Mechanical reading of ferroelectric polarization (F)

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Mechanical reading of ferroelectric polarization

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ABSTRACT

Flexoelectricity is a property of dielectric materials whereby they exhibit electric polarization induced by strain gradients; while this effect can be negligible at the macroscale, it can become dominant at the nanoscale, where strain gradients can turn out to be tremendous. Previous works have demonstrated that flexoelectricity coupled with piezoelectricity enables the mechanical writing of ferroelectric polarization. When considering ferroelectric materials with out-of-plane polarization, the coupling of piezoelectricity with flexoelectricity can insert a mechanical asymmetry to the system and enable the distinction of oppositely polarized domains, based on their nanomechanical response. Using atomic force microscopy and, more specifically, contact resonance techniques, the coupling of flexoelectricity to piezoelectricity can be exploited to mechanically read the sign of ferroelectric polarization in a non-destructive way. We have measured a variety of ferroelectric materials, from a single crystal to thin films, and domains that are polarized down always appear to be stiffer than oppositely polarized domains. In this article, we demonstrate experimentally that the phenomenon is size-dependent and strongly enhanced when the dimension of the material is reduced to nanoscale in thin films. Ultimately, we demonstrate how the sensitivity in mechanical reading of ferroelectric polarization can be improved by appropriately tuning the mechanical stiffness of the cantilevers.

I. INTRODUCTION

Ferroelectric materials show a spontaneous electric polarization switchable by the application of an external electric field. Due to their robust and reversible electric polarization and their very high dielectric constant, they have a wide range of technological applications, including many in the form of thin films.[1,2] The ferroelectric polarization is intrinsically coupled to the deformation of the material, since all ferroelectrics are also piezoelectrics. Nevertheless, the spontaneous strain due to polarization is not dependent on the sign of polarization; for classical perovskite ferroelectrics such as $BaTiO_3$ or $PbTiO_3$, the tetragonality does not depend on whether polarization points up or down. Flexoelectricity, on the other hand, causes the appearance of polarization in any material (ferroelectric or otherwise) in response to

strain gradients,[3] which can be notably large at the nanoscale. This is the case when forces are applied with an atomic force microscope (AFM) sharp nanometric tip, and the exploitation of flexoelectric phenomena by AFM tools has led to a number of emerging phenomena such as the mechanical writing of ferroelectric polarization,[4] the mechanical gating of FET transistors,[5] and, more recently, the discovery of the flexo-photovoltaic effect.[6]

As piezoelectric materials, the mechanical properties of ferroelectrics are strongly entangled with their polarization, and mechanical deformation of these materials has to be energetically regarded not only from the structural but also from the electric point of view. In particular, uniform deformation of a piezoelectric causes polarization that, if unscreened, generates a depolarization field that has an associated electrostatic energy cost; for this reason,

the effective Young's modulus of a ferroelectric without electrodes is higher than the same ferroelectric with shorted electrodes.[7] For this reason, also, the mechanical response of 180° domain walls, where the ferroelectric polarization is cancelled, is softer than that of the domains they separate.[8] The nature of the mechanical properties under non-uniform deformations including the ensuing flexoelectric effects is considerably even more complex than those of homogeneously strained materials and remains far-less explored. Not only is the strain distribution more complex, the strain gradient itself has its own mechanical contribution proportional to the square of the gradient, but also, in the particular case of ferroelectrics, the flexoelectric strain and the piezoelectric strain act simultaneously, with their interaction leading to qualitatively different mechanical responses from those that can be expected in a homogeneous strain scenario.

In a seminal work, Cordero-Edwards et al. studied the effect of a non-uniform mechanical load on the mechanical properties of a ferroelectric single crystal as a function of the sign of the out-of-plane ferroelectric polarization.[9] Nano-indentation (destructive) measurements on a ferroelectric single crystal of stoichiometric lithium niobate demonstrated that the overall elastic and plastic mechanical responses were asymmetric, arising from the coupling of the piezoelectric coefficient (the sign of which depends on ferroelectric polarity) with symmetry flexoelectric polarization, which is independent of ferroelectric polarity and therefore can either be additional to or substractive from piezoelectric polarization depending on domain orientation, explaining the observed mechanical asymmetry.[10] The results showed that up-polarized ferroelectric domains were more elastic and tougher, while down-polarized ferroelectric domains exhibited a stiffer and more brittle response under non-uniform deformations. The same behavior but focusing only on elastic deformation was also observed by non-destructive indentation using the tip of an atomic force as a means of delivering strain.[9]

The result of Cordero-Edwards et al. paved the way for non-destructive mechanical reading of polarization, whereby the polarity of a ferroelectric domain can be determined without having to apply any voltage to it. On the other hand, the mechanical reading based on flexoelectricity also presents questions. In particular, a derivative of the previous work lies in the definition of the percentage of asymmetry generated by the coupling of flexoelectricity with piezoelectricity;[9] indeed, since flexoelectricity depends on size, the mechanical asymmetry of ferroelectrics also can vary in non-trivial ways as a function of film thickness. In the present article, we examine how.

On the nanotechnology front, AFM provides several operation modes to give insight into a myriad of mechanical attributes, from elastic properties and the determination of the Young modulus of organic or inorganic systems to adhesion, friction, or breakdown properties. The most relevant to explore oxide thin films, with typical Young modulus in the range of tens to hundreds of GPa, are those exploiting the mechanical resonance of the cantilevers in strong coupling with the sample under study, named as Contact Resonance AFM (CR-AFM),[11–13] atomic force acoustic microscopy,[14–16] or eventually ultrasonic force microscopy.[17] The former has indeed been the key tool to determine the mechanical softening of the domain walls of ferroelectric materials compared to their neighbor ferroelectric domains due to their lack of polarization, bringing them somehow closer to the paraelectric state of the crystal.[8]

II. EXPERIMENTAL

An important part of this study is to evidence that the polarization-induced asymmetry in the mechanical response of ferroelectrics is universal. We have therefore studied ferroelectric samples of different materials and different morphologies: commercially acquired single crystals of $LiNbO_3$ and $BaTiO_3$ and ferroelectric thin films of $BiFeO_3$ and $PbTiO_3$. After an initial proof of concept using a periodically poled lithium niobate single crystal (PPLN) with opposite out-of-plane polarized domains to correlate our data with nanoindentation measurements, further exploration included barium titanate ($BaTiO_3$) single crystals with a–c domains, including areas with c up and c down polarization. Obtained data were complemented with experiments on thin films. We used a bismuth ferrite ($BiFeO_3$) (111) thin film of 70 nm with ferroelectric polarization aligned exclusively in the out-of-plane axis, and two lead titanate thin films ($PbTiO_3$) with different thicknesses, 20 and 50 nm, to explore the size effect on mechanical reading of polarization. Note that in both cases ($BiFeO_3$ and $PbTiO_3$), the $SrRuO_3$ bottom electrode is intercalated between the substrate and the ferroelectric film. The $PbTiO_3/SrRuO3$ bilayers were coherently grown onto a 001-oriented $SrTiO_3$ single crystal substrate using reactive molecular-beam epitaxy. The compressive strain exerted by the substrate impose the polarization in the $PbTiO_3$ film to be along the out-of-plane direction solely (pure c-domain scenario). The growth conditions and the structural characterization can be found elsewhere.[18,19] $BiFeO_3$ (111) films were epitaxially grown by pulsed layer deposition on the $LaSrMnO_3$ bottom electrode.

All AFM measurements were done on an MFP-3D Asylum AFM (Asylum Research—Oxford Instruments). Two types of tips were used, PPP-EFM tips (Nano sensors; Schaffhausen, Switzerland) with a stiffness constant of k ∼ 2 N/m and coated with Ptlr and PPP-NCL tips (Nano sensors; Schaffhausen, Switzerland) with a stiffness constant k ∼ 45 N/m and the same coating.

A. Dual amplitude resonance tracking piezoresponse force microscopy measurements

As a starting point, we used Piezoresponse Force Microscopy (PFM)[20] to test the ferroelectric polarization of different samples in the as-grown state and after electric field lithography of new ferroelectric domains. PFM is a contact mode in which the sample is excited by an AC voltage applied by the AFM tip, and it is used as a top mobile electrode. The so induced inverse piezoelectric effect on the ferroelectric samples translates into surface deformation (expansion and contraction), which is picked up by the cantilever and rendered into an amplitude and phase of the oscillation signal. When the excitation is driven close to the cantilever's resonance frequency, the intrinsically low deformation signal, typically in the range of pm, is strongly amplified by the Q factor of the resonance of particular importance when dealing with thin films. While the amplitude accounts for the magnitude of deformation and is thus proportional to the value of ferroelectric polarization, the phase

indicates the direction of polarization, being the phase of up and down domains shifted by 180°. In order to follow the frequency shifts of the resonance induced by changes in tip-sample mechanical coupling and topography features, Dual Amplitude Resonance Tracking (DART) mode applies two exciting frequencies right above and below the resonance peak and builds up a feedback loop to keep the amplitude equal on both points. When the sample is electrically excited that leads to DART PFM measurements, the same signal operation mode can be applied to track the contact resonance frequency in CR-AFM as described below.

B. Contact resonance AFM

The track of mechanical properties was achieved using the CR-AFM mode.[16] In this mode, the tip is in strong contact with the sample and the whole system is now mechanically excited.[21,22] While scanning, the force applied by the tip is being kept constant. The vibration modes of this system depend both on the geometrical characteristics of the tip (which are assumed to remain unchanged through the whole measurement) and on the nature of the tip-sample mechanical contact. Here, the so-called mechanical contact resonance frequency is the key quantity of interest, as it depends on the sample's elastic properties: thus, shifts in contact resonance frequency directly correlate with Young's modulus of the material; more specifically, lower resonance frequencies correspond to softer materials and higher resonance frequencies to stiffer ones.

III. RESULTS AND DISCUSSION

A. Stiffness as a function of polarization direction

Stress induced by an AFM tip can cause deformation of the material[23] and even lead to giant change on its functional properties.[24] The so induced homogeneous deformation of a piezoelectric material has an energy cost with two components: the elastic one, which is related with deformation itself and is described by Hooke's law, and the electrostatic one, related with induced changes in polarization due to electromechanical coupling. Both are symmetric with respect to space inversion: the elastic energy is symmetric because the deformation due to polarization is identical for both directions and so is the electrostatic energy since it is proportional to polarization squared ($\sim 1/2\chi^{-1}P^2$, where χ is the dielectric susceptibility) canceling the influence of the sign of polarization.

In the case of an inhomogeneous deformation, though, as the one caused by a sharp AFM tip, huge strain gradients are induced[23] and flexoelectricity has to be taken into account. Now resultant polarization has two sources: strain by means of piezoelectricity and strain gradients by means of flexoelectricity. When considering AFM tip-induced strain gradients, they are singularly oriented toward the tip contact point, inducing in all cases a net down polarization (as long as the flexoelectric coefficient of the material is positive). In a ferroelectric, since the piezoelectric coefficient links to ferroelectric polarization and can thus be reversed, former contributions can be parallel or antiparallel. In this way, the same inhomogeneous deformation can enhance or decrease the total induced polarization of the material, depending on the sign of ferroelectric polarization. This flexoelectric modulation of the total

ferroelectric polarization has consequences on the mechanical attributes of the sample as a function of the domains.[9] More specifically, in down polarized areas, flexoelectric and piezoelectric polarization have the same orientation, resulting into an increase in total ferroelectric polarization and the ensuing increase in electrical energy cost of deformation, compelling a stiffer mechanical response of down domains. Oppositely, domains that are polarized up, where piezoelectricity and flexoelectricity are antiparallel, appear to be softer. This phenomenon endows the mechanical response as measured by AFM tips to account for the ferroelectric polarization of materials, as illustrated in Fig. 1.

Top row images of Fig. 1 show the ferroelectric domains' orientation of different materials with pure out-of-plane alignment of polarization as measured by PFM measurements, where the purple PFM phase signal stands for down polarization and the yellow signal denotes up polarized domains. We tested a $BaTiO_3$ single crystal [Figs. 1(a) and 1(b)], a $BiFeO_3$ (111) thin film, [Figs. 1(c) and 1(d)] and a $PbTiO_3$ thin film with thickness of 20 nm [Figs. 1(e) and 1(f)]. Bottom row shows the corresponding CR-AFM images of exactly the same areas for each sample. It stems from Fig. 1 that areas that are up polarized show lower resonance frequency in CR-AFM measurements, meaning that they are softer, as expected. More precisely, in the BTO single crystal, the shift in the contact resonance frequency between up and down domains reaches about 350 Hz. It is worth to mention that the diagonal stripe on the downright edge of Fig. 1(b) corresponds to an in-plane polarized domain, which is known to be about 150% stiffer than out-of-plane polarized domains.[7] In the $BiFeO_3$ thin film, opposite domains differ by 500 Hz, while in the $PbTiO_3$ thin film, the difference amounts around 2 kHz.

Remarkably, besides the difference in mechanical stiffness between domains, there is also a difference in the mechanical response between domains and domain walls. This phenomenon has been studied in detail in our previous work[8] and is not directly related with the coupling of piezoelectricity with flexoelectricity. In the case of domain walls, there are two mechanisms, not mutually exclusive, that contribute in domain walls' softness. The first one is related with the motion of domain walls: when force is applied by the AFM tip over a polarized area, polarization acts against this deformation and appears to be stiff. But when the force is applied next to a domain wall, the cubic structure is favored so the domain wall moves or broadens toward this direction, making the cost of deformation smaller, showing a softer mechanical response. The energy cost of moving a domain wall is lower than the energy cost of deforming a polarized domain. The second mechanism is related to the electrostatic cost of deformation: for a polarized area, the electrostatic energy is proportional to the square of polarization. Over a domain wall though, the total amount of polarization is zero; thus, the associated electrostatic energy is zero, and domain walls appear to be easier to deform.

B. Size dependence of stiffness asymmetry between up and down domains

Scrutinizing the results of Fig. 1, one can observe that the difference in mechanical response between up and down polarized domains (proportional to contact resonance frequency) is enhanced
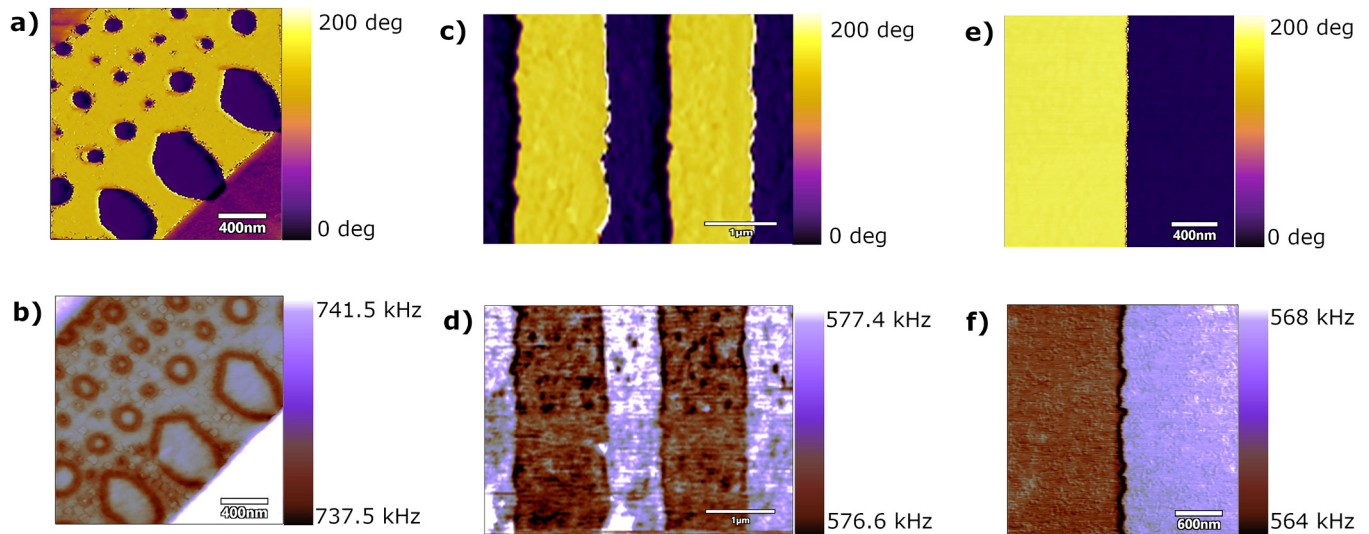
FIG. 1. Ferroelectric domains of different materials as observed by PFM and CR-AFM. (a) PFM phase image of BaTiO$_3$ single crystal with c domains polarized up (yellow) and down (purple). Diagonal stripes at the top left and bottom right corners correspond to a domains with polarization in-plane. (b) CR-AFM image of the same area demonstrating the differences in mechanical properties of ferroelectric domains. The dark brown lines correspond to the softer domain walls. (c) PFM phase image and (d) CR-AFM image of a BiFeO$_3$ (111) thin film on the LaSrMnO$_3$ substrate showing ferroelectric strip domains written with an applied voltage. (e) PFM phase image and (f) the corresponding CR-AFM image of a PbTiO$_3$ thin film on the SrTiO$_3$ substrate around a domain wall (brown) separating an up-polarized domain (left area) from a down-polarized domain (right area).

in the case of thin films, as compared to single crystals. The size dependence of the contrast arises from the dimensional balance between the tip-induced curvature with respect to film thickness, entangled in different aspects. On one hand, the determination of the AFM tip-induced strain gradients in each case constitutes the primary concern to account for the flexoelectric coupling effect into mechanical attributes. On the experimental front, we know that the tip radius suffers wearing effects promoted by scanning over the surface in the contact mode. Stabilization of tip radius in the order of ~150 nm for regular experiments is predicated upon our previous knowledge obtained after analyzing the AFM tips by SEM after the experiments. Additionally, in all cases, measurements were done with PPP-NCL tips with k ~ 45 N/m and applied forces in the range of 900 nN (slightly fluctuating among different experiments). On the basis of the above, we can therefore argue that the induced strain gradients are within the same order of magnitude for all materials under this regular operation conditions. The second main factor to take into consideration to explain this observation is the flexoelectric coefficient: under the same strain gradients, the total induced flexoelectric field will scale the following equation:

$$E_{flexo} = f \frac{\partial s}{\partial z}, \tag{1}$$

where f stands for the flexocoupling coefficient and $\partial s/\partial z$ is the strain gradient, which for loads of ~900 nN on a contact area with radius of ~25 nm (as derived from the Hertz contact model on a reference sample with Young modulus E = 100 GPa and ν = 0.3),

can take a value of the order of 10^5–10^6 m^{-1} (Ref. 23). In spite of arising efforts to frame a database with the flexocoupling coefficients of most prominent materials, significant divergences arise from experimental and theoretical determination of this parameter, a question that continues to defy scientific efforts. Yudin and Tagantsev have reported a flexocoupling coefficient for the BaTiO$_3$ single crystal of $f = 7$ V at room temperature.[25] On the other hand, PbTiO$_3$ seems to exhibit a lower flexocoupling coefficient of about $f = 5$ V.[26] Although the flexocoupling coefficient of BaTiO$_3$ is significantly bigger than the other two materials, the asymmetry between different domains and, thus, the difference in their nanomechanical response, appear enhanced in the case of BiFeO$_3$ and PbTiO$_3$ due to sample size reduction; the flexoelectric field generated, under the same applied load, becomes more relevant in the cases of thin films.

To further investigate size effects, it is crucial to perform experiments on the same material to exclude the difference in mechanical response due to different piezoelectric coefficients. To be able to account for data in a consistent and quantitative manner, we performed CR-AFM measurements on two different PbTiO$_3$ thin films varying in thickness of 20 and 50 nm, respectively. Results are illustrated in Fig. 2.

Figures 2(a) and 2(b) show the PFM phase and CR-AFM image of the 50 nm thick PbTiO$_3$ thin film. Histograms of the contact resonance frequency signal for the up and down domains [Fig. 2(c)] show a mean shift of 1.04 kHz among them, with down polarized domains appearing always stiffer. Figures 2(d)–2(f) illustrate the corresponding analysis for the thinner PbTiO$_3$ thin film, with a thickness of 20 nm. While in both experiments, the force
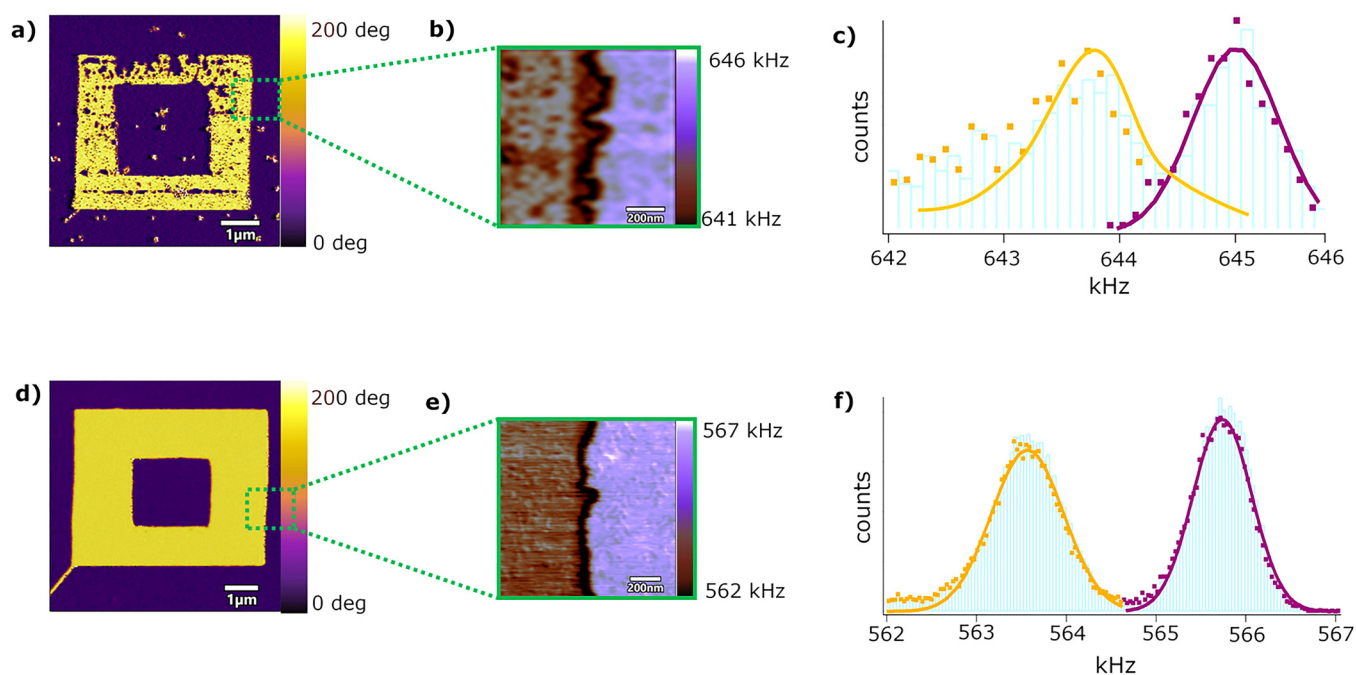
FIG. 2. (a) PFM phase image of the PbTiO$_3$ thin film of 50 nm thickness grown on the SrTiO$_3$ substrate. (b) The corresponding CR-AFM in a zoomed in area showing a significant shift of the measured contact resonance frequency to lower frequencies for up domains. (c) Histograms of the CR-AFM signal for the up and down domains, respectively, denoting a relative shift of $\Delta f = 1.04$ kHz among opposite polarized domains. The points observed at the lowest frequency range correspond to the contribution of the domain walls' contact resonance frequency to the histogram. (d) PFM image of the PbTiO$_3$ thin film of 20 nm thickness grown on the SrTiO$_3$ substrate with (e) the mechanical response of a zoomed area as measured by CR-AFM. (f) Histograms of image (e) for the up and down domains, respectively, showing a difference in stiffness between up and down domains, associated to a shift of the order of $\Delta f = 2.17$ kHz. In all cases, a PPP-NCL tip with k = 45 N/m was used for the CR-AFM measurements, obtained with an applied force of 900 nN. The apparent enhancement in the domain wall width in (b) compared to (e) is due to the lower resolution of the former image.

applied by the tip was the same, and in the latter case, the difference in the contact resonance frequency between opposite polarized domains rises up to 2.17 kHz, confirming the predicted size dependence of the flexoelectric-induced asymmetry in mechanical stiffness. This finding is in line with the behavior exhibited by the fracture toughness upon dimensional reduction as studied by Abdollahi et al.,[10] where the energy release rate was observed to decrease with the beam thickness when flexoelectricity was introduced. In that case, the difference in fracture toughness between up and down polarized BaTiO$_3$ thin films doubles upon decrease in the film thickness between 100 nm and few tens of nanometers, reaching an asymmetry factor of almost 80% for the later one. This effect is directly correlated with the fact that as the sample thickness decreases, the relative size of the flexoelectrically polarized region around the tip increases, and thus, it can be extrapolated to other mechanical properties such as stiffness.

Fundamental understanding of how nanoscale stiffness under strain gradients of ferroelectrics depends on size is an important challenge that remains to be tackled with simulations but may be regarded qualitatively. A possible explanation for the enhanced contrast is a geometric size effect in the relative volume impacted by the strain gradients as compared to the ferroelectric volume: in this sense, the consequences of flexoelectric effects[27–29] are indeed

significantly enhanced with size reduction up to the point that they can even induce full ferroelectric switching for thin enough samples. The observed contrast in mechanical stiffness is predicated upon coupling between piezoelectricity and flexoelectricity. While the radius of the tip is the main length scale for the volume affected by flexoelectricity, the mechanical contrast does not depend solely on flexoelectricity but on the competition of flexoelectricity and piezoelectricity. Strain gradient has a finite penetration depth that is roughly proportional to the radius of the tip. Homogeneous compressive strain, on the other hand, elicits a piezoelectric response from the entire thickness of the sample. When applying force with an AFM tip, there is a part of the out-of-plane strain component (e_{33}) that penetrates the entire thickness of the sample.[4,30] Thus, when the radius of the tip is comparable to the thickness of the sample, flexoelectricity and piezoelectricity affect roughly the same volume, and this maximizes the competition between flexoelectricity and piezoelectricity, that is at the root of the observed mechanical contrast: the induced flexoelectric field in thin films becomes dominant over ferroelectric polarization for the domains in which both are antiparallel (leading ultimately to the well-known mechanical switching of ferroelectric polarization),[4] and, conversely, it might nearly double the polarization in the domains where both couple in parallel. This enormous

flexoelectric-induced polar contrast of thin films is thus translated into an enhanced mechanical contrast. By contrast, in very thick samples, flexoelectricity only comes from a relatively small fraction of the overall thickness, while the d_{33} component of piezoelectricity still comes from the entire thickness, and hence, the relative impact of flexoelectricity (and thus the associated mechanical contrast) diminishes.

C. Tuning the sensitivity on stiffness-induced contrast in CR-AFM

Results shown earlier clearly describe how the mechanical reading of ferroelectric polarization is enabled on the base of fundamental physics. Contrast is naturally enhanced by sample size reduction, but the overall mechanical response of the cantilever-
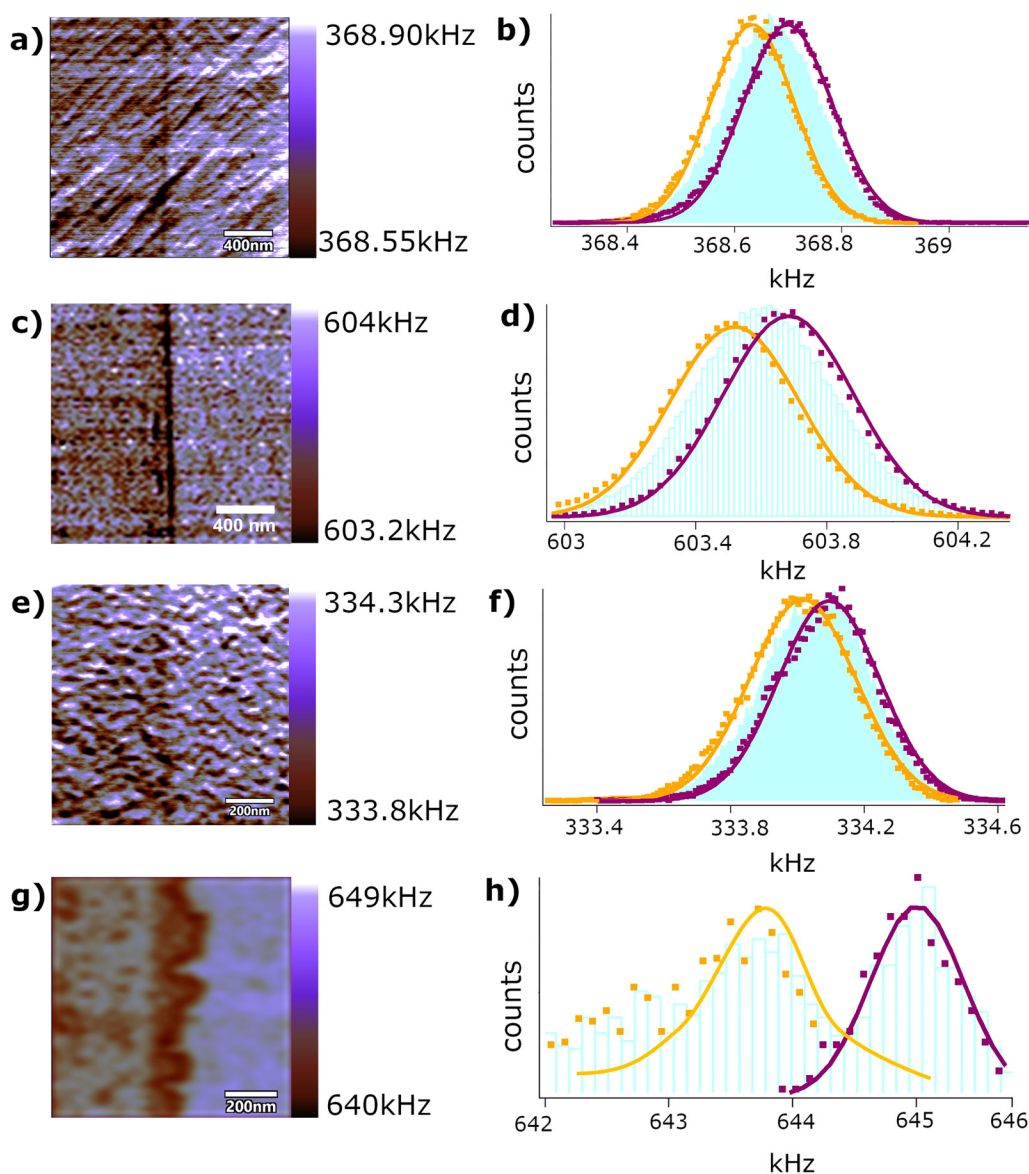
FIG. 3. Left column: CR-AFM frequency images of a PPLN single crystal in (a) and (c) and of a PbTiO$_3$ thin film grown on the SrTiO$_3$ substrate with a thickness of 50 nm in (e) and (g). The images are measured using cantilevers of different stiffness: (a) and (e) are obtained with a Nanosensors PPP-EFM tip with stiffness k ∼ 2 N/m, under an applied force of 900 nN, and (c) and (g) with a Nanosensors PPP-NCL tip soft tip with k ∼ 45 N/m. The right column shows the histograms corresponding to each of the CR-AFM images of the left column. The points observed at the lowest frequency range in (h) correspond to the contribution of the domain walls' contact resonance frequency to the histogram.

sample system captured by CR-AFM also embeds cantilever geometrical features that define its mechanical dynamics and resonant bending modes. The mechanical resonant frequency of a cantilever in strong coupling with a stiff sample can be approached using an Euler–Bernoulli elastic beam model for the cantilever, describing the tip-sample mechanical junction as an effective spring $k^\star$ connected in series with a dashpot to account for damping.[12,16,31–34] For a constant sample stiffness, the full resonant response of the whole system will be essentially dominated by cantilever stiffness: stiffer cantilevers result into higher resonant frequency of the system and enhance sensitivity to changes on sample stiffness. Stiffer cantilevers will cause higher frequency shifts upon the same alteration of sample stiffness, thus increasing the contrast in the mechanical reading of ferroelectric polarization.

To prove this end, we performed the mechanical reading of ferroelectric polarization experiments with different types of AFM tips with varying stiffnesses. Figure 3 shows the CR-AFM images for two samples, a PPLN single crystal and a $PbTiO_3$ thin film obtained using cantilevers with low spring constant ($\sim 2\,N/m$) and high spring constant ($\sim 45\,N/m$). In the case of PPLN [Figs. 3(a)–3(d)], the measured frequency shift between up and down domains using a stiff tip is almost 250 Hz. With a soft tip, the difference falls in the resolution limit, around 50 Hz, and is hardly distinguished. The corresponding experiment on a ferroelectric thin film, in this case $PbTiO_3$ [Figs. 3(e)–3(h)], for which we already count on the size effect enhancement of the contrast, the observed difference between opposite polarized areas amounts to 100 Hz using a soft tip and rises up to 1.04 kHz when a stiffer tip is used.

Figure 3 serves to illustrate that in both cases, that is, for single crystals and thin films, the mechanical reading contrast of the ferroelectric domains is noticeably stronger when using stiff cantilevers. This can be explained by the mechanics behind the dynamics of the cantilever in contact with the sample. In CR-AFM, the beam mechanical bending modes (and associated resonant frequencies) emanate from the coupling of two springs in series.[35] The first spring is the cantilever, represented by the elastic beam with a corresponding spring constant (k_{lever}). The second spring considers the effective mechanical coupling between the tip and the sample using $k^\star$, which embraces the mechanical properties of the sample (k_{sample}). When the spring constant of the cantilever is lower than the effective stiffness $k^\star$, then all energy that should be transferred to excite the contact and the sample is absorbed by the soft cantilever and the probe becomes less sensitive to any sample changes. In other words, in order to mechanically characterize stiff materials, we need cantilevers that are as stiff as possible.

IV. CONCLUSIONS

The purpose of this article was to illustrate the relevant aspects that must be considered when exploiting flexoelectricity to achieve the mechanical reading of ferroelectric polarity, which is the counterpart to the mechanical writing of ferroelectric domains. Our results show that the effect is universal: from bulk single crystals of $LiNbO_3$ and $BaTiO_3$ to epitaxial thin films of $BaTiO_3$, $PbTiO_3$, and $BiFeO_3$, we see in all cases that the mechanical contact resonance frequency is always higher for up-pointing domains than for downward-pointing ones. This observation brings out the

interesting and non-trivial conclusion that the effective flexoelectric coefficient has the same sign for all of these materials, despite their difference in composition, elemental charge, and even crystal orientation. Considering that the direct measurement of flexoelectricity in polar materials is inherently complicated,[36] this information is already valuable. In addition, by comparing the results of single crystals with very different dielectric constants (and, therefore, very different expected flexoelectric coefficients),[3] we see that, as expected, the mechanical contrast between up and down domains is larger for the material with larger dielectric constant.

Moving on to geometrical considerations, mechanical contrast relies on the interaction between piezoelectric polarization and the flexoelectric polarization, both induced by tip compression. The tip-induced strain gradient, however, by its very nature relaxes within a small distance, typically of the order of magnitude as the indentation radius. Outside of that volume, the strain state is homogeneous. This means that the smaller the film thickness, the larger the relative volume of material where flexoelectricity is active and can compete with piezoelectricity. In practical terms, this means that (i) mechanical contrast is larger in thin films than in bulk single crystals, and (ii) the thinner the film, the larger the contrast.

Finally, in practical terms, it is important to notice that the measured contact resonance frequency depends on both the elastic constant of the cantilever and that of the sample, which act in series. For very rigid ceramic samples, the softer spring constant of the two is the bending mode of the cantilever, which therefore dominates the measured resonance frequency. Conversely, in order to emphasize the sample contribution, we need to use cantilevers that are as stiff as possible; as our results show, for the same sample, the contrast between the resonance frequency of oppositely polarized domains in the same sample can be detected or invisible depending on whether the cantilever used is stiff or soft.

The present results establish both the universality of the effect (i.e., for all ferroelectrics, the polarity of ferroelectric domains can be detected by purely mechanical means) and also the physical and practical considerations that must be considered when investigating the nanomechanics of ferroelectrics. We hope that these will inspire further research into this interesting emerging phenomenon and help guide prospective scientists around the practical problems involved.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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