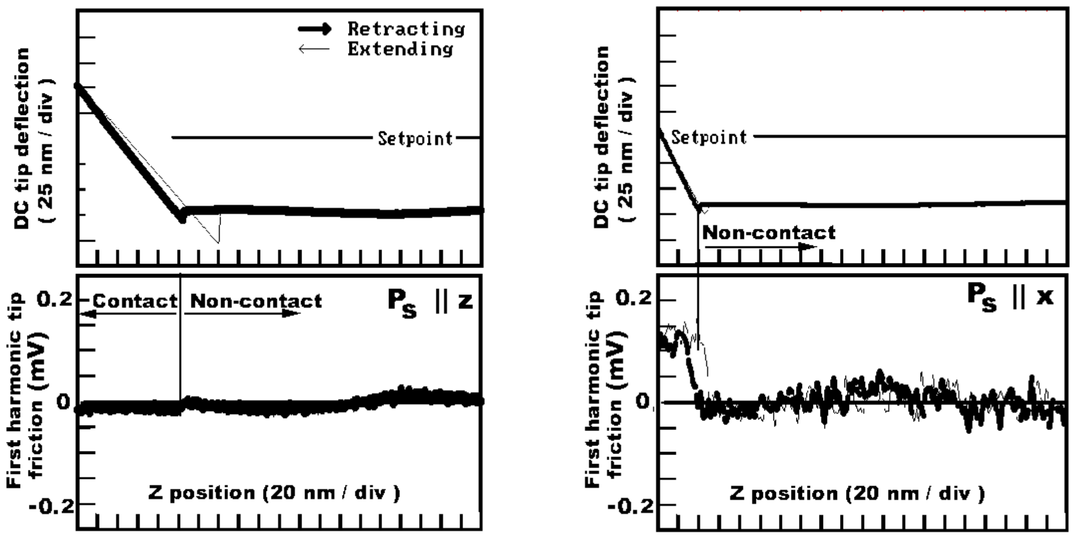
(a) (b) (c) (d)

Figure 14 Deflection versus z-scanner position above a negative ferroelectric domain (polarization downward) in a $BaTiO_3$ single crystal: **(a)** DC component (force curve). **(b,c,d)** First harmonic component at different V_{DC}: **(b)** $V_{DC} = 0$, above the surface (non-contact) the signal is 180° phase shifted with respect to the signal when the tip is in contact with the surface. **(c)** $V_{DC} = -2V$, and **(d)** $V_{DC} = 2V$. *The first harmonic signal in contact mode is not influenced by the DC bias.* These measurements prove the piezoelectric nature of the first harmonic signal in contact mode.

The DC component of the deflection was not influenced, within the experimental errors, by the DC voltage, and the plot in Figure 14a represents a usual force curve (compare with Figure 3 in Sect. 3.1.1). Above the sample surface, in non-contact, only the electrostatic interaction is present in the first harmonic signal. For $V_{DC} = 0$ the phase shift changes from 0° to 180° (Figure 14c, the first harmonic changes from positive to negative) as the tip approaches the surface and is pushed into it, *in complete agreement with the expected phase shifts* of the two signals for a negative domain (see Eq. 12 in Sect. 3.2.3 and Eq. 20 in Sect. 3.2.4).

Moreover, as can be seen in Figure 14c-d, the bias voltage has a strong influence on the first harmonic, in agreement with the strong dependence of F_{ω} on V_{DC} in Eq. 20*. In contrast, in the contact region of the curves, the first harmonic signal is independent of the bias voltage (with the restriction that it is lower than the coercive voltage, of course). This is an incontestable proof that the electrostatic interaction has no visible influence on the signal and the tip truly follows the surface vibrations when operated in contact mode.

The cantilever torsion and therefore the lateral deflection signal could, in principle, also be influenced by an electrostatic interaction [55]. Figure 15 proves that the x-deflection signal is non-zero *only* when the tip is in contact with the surface and the polarization is in the film plane.



(a) **(b)**

Figure 15 First harmonic component of the x-deflection signal (lower plots) versus z-position of the scanner: **(a)** above a domain with polarization perpendicular, and **(b)** above a domain with polarization parallel to the sample surface ($BaTiO_3$ single crystal). The upper plots show the tip-to-sample contact position. Above the sample, in the non-contact region, the x-deflection signal is always zero.

In conclusion, when the tip is in contact with the surface, *only the piezoelectric effect* is responsible for the first harmonic of both the in- and out-of-plane cantilever deflections.

* Because the DC bias is applied to the bottom electrode, the sign of V_{DC} in Eq. 20 has to be changed from positive to negative.

4.2 Imaging of the ferroelectric domain structure

As it was demonstrated in the previous section (4.1) the first harmonic component of both deflection signals (corresponding to the vertical and lateral movements) indeed represents the induced piezoelectric vibrations of the ferroelectric sample. Therefore, the first harmonic signals recorded above a given point of the surface describe the two components of polarization perpendicular to the cantilever axis at that point.

To obtain the distribution of ferroelectric domains at the surface of a sample using SFM it is necessary to associate the position of the SFM tip to the signal containing information about the ferroelectric state. This can be most easily achieved using one of the built-in input channels of the SFM system. Alternatively, the same task can be fulfilled using a second computer to collect and store the (x, y) position from the SFM scanner, and the piezoresponse signal (i.e. domain information). The image of the domains is usually visualized by associating different colors to different levels of the signal.

Out-of-plane domains

Monitoring the first harmonic of the z-deflection signal while scanning the surface results in an image of the effective longitudinal piezoelectric coefficient d_{zz}. Using Eq. 12 and Eq. 14 (Sect. 3.2.3), the relationship between the measured signal v^z_ω and d_{zz} is given by Eq. 22:

$$v^z_\omega = \delta d_{zz} V_{AC} \qquad \text{Eq. 22}$$

where δ, the sensitivity of the optical detector, is in fact the conversion factor between the mechanical displacement of the SFM tip and the electric deflection signal.

An information about the polarization state is obtained from the linear relation between the piezoelectric coefficient and the spontaneous polarization. It is well known that for ferroelectric materials having a tetragonal symmetry (point group 4mm) and with a centrosymmetric paraelectric phase the piezoelectric effect can be considered as the electrostriction effect biased by the spontaneous polarization $\boldsymbol{P_S}$ as shown in Sect. 2.2 (Eq. 10a). If the region being probed is not *c*-oriented ($\boldsymbol{P_S}$ is not normal to the film plane), an effective piezoelectric coefficient has to be considered. As shown in Appendix B, magnitude and sign of the piezoelectric coefficient along a certain direction (denoted d_{zz}) is related (but not directly or simply related) to the angle between the spontaneous polarization and the normal to the film surface. Therefore, the distribution of d_{zz} represents in fact a more or less faithful* image of the out-of-plane polarization distribution at the sample surface, at least for the materials that belong to the 4mm point group symmetry.

In-plane domains

The first harmonic of the lateral deflection signal being proportional to the shear piezoelectric coefficient (see Eq. 16), the above considerations hold for the in-plane domains, too. As it was deduced thermodynamically for the same tetragonal symmetry in Sect. 2.2, the shear piezoelectric coefficient d_{15} is given in Eq. 10b for the case of the cantilever axis

* depending on the balance between d_{33}, d_{31}, and d_{15} in Eq. A 7 (Appendix B).

perpendicular to the spontaneous polarization, which is parallel to the film plane (geometry shown in Figure 6, Sect. 3.2.3). In the general case where the spontaneous polarization is oriented in the film plane along an arbitrary direction relative to the cantilever (see the *xyz* system of coordinates in Figure 6), an effective shear coefficient d_{xxz} is detected. Magnitude and sign of d_{xxz} depend on the angle between the *x*-axis and the spontaneous polarization [86].

Therefore, the in-plane domains can be visualized in the same manner as the out-of-plane domains, a mapping of d_{xxz} being a more or less distorted image of the in-plane polarization. However, special care has to be taken when interpreting the in-plane domains if the scan direction is not along one of the principal crystallographic directions, due to the complex nature of the friction-induced cantilever vibrations.

4.3 Local measurements

The usual macroscopic techniques used for the measurement of the electromechanical properties [7,87,88] cannot be applied in the case of SFM, due to the fact that the geometry of the region being measured is depending on its position. In this case, the SFM conductive tip represents in fact a nanometer-sized movable top electrode used for probing the sample surface by applying an AC voltage. This top electrode can be fixed over any desired place of the sample surface, in order to explore only that area. Taking into account that the sample is tested by detecting the induced mechanical oscillations, several procedures can be used to measure the local properties.

4.3.1 Local piezoelectric coefficient

The local piezoelectric coefficient can be determined with a high accuracy by sweeping the amplitude of the testing AC voltage from zero up to the local coercive voltage of the sample. The piezoelectric constant can be easily calculated from the slope of the linear dependence expressed in Eq. 22 (Sect. 4.2). In the case of ferroelectrics, as soon as the AC amplitude is higher than the local coercive voltage, the polarization starts to switch with the same frequency as the AC voltage, leading to a decrease of the first harmonic response.

4.3.2 Stress dependence of piezoelectric coefficient

The influence of the mechanical stress on the longitudinal piezoelectric coefficient can be studied by varying the contact force between the tip and the sample while recording the piezoresponse signal. Since the stress applied strongly depends on the real contact area, which is very difficult to estimate, the contact force dependence is used instead. The range of contact forces that can be used depends on the elastic constant of the cantilever.

In general, the piezoelectric coefficient decreases when the stress (or the contact force) increases*.

* In the thermodynamic treatment of ferroelectricity, an increase of the stress X is equivalent to an increase of the temperature T (Eq. 2, Sect. 2.1), therefore the ferroelectric is closer to its paraelectric phase and has a smaller spontaneous polarization (and implicitly also a smaller piezoelectric coefficient).

4.3.3 Hysteresis loops

The most important characterization and also a proof of ferroelectricity is the presence of a piezoelectric *hysteresis*. This measurement is generally performed using a DC bias source connected in series with the AC voltage source. The hysteresis loops are obtained by sweeping the bias voltage and recording the piezoresponse signal. There are two main procedures that may be used:

1. In-field hysteresis. In the first procedure, the probing AC voltage is superimposed on the DC bias which is varied in steps from zero to V_{max}, then decreased down to V_{min} and increased again up to V_{max}, in order to measure the piezoelectric coefficient as a function of the DC field applied *simultaneously*. Each step of the bias has a duration t_{bias} (Figure 16a). The loop obtained in this manner is further referred to as *in-field* hysteresis loop and represents a normal *d - E* curve [89], as it is often used for the characterization of the macroscopic piezoelectric properties of thin films.

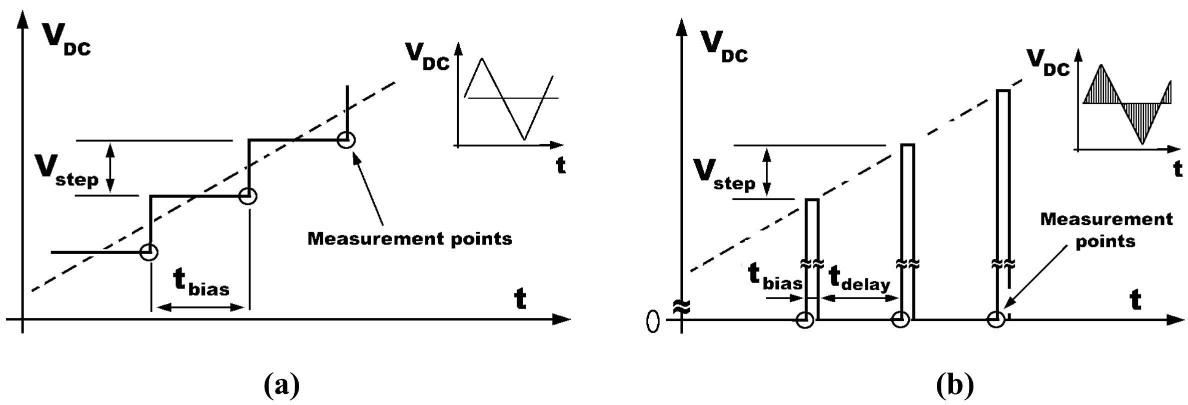


Figure 16 The waveform of V_{DC} in hysteresis loop measurements: **(a)** for the in-field loops, and **(b)** for remanent loops

2. Remanent hysteresis. In the second procedure, the DC bias voltages are in fact pulses with a duration t_{bias} and an interval of time t_{delay} between them. The piezoresponse signal is recorded and stored just before the application of the next polarizing pulse (Figure 16b) [49,90]. The amplitudes of the pulses are varied in steps in the same way as in the first procedure. Using this measuring method, the electrostatic interactions between tip-cantilever and the bottom electrode are avoided during the measurement and only the *remanent* piezoelectric coefficient is measured as a function of the DC voltage pulse *previously* applied to the sample. The loop obtained accordingly is further referred to as *remanent* hysteresis loop. This kind of measurement reveals the retention characteristics of ferroelectric thin films.

Whereas the remanent loop is saturated for high values of the poling voltage, the in-field loop contains a linear part. The linear part can be used to estimate the electrostriction coefficient of the material, as shown in the next section.

It should be mentioned that rather recently the remanent hysteresis loop procedure was applied to macroscopic measurements, too [91]. Its main scope was to minimize leak charges and therefore to obtain more realistic polarization data even in very leaky ferroelectric samples.

4.3.4 Estimation of the electrostriction coefficient

The electrostrictive effect is present in all materials, regardless of the symmetry and is an example of nonlinear coupling between elastic and electrical fields. Generally, if an electric field E_i is applied to a material, the electrostrictive strain S_{ij} is defined by:

$$x_{ij} = M_{ijkl} E_k E_l \qquad \textit{Eq. 23}$$

The electrostrictive effect can also be expressed in terms of the induced polarization:

$$x_{ij} = Q_{ijkl} P_k P_l \qquad \textit{Eq. 24}$$

where the polarization-related electrostrictive coefficients Q_{ijkl} are given by:

$$M_{ijpq} = \chi_{ip} \chi_{lq} Q_{ijkl} \qquad \textit{Eq. 25}$$

In the case of ferroelectric materials, however, Eq. 23 and Eq. 24 are not simultaneously valid, due to the strong nonlinear dependence of the susceptibility tensor χ_{ij} on the electric fields. Experimental data have shown that the polarization-related electrostrictive coefficients Q_{ijkl} are, within the experimental errors, independent on temperature [92] and electric field [93,94]. For this reason they are mostly used for the description of the electromechanical properties of ferroelectric materials, though they were found to depend on the number of polarization switches in some cases [95].

For a single-crystal ferroelectric in the monodomain state, Eq. 10a (Sect. 2.2) between the electric-field-induced strain along the z-axis x_{33} and the spontaneous polarization P_S is extended to include the effect of an applied electric field as follows [96,97]:

$$x_{33} = \varepsilon_{33} Q_{33} (2P_S + \varepsilon_{33} E_3) E_3 \qquad \textit{Eq. 26}$$

The first term represents the linear, piezoelectric strain with respect to the external electric field E_3. The second term is the pure electrostriction component of the strain. In Eq. 26 the electrostriction coefficient is written using the matrix notation.

The experimental setup used for piezoelectric measurements with a SFM allows the application of an AC signal biased by a DC voltage, and the detection of a certain harmonic (usually the first) of the mechanical response of the sample. Next, these experimental aspects will be taken into account to demonstrate a possibility for the estimation of the electrostriction coefficient. If we replace in Eq. 26 the electric field as shown in Eq. 27:

$$E_3 = E_{DC} + E_{AC} \sin(\omega t) \qquad \textit{Eq. 27}$$

the total strain induced can be written as:

$$x_{33} = x_0 + x_\omega \sin(\omega t) + x_{2\omega} \sin\left(2\omega t - \frac{\pi}{2}\right), \text{ where} \qquad \textit{Eq. 28}$$

$$\begin{cases} x_0 = \varepsilon_{33} Q_{33} (2P_S + \varepsilon_{33} E_{DC}) E_{DC} + \frac{1}{2} \varepsilon_{33}^2 Q_{33} E_{AC}^2 \\ x_\omega = 2\varepsilon_{33} Q_{33} (P_S + \varepsilon_{33} E_{DC}) E_{AC} \\ x_{2\omega} = \frac{1}{2} \varepsilon_{33}^2 Q_{33} E_{AC}^2 \end{cases} \qquad \textit{Eq. 29}$$

The longitudinal piezoelectric coefficient can be obtained as the amplitude of the first harmonic of the strain divided by the amplitude of the driving AC electric field:

$$d_{33} = \frac{x_{\omega}}{E_{AC}} = 2\varepsilon_{33}Q_{33}(P_S + \varepsilon_{33}E_{DC}) \qquad \textit{Eq. 30}$$

In Eq. 30 it can be seen that, for a constant ferroelectric polarization P_S, the dependence of the piezoelectric coefficient on the DC electric field is linear. On a *d(E)* in-field hysteresis curve, the slope of this linear component can be obtained by differentiating Eq. 30 with respect to E_{DC}, for those regions of the hysteresis loop, for which the ferroelectric polarization is not switching (at saturation).

$$\frac{\partial d_{33}}{\partial E_{DC}} = 2Q_{33}\varepsilon_{33}{}^{2} \qquad \textit{Eq. 31}$$

The electrostriction coefficient can be estimated from the slope of the saturated regions of the in-field piezoelectric hysteresis loops provided the permittivity is known from other measurements. In principle, the electrostriction coefficient could be estimated from the second harmonic, too, if the noise level is low enough. The strain to be measured is proportional to the product $E_{DC}E_{AC}$ if the first harmonic is used, whereas it is proportional to $E_{AC}{}^2$ if the second harmonic is detected. The problems that arise are, first, that the AC voltage has to be smaller than the coercive voltage (to prevent switching), and second, that a higher AC voltage may produce breakdown in the film. In contrast, using a high DC voltage avoids these problems.