Contact resonances in voltage-modulated force microscopy

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A study of the frequency dependence of the signal in piezoresponse scanning force microscopy of ferroelectric materials has been performed. It is found that, for soft cantilevers, the signal is governed by the cantilever elastic properties. Both ferroelectric-electromechanical and electrostatic interaction contributions to the overall signal were found to depend on the frequency of the testing voltage. Indications for optimal measurement regimes are given. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1592307]

Piezoresponse scanning force microscopy (PFM) is now a standard method for the study of ferroelectric phenomena.[1] A small oscillating testing voltage is applied between the conductive tip of a scanning probe microscope and the bottom electrode of a ferroelectric sample. This ac voltage induces mechanical oscillations of the cantilever, which are then retrieved from the global deflection of the cantilever using a lock-in technique. The scenario initially proposed was that the surface of the ferroelectric sample is oscillating due to the converse piezoelectric effect (CPE), and that these oscillations are transmitted to the cantilever.[2,3] Meanwhile it was shown that the electrostatic (ES) interaction between the tip/cantilever and the bottom electrode of the sample may play a significant role in the formation of the PFM contrast.[4–6] Hong *et al.* even neglected the influence of the CPE on the cantilever vibration, and used the term "dynamic-contact electrostatic force microscopy" (DC–EFM)[7,8] for the same technique (same experimental setup). Recently, the contrast in PFM was thoroughly analyzed and the limits for different contrast mechanisms were defined.[9] Given the earlier findings, we use in the following the more general term contact-voltage modulated force microscopy (c-VMFM) instead of PFM or DC–EFM.

Labardi *et al.*[10] provided a first report concerning the frequency dependence of the c-VMFM signal from TGS single crystals. However, they did not discriminate between the CPE and ES contributions. In this letter we will show that the properties of the cantilever strongly influence the VMFM measurements. The spring constant of the cantilever does not only control the (static) force applied to the sample, but also its own dynamical properties. In turn, the latter influence the magnitude and the phase of the VMFM signal. In order to study this influence we performed an analysis of the frequency dependence of the c-VMFM signal. We show that both CPE and ES interaction have frequency-dependent contributions to the c-VMFM signal, and that they can be separated by local hysteresis measurements.

The experimental setup is similar to that used in Refs. 1–11. A commercial scanning probe microscope (Autoprobe CP Research, Thermomicroscopes) working in contact mode and a lock-in amplifier (EG&G Instruments, model 7260) were employed to measure the vibrations of the cantilever. The mechanical oscillations were induced by applying a small ac voltage between the tip (Micromash, CSC12- and CSC11-series coated with W_2C) and the bottom electrode of the sample. The ac amplitudes applied ranged from 50 mV up to 1 V, in order to keep the cantilever vibration within 3% of the static deflection. The ac voltage applied did not result in a change of the ferroelectric domain structure in our experiments. The spring constants of the cantilevers ranged from $k=0.02$ N/m up to $k=0.5$ N/m corresponding to first free resonance frequencies ($f_{1\omega}^{nc}$) of 9 up to 32 kHz. Hysteresis loop measurements were performed using a computer-controlled Keithley 2400 source meter in series with the ac source. The frequency of the triangular wave was 5 mHz. The samples used for investigations were chemical solution deposited lead zirconate titanate films, 100 nm thick, incompletely crystallized, showing rosette-type ferroelectric islands (1–2 μm in lateral size) surrounded by a pyrochlore phase. These samples were chosen because they permitted a comparison, on the same sample, of the induced cantilever vibrations for a contact of the tip with ferroelectric and nonferroelectric materials, respectively, preserving exactly the same ES interaction between the cantilever and the platinum bottom electrode.

The cantilever is the most important element of an atomic force microscope (AFM). Its role is twofold: (a) carrying the tip, it controls the interaction between tip and surface and (b) it provides information to the system about the tip displacement. Most commercial AFMs use an optical beam to detect the cantilever bending which is directly related to the force exerted on the tip and the tip displacement. In this work we refer only to this type of detection. This method works quite well in the quasistatic regime (vibrations below 1 kHz) such as in the usual topography imaging contact mode. Being an elastic beam, the cantilever has its own resonance frequencies corresponding to different vibration modes. The cantilever vibrations are governed by the boundary conditions (forces acting on the cantilever) and they have to be taken into account in the detection process. This is especially important when the cantilever is driven into oscillation at or near one of its resonance frequencies, when the vibration is most sensitive to changes in boundary condi-

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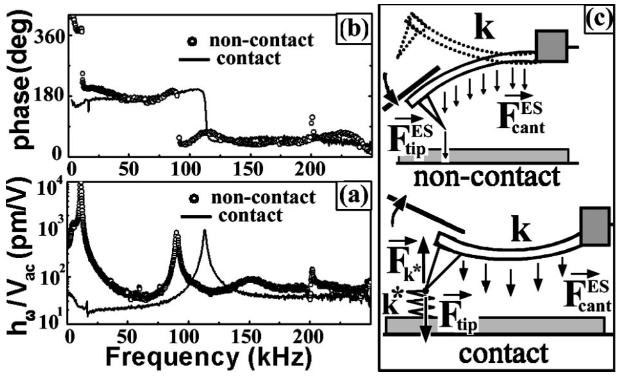

FIG. 1. Amplitude (a) and phase (b) of the oscillation of a soft cantilever (CSC12d, $k=0.03$) when excited electrostatically in noncontact (⦿) and in contact (—) with a nonferroelectric surface. The absolute amplitude h_ω is divided by the amplitude of the ac driving voltage. (c) Bending of the cantilever when it vibrates near $f^{nc}_{1\omega}$ and $f^{c}_{1\omega}$ in noncontact and contact with a sample surface, respectively.

tions, and this fact is already exploited in noncontact-VMFM (EFM and Kelvin force microscopy).

Figure 1 compares the frequency dependence of the noncontact-VMFM signal with the *c*-VMFM signal. The spectra were obtained while keeping the cantilever fixed above (⦿) and in contact with (—) the pyrochlore region of the sample surface, and are typical for all cantilevers measured in this work. The vibration modes (and therefore the resonance frequencies) of a cantilever are different in contact and in the noncontact case,[12] as sketched in Fig. 1(c) for the first flexural modes. It has been calculated that the n^{th} contact resonance ($f^{c}_{n\omega}$) lies between $f^{nc}_{n\omega}$ and $f^{nc}_{(n+1)\omega}$ of the free cantilever (cantilever fixed only at one end).[12] The reason why in our experiments $f^{c}_{1\omega}$ is higher than $f^{nc}_{2\omega}$ is the fact that in contrast to Ref. 12, the forces driving the cantilever into oscillation in VMFM of nonferroelectric surfaces are electrostatic, acting on both tip and cantilever. The force acting on the cantilever is distributed along its length and this significantly changes the induced deflection. Assuming a planar geometry the first harmonic of the ES force has the form $F_\omega=-\alpha(V_{\text{dc}}\text{-CPD})V_{\text{ac}}\sin(\omega t)$, where $\alpha=(1/2)\partial C/\partial z<0$ is the derivative of the system capacitance with respect to the coordinate z normal to the surface, V_{dc} and V_{ac} are the dc and the amplitude of the ac component of the applied voltage, and the contact potential difference (CPD) was typically -0.5 V in our experiments. The response of the cantilever to this excitation force is supposed to be $h_\omega=F_\omega/k$, where k is the equivalent spring constant of the cantilever.[6] As this formula has a static origin, it can only be valid at low frequencies. The frequency dependence of the cantilever response A_ω to an ac excitation may be empirically described near a resonance by the formulas $A_\omega=A_0[(\omega_0^2-\omega^2)^2+(\gamma\omega)^2]^{-1/2}$ and $\tan\varphi=\gamma\omega/(\omega^2-\omega_0^2)$. Here, A_0 is the amplitude of oscillation at the resonance $f_0=\omega_0/2\pi$, γ is a damping coefficient, and ω is the driving angular frequency. This means that the phase of the cantilever oscillation for $\omega<\omega_0$ is shifted 180° compared to the phase at $\omega>\omega_0$. This 180° phase shift can be clearly seen in Fig. 1(b) for both contact and noncontact cases. This leads to the conclusion that the amplitude $h_\omega=\beta_\omega F_\omega/k$ and the phase φ_ω of the electrostatically induced cantilever deflection have a complex dependence on frequency. Near resonances, β_ω and φ_ω

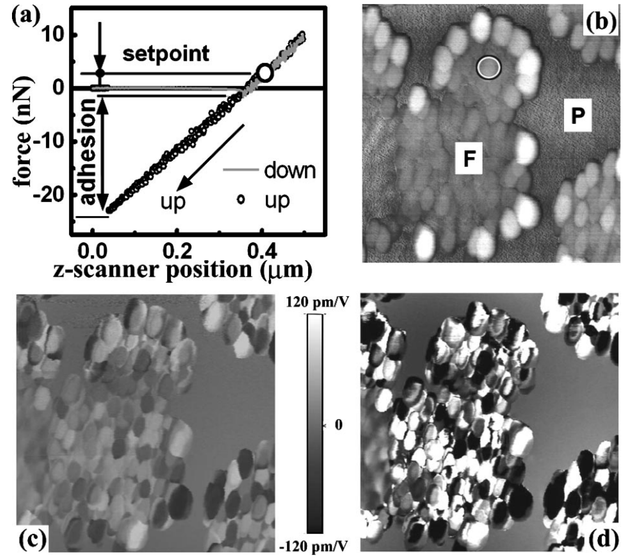

FIG. 2. (a) Typical force vs separation curve. Note the huge adhesion force (~20 nN) compared to the setpoint force (2 nN). (b) Topography image of a $3\times3\ \mu\text{m}^2$ area of an incompletely crystallized ferroelectric thin film (*F*—ferroelectric, *P*—pyrochlore, *z* range=40 nm). (c) and (d) *c*-VMFM images of the same area taken using an ac testing signal with $f=5.6$ kHz (c) and $f=145.6$ kHz (d). Images (c) and (d) have the same color bar.

have the form of A_ω and ϕ. The phase φ_ω of the oscillation is especially important in VMFM, because it provides information on the sign of the CPD, surface charge, or polarization. Below any resonance, it can be noted that the cantilever oscillations in contact and in noncontact mode have a phase difference of 180°. This is caused by the different boundary conditions and by the fact that the local angular deflection and not the tip position of the cantilever is detected [Fig. 1(c)]. The 180° phase change of the cantilever oscillation at the resonance frequency means that the slope of the bias dependence $\eta_\omega=\partial h_\omega/\partial V_{\text{dc}}$ changes its sign when passing through resonance.

If a Hertzian contact is assumed, the contact stiffness is $k^*=\sqrt[3]{6E^{*2}RF_0}$,[9,12–14] where E^* is the reduced Young modulus of the tip-to-sample contact, R is the radius of the tip apex, and F_0 is the static (indentation) force. This implies that increasing F_0 leads to an increase of k^*, i.e., a shift of $f^{c}_{1\omega}$. In the point mass model, an increase of F_0 by a factor of 2 should result in an increase of $f^{c}_{1\omega}$ by roughly 12% (neglecting the increase of R). However, we did not detect any noticeable shift of $f^{c}_{1\omega}$ with increasing F_0 up to a factor 3. The reason for this behavior can be found in Fig. 2(a), showing a force spectroscopy measurement. From this calibration curve it is clearly seen that the contact force (the "setpoint" value) is ten times smaller than the adhesion force between tip and sample surface (2 nN compared to 23 nN). This means the static force between cantilever and sample is essentially the adhesion force[14] when soft cantilevers are used under ambient atmosphere. Unfortunately, cantilevers capable of higher loading forces have $f^{c}_{1\omega}$ above the upper frequency limit of our experimental setup.

Recording the sample topography and the *c*-VMFM signal for different ac testing frequencies revealed an enhancement of the VMFM contrast near $f^{c}_{n\omega}$. Figure 2(b) shows the sample topography with a flat (nonferroelectric) background ("*P*") and clusters ("rosettes") of ferroelectric grains about 200 nm in lateral size ("*F*"). Figures 2(c) and 2(d), repre-

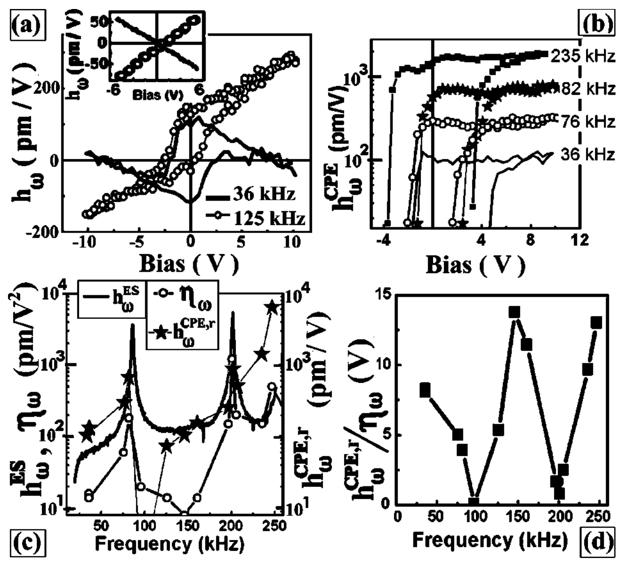

FIG. 3. (a) Hysteresis loops recorded below (—) and above (-○-) the first contact resonance of a CSC12f cantilever. The inset shows the same measurements performed in contact with a non-ferroelectric region. (b) Bias dependence of h_ω^{CPE} at different testing frequencies (ferroelectric hysteresis loops, linear part subtracted). (c) Comparison between the frequency dependence of the cantilever vibration in contact with a pyrochlore region (—) and a ferroelectric grain (-○-,-★-). (d) Frequency dependence of the ratio between the ferroelectric and electrostatic contributions. Measurements above ferroelectric regions were obtained from hysteresis measurements.

sented at the same color scale, show the c-VMFM signal from the same area of the sample, obtained with an ac signal at 5.57 kHz (far below $f_{1\omega}^c$) and 145.6 kHz (near $f_{1\omega}^c$ of this cantilever), respectively. Both images reveal the same ferroelectric domain structure, suggesting that the probed volume of the sample does not depend on the testing frequency. In order to clarify the nature of the contributions to the c-VMFM signal above the ferroelectric surface, we recorded several in-field hysteresis loops[11] from a selected grain [indicated by a circle in Fig. 2(b)]. Figure 3 exemplifies the different contributions to the c-VMFM signal. Figure 3(a) establishes that for soft cantilevers (in this experiment $k = 0.023$ N/m) the linear part of the hysteresis loop is in fact the ES contribution. The two hysteresis loops were obtained using testing ac frequencies below (36 kHz) and above (125 kHz) $f_{1\omega}^c = 84$ kHz. As discussed previously, the 180° shift of φ_ω at $f_{1\omega}^c$ is seen in the c-VMFM signal as a change in the sign of the linear slope of the V_{dc} dependence. The inset in Fig. 3(a) shows the same "hysteresis" measurement in contact with the pyrochlore region. In contrast to the inset, the "sign" of the CPE contribution does not change. The total response can be decomposed in $h_\omega/V_{ac} = h_\omega^{CPE} + \eta_\omega \cdot dc$, where $dc = (V_{dc} - CPD)$, and the superscript "CPE" stands for the ferroelectric contribution. The strong frequency dependence of the CPE contribution (ES part subtracted) shown in Fig. 3(b), is a clear evidence that the modulation amplitude of the cantilever vibration induced by the ferroelectric domains strongly depends on the driving frequency, and therefore a comparison between measurements performed with different cantilevers is principally not possible.

A comparison between the CPE and ES contributions to the cantilever vibration over the frequency range accessible is shown in Fig. 3(c). The ES contribution to the response signal $h_\omega^{ES} = (h_\omega/dc)/V_{ac}$ was measured with the tip in contact with the pyrochlore region (—) and was normalized in order to have the same unit as the slope $\eta_\omega = (\partial h_\omega/\partial V_{dc})/V_{ac}$ of the saturated part of the hysteresis loops (-○-). The CPE contribution (-★-) was calculated as $h_\omega^{CPE,r} = (h_\omega^+ + h_\omega^-)/(2V_{ac})$, where $h_\omega^{+,-}$ are the remanent values on the hysteresis loops of the cantilever response. The following important features can be derived from Fig. 3: (i) When in contact with the ferroelectric grain, the ES contribution is smaller than the cantilever response in contact with the non-ferroelectric region, because the permittivity of the ferroelectric phase is at least one order of magnitude larger.[15] (ii) The magnitude of each of the contributions follows the shape of the frequency spectrum for nonferroelectric contact, proving that the VMFM signal is governed by both the properties of the material under the tip and those of the cantilever. (iii) As shown in Fig. 3(d) the frequency dependence of the ratio $h_\omega^{CPE,r}/\eta_\omega$ is not constant, but has local minima and maxima in strong correlation with the vibrational mode.

In conclusion, we have shown that c-VMFM measurements performed with soft cantilevers are strongly influenced by the experimental conditions via the dynamical properties of the whole (electro)mechanical system composed of cantilever, tip, sample and adhesion layer. For the imaging of the ferroelectric domain structure we propose the use of a frequency near a contact resonance of the system, but not exactly on the peak, because its position is controlled by the nonuniform adhesion. An important advantage of the contact resonance is that the ac amplitude needed for testing can be very much reduced (in our case down to 50 mV), and this makes the method suitable for very thin films, below 50 nm in thickness. Quantitative measurements of the material properties should be performed with stiff cantilevers (in the strong indentation regime)[9] but only for testing frequencies at least one order of magnitude below $f_{1\omega}^c$. The drawback is that the measurement will be affected by the large contact force applied, typically in the 1 μN range.

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