Nanoscale polarization profile across a 180° ferroelectric domain wall extracted by quantitative piezoelectric force microscopy

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The structure of a single antiparallel ferroelectric domain wall in LiNbO3 is quantitatively mapped by piezoelectric force microscopy (PFM) with calibrated probe geometry. The PFM measurements are performed for 49 probes with the radius varying from 10 to 300 nm. The magnitude and variation of the experimental piezoelectric coefficient across a domain wall match the profiles calculated from a comprehensive analytical theory, as well as three-dimensional finite element method simulations. Quantitative agreement between experimental and theoretical profile widths is obtained only when a finite disk-type tip radius that is in true contact with the sample surface is considered, which is in agreement with scanning electron microscopy images of the actual tips after imaging. The magnitude of the piezoelectric coefficient is shown to be independent of the tip radius, and the PFM profile width is linearly proportional to the tip radius. Finally we demonstrate a method to extract any intrinsic material broadening of the ferroelectric domain wall. Surprisingly wide wall widths of up to 100 nm are observed in the limit of zero tip radius. © 2008 American Institute of Physics. [DOI: 10.1063/1.2979973]

I. INTRODUCTION: FERROELECTRIC WALL WIDTH AND COERCIVE FIELDS

The extremely small width of ferroelectric domain walls, typically of the order of one to two lattice units,1,2 has attracted significant interest in these materials as potential data storage media. The “up” and “down” polarization states in a ferroelectric created by localized field as well as data storage bits, with >10 Tbits/in.2 storage density demonstrated recently.3 Domain shaping on diverse shapes and length scales is also critical to terahertz surface acoustic wave devices, nonlinear optical frequency conversion, as well as electro-optic steering, dynamic focusing, and beam shaping devices. In these applications, domain wall width determines the minimum feature size and maximum operation frequency of the device.4 Domain wall width also directly influences the dynamics of wall motion.5,6 Further, even minute broadening of a domain wall is predicted7,8 to dramatically lower the coercive fields in ferroelectrics through lowering of the threshold field for wall motion against intrinsic lattice friction. Thus determining the nanoscale structure of a wall is of fundamental interest to the field of ferroelectrics.

To date, the primary means of investigating wall widths on unit cell level has been transmission electron microscopy (TEM).9,13 The original TEM studies of a ferroelectric 180° domain wall in a related material, lithium tantalate, concluded that wall width cannot be resolved down to their resolution limit of 0.28 nm.10 Recently, an improved TEM technique has demonstrated that charged 180° walls in lead zirconate titanate (PZT) thin films can be up to 4–5 nm.14 In parallel, direct imaging of strain at these walls using synchrotron x ray,15,16 index contrast using near-field scanning optical microscopy,17 and excitation emission spectroscopy18,19 reveal property changes on length scales of 1–30 μm. Thus the scale of 1 nm to 1 μm linking atomic structure of the wall and macroscopic properties of the ferroelectric has been less explored. Atomic force microscopy measurements of surface topography at twinned 90° walls have been used to derive wall widths of ~1.5 nm and determine defect effect on wall broadening.20,21 However, there is no intrinsic topography associated with 180° domain walls, necessitating detection of primary order parameter, Pi. Recent work using a new technique, namely, scanning nonlinear dielectric microscopy (SNDM) has shown domain wall widths of up to 150 nm.22 While SNDM has excellent resolution of better than 1 nm based on published evidence,23,24 a direct interpretation of the SNDM signal in terms of intrinsic material properties, especially polarization, is presently not possible. A quantitative theory for this technique is also not developed.

In this work, we analyze the structure of a 180° domain wall on the 1–100 nm length scales by piezoelectric force microscopy (PFM) with calibrated probe geometry. The technique is quantitative, and allows direct extraction of the po-
larization profile across a ferroelectric wall. PFM detects the surface displacements, $U_i$, related to piezoelectric strain $\varepsilon_{ij} = d_{ij} E_k$ induced by applying an oscillating electric field $E_k$ to the tip in contact with the sample surface. $^{25,26}$ Since piezoelectric coefficients are related to the order parameter polarization, and $\gamma_{ijkl}$ is the electrostrictive coefficient of the material, measurement of the piezoresponse across a wall is expected to provide direct information on the primary order parameter, $P_i$, across a wall. (The fourth-order electrostrictive tensor, $\gamma_{ijkl}$ is not expected to change across the wall, since it is a property of the prototype paraelectric phase and is invariant with respect to inversion symmetry across the wall). PFM technique has been reviewed in many places, and has been extensively used to study ferroelectric domains. $^{27-31}$ However, to date there has been very little experimental and theoretical investigation of the resolution limits of PFM $^{32-35}$ in order to understand widely varying wall width studies, thus the exact limits of domain wall width are still highly debated. In this work, we present, to date, the most rigorous and complete quantitative theory (both analytical and numerical) of PFM imaging. This enables extraction of the polarization profile across a single ferroelectric domain wall, which is not possible with any of the previous techniques employed.

Since the goal is to extract information regarding the intrinsic wall width of an antiparallel wall, the first step is to quantitatively understand the PFM imaging technique, and its resolution limits. The measurements are performed using 49 probes with calibrated probe geometry in the 10–300 nm range. By varying the effective radius of the probe, carefully characterizing the details of the tip shape and tip-sample contact region (Sec. II), and combining it with three-dimensional (3D) finite element modeling (Sec. III), and analytical theory (Sec. IV), we demonstrate that the PFM profiles can be quantitatively understood. We demonstrate that the intrinsic or extrinsic wall broadening can be extracted by a careful comparison of experiments and theory (Sec. V).

II. PFM EXPERIMENTS

A. Tip shape and contact

Antiparallel domain walls in congruent lithium niobate are the focus of this study. The point group symmetry of LiNbO$_3$ is $3m$ and the polarization is along the $+z$ direction ($+P_z$) or $-z$ direction ($-P_z$). The walls are typically parallel to the crystallographic $y$-$z$ mirror planes. Hence the wall coordinates are defined as $x$ perpendicular to the wall, $y$ along the wall, and $z$ along the polarization direction.

The origin of the contrast in vertical PFM arises from piezoelectric deformation due to the converse piezoelectric effect. The application of a localized external electric field to a piezoelectric material results in a local strain, and consequently displacement of the surface. In a contact atomic force microscopy (AFM) mode, the tip is expected to follow this deformation of the surface. The vertical PFM (bending mode) detects the displacement of sample surface perpendicular to the sample surface. The displacement detection sensitivity of $\sim$ pm is enabled through the use homodyne detection using lock-in amplifier. For lithium niobate (point group $3m$), the piezoelectric tensor has four independent nonzero coefficients ($d_{33}$, $d_{35}$, $d_{32}$, and $d_{33}$).

Since PFM is a contact mode technique, abrasion of the tip occurs during imaging, $^{36,37}$ which changes the tip shape and the field distribution under the tip. The tip apex is typically approximated by an ideal sphere or disk with a radius $r$. The contact of the tip to the sample is either considered to be an ideal point contact, or more commonly, a dielectric gap of the order of 0.1–1 nm is assumed between the tip and the sample. Exact analytical expressions for the field distribution around such tip shapes are well known. $^{38,39}$ However, below, we show that these assumptions of tip shape and tip-sample contact region are limited.

In order to rigorously describe the tip shape, we imaged the end of each tip using field emission scanning electron microscope (FESEM), after scanning a few PFM line scans across a domain wall. These tips can be divided into two sets, 1 and 2, as they are referred to in Fig. 1. As seen in Fig. 1(a), tip set 2 looks more disk-like, in that its end is flat with a circular contact area of radius $r$. A majority of the tips were of this type. It is modeled as a disk of charge of radius $r$ on the surface of the sample. Tip set 1, seen in Fig. 1(b) appears spherelike, and was usually seen for very small tip radius. The radius of the contact area for tip set 2 can be determined by intersecting a straight line (surface of the sample) with the end of the tip in the image; however, a more systematic method that yielded the same results was followed: drawing an imaginary circle at the end of the tip, and taking the cross-sectional area of radius $r$ at a depth of $h$–1–2 nm (1–2 $c$ lattice units) depth from the tangent to the surface of the circle. The $h$ should, however, not be construed as a real indentation, but is rather chosen phenomenologically as an engineering parameter that accounts for the SEM image diffuseness at the end of the imaged tip. This is used to estimate the contact area formed during the wear process. We find that this uncertainty in $h$ (1–2 nm) and hence in $r$ does not affect our conclusions, which are dominated by experiments with tip set 2, that are unambiguous in their actual tip size. In particular, for $r$–10 nm, the observed PFM domain wall resolution is ~100 nm, well beyond broadening anticipated from conventional indentation models (e.g., Hertzian).

B. PFM profiles across a wall

The PFM signal is typically a complex displacement, $\vec{U} = U_\theta + i U_i = U_i e^{i\theta}$. The phase, $\theta$, refers to the relative phase

![FIG. 1. (Color online) (a) FESEM image of a used PFM tip from tip set 2, with a circular disklike end with a radius $r$. (b) FESEM image of a used spherelike PFM tip from tip set 1. The radius $r$ of the contact circle for a weak indentation ($h$–1–2 nm or 1 unit cell depth) is used to characterize the radius $r$ of the tip as shown. ($h$ is not to scale in the figure).](Image 352x665 to 520x742)
of the tip displacement with respect to the phase of the alternating voltage applied to the PFM tip. The pure electromagnetic signal $\tilde{U}$ can be clearly distinguished in the complex plane from any background signal as described in literature. This background subtraction described in Ref. is critical for quantitative analysis of the PFM profiles, and performing it eliminates the frequency dependence of the PFM signal in the frequency range of 20–100 kHz used in this study. A monotonic frequency dispersion of the pure PFM signal still remains below the frequency of 20 kHz presumably due to lock-in nonidealities, and hence this frequency range is excluded from this study. Figure 2 depicts example profiles of the $U_R$ and $UI$ as a function of the wall normal coordinate $x$. Note that with appropriate background subtraction, the pure electromechanical displacement is entirely along the real part $U_R=U_o \cos \theta$ while $UI=U_o \sin \theta$. Measurements were made with a Ti/Pt coated Si tip with a tip disk radius of 50–60 nm. An oscillating voltage of 5 Vrms, at 42.35 kHz was applied to the tip.

C. Tip size dependence of the PFM amplitude and width

Experimentally, there are two important experimental parameters that were extracted from these profiles: amplitude, $|U_z|$ and width, $\omega_{PFM}$. The PFM amplitude was calibrated using a poled PZT ceramic sample uniformly electroded on both sides, whose piezoelectric coefficient in pm/V was independently measured using a piezometer, which applies a stress and measures the open loop potential generated across the material. The surface displacement of this PZT sample in response to an applied voltage from a PFM tip was then used to calibrate the PFM signal. This calibration, in turn, was used to quantify the piezoelectric coefficient of the LiNbO$_3$ sample. The calibrated amplitude of the PFM response away from the wall in units of $d_{eff}$ (pm/V) is plotted as a function of the experimentally determined tip radius $r$ in Fig. 3. An important conclusion seen from Fig. 3 is that the $d_{eff}$ is independent of the tip radius used. Remarkably, thus calibrated magnitude of the $d_{eff}$ in pm/V as well as its invariance with respect to tip radius also agrees with both the analytical theory and numerical simulations described next in Secs. III and IV.

FIG. 2. (Color online) An example of complex PFM displacement, $\tilde{U}=U_R+iUI=U_o e^{i\theta}$ as a function of wall normal coordinate, $x$ across a 180° domain wall in lithium niobate. (a) $U_R=U_o \cos \theta$, (b) $UI=U_o \sin \theta$, (c) $U_o$, and (d) $\theta$. Measurements were made with a Ti/Pt coated Si tip with a tip disk radius of 50–60 nm. An oscillating voltage of 5 Vrms, at 42.35 kHz was applied to the tip.

FIG. 3. (Color online) The maximum amplitude, $|U_z|$, away from the wall as a function of tip radius, $r$ is shown. Also shown overlapped is the analytical theory and FEM predictions.
Figure 4 shows the width \( \omega_{PFM} \) of the PFM response across a single 180° domain wall as a function of the experimentally determined tip radius \( r \). The \( \omega_{PFM} \) refers to the half width where the PFM response reaches \( \pm 0.76 \) of the saturation PFM value away from the center of the wall. Note the \( \tanh(1) \approx 0.76 \), which is motivated from the fact that phenomenological Ginzburg–Landau–Devonshire theory of polarization variation across the wall follows the expression \( P/P_s \sim \tanh(x/\omega_o) \). This saturation value was taken as the PFM value at \( \sim 1.8 \) \( \mu \)m from the center of the wall. The PFM width decreases linearly with the tip radius, except at the smallest tip radii, where deviations from linearity are observed. The relationship between these deviations and the intrinsic wall width is discussed in Sec. V. Two modeling approaches were employed, namely, analytical theory and finite element modeling (FEM) as described in the next section.

In comparing Fig. 4 with a similar measurement reported in Ref. 35, Fig. 3, we note the following primary differences: Ref. 35 uses full width at half maximum (\( \pm 50\% \)) as the PFM width, takes the saturation value of PFM signal as the value at \( \sim 100\)nm from the wall center where PFM signal still appears to vary with distance, and plots the tip radius based on tip manufacturer’s specification assuming a spherical tip. This work uses \( \pm 76\% \) as the width, takes the saturation value of PFM signal as the value at \( \sim 1.8\) \( \mu \)m from the wall center where PFM signal no longer varies with distance, and characterizes each tip after it is used by FESEM, which reveals a disk-like tip whose radius is plotted. When the differences in the definition of wall width and saturation PFM value are accounted for, the PFM widths in Ref. 35 are similar to this work. There is no obvious way for us to account for the differences in the way the tip radius is characterized and plotted in these two works.

III. FINITE ELEMENT SIMULATION OF THE PFM RESPONSE

In order to understand the PFM response quantitatively, we also perform FEM modeling of the imaging process using the commercial ANSYS program as well as analytical theory using the decoupled approximation.\(^3^0\) The FEM approach described in Ref. 30 in detail includes a complete description of the geometry of the tip, the sample, and the contact region, numerical calculation of the electric field distribution with a constant potential applied to the tip, and using the computed potential distribution on the sample surface as boundary condition to calculate the piezoelectric deformation of the surface [Fig. 5(a)]. Input to the FEM includes the complete dielectric tensor, elastic tensor, and piezoelectric tensor of the sample, thus providing a rigorous 3D approach. (The \( d_{22} \) coefficient ignored in analytical theory was included in FEM, and its effect on the PFM was shown to be minimal as well and is confirmed later that this is a valid assumption.) A single domain wall parallel to one of the three degenerate \( y-z \) physical crystal planes was defined in the simulation by flipping the crystal physics axes, \( y \) and \( z \) across the wall. Figure 5(b) depicts the surface deformations simulated by FEM for three different locations of the tip across a single steplike 180° domain wall. (Three separate simulations for the three tip positions have been merged in this plot). Using a series of positions of tip across the wall, continuous FEM line profiles of \( U_z \) were generated (see video clip; online supplementary information).\(^5^0\) All simulations with FEM were performed only with steplike wall, and did not include any intrinsic broadening or diffuseness, since it was not numerically feasible in the software used. Diffuseness is included in the analytical theory, described later.

We explore two different models for the tip-sample surface interaction: (a) the sphere-plane model and (b) the disk-plane model, where the sphere or the disk refers the tip shape and the plane refers to the sample surface. In both models, there are three electrostatic boundary conditions to satisfy:
(1) An equipotential AFM tip surface equal the electrical potential, \( V \), applied to the tip.
(2) The tangential component of electric field \( E \) is continuous across the interface between the dielectric medium (air) and the dielectric specimen.
(3) The normal component of electric displacement \( D \) is continuous across the interface between the dielectric medium and dielectric specimen.

The conical part the AFM tip contribution in a spherical tip can be modeled using the line charge model developed by Huang Wen et al.\(^{42}\). The conical part of AFM tip contribution in a disk tip was modeled using ANSYS. The conical part was simplified as a 20 \( \mu \)m long metallic coated silicon with a full cone angle of 30\(^\circ\). By applying the calculated potential as the boundary condition for the piezoelectric coupling simulation using ANSYS, the deformation of the ferroelectric resulting from the AFM tip can be simulated. Piezoelectric response of a single domain lithium niobate in true contact with the tip was simulated with finer meshing of the sample surface below the tip and coarser meshing away from the tip. The meshing was adjusted until the results converged and became independent of the fineness of the meshing system.

IV. ANALYTICAL THEORY OF THE PFM RESPONSE ACROSS A DIFFUSED DOMAIN WALL

A. Resolution function approach

Since the goal of this work is the extraction of an 180\(^\circ\) domain wall diffuseness, we consider a single domain wall with the strain piezoelectric coefficient tensor terms \( d_{ij} \) dependent only on lateral coordinates \( x \) and \( y \) perpendicular to the polarization direction. The system is considered uniform in the polarization direction, \( z \). In LiNbO\(_3\), in particular, the domain walls tend to be parallel to the crystallographic \( y-z \) planes, hence the spatial dependence needs to be considered only as a function of the wall normal coordinate, \( z \). The surface displacement vector \( U_f(z) \) (measured PFM piezoresponse) is given by the convolution of piezoelectric tensor coefficients \( d_{ij}(x) \) with the resolution function components \( W_{ijk}(x,y) \) as proposed in Ref. 33. Since in many cases, the inhomogeneous distribution of piezoelectric coefficients are similar, e.g., for ferroelectrics they are determined by the polarization distribution, hereafter we denote the inhomogeneous part of the piezoelectric coefficients as function \( \beta(x) \). In this approximation, the components of the surface displacement below the tip can be written as follows:\(^{33}\)

\[
U_f(x) = \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy W_{ijkl}(-x',-y) d_{ijkl}^{\text{bulk}} \beta(x-x'),
\]

(1) Here \( d_{ijkl}^{\text{bulk}} \) are constant piezoelectric coefficients of bulk material. The resolution function is introduced as

\[
W_{ijkl}(x,y) = c_{kijn} \int_{0}^{\infty} dz \frac{\partial G_{ijn}(-x,-y,z)}{\partial x_n} E_j(x,y,z).
\]

(2) Here \( E_j \) is the component of the external electric field produced by the probe, \( c_{kijn} \) are stiffness tensor components, and \( \partial G_{ijn} / \partial x_n \) is a semispace elastic Green tensor derivatives on Cartesian coordinate \( x_n = (x,y,z) \). For most inorganic ferroelectrics, the elastic properties are weakly dependent on orientation and hereinafter the material can be approximated as elastically isotropic. Corresponding Green’s tensor \( G_{ij}(x,y,z) \) for elastically isotropic half-plane is given by Lur’\( ^e \)\(^{38} \) and Landau and Lifshitz.\(^{44}\)

Using decoupling approximation,\(^{45,30} \) and resolution function approach\(^{32} \) for transversally isotropic media,\(^{33} \) vertical piezoelectric response of isolated 180\(^\circ\)-domain wall in the inhomogeneous electric field of the probe tip has the form\(^{46,40} \)

\[
d_{35}^{\text{eff}}(x) = \frac{U_f(x)}{V} = \frac{1}{2V} \int_{-\infty}^{\infty} U_3^{\text{step}}(x-x') \frac{\partial \beta(x')}{\partial x'} dx'.
\]

(3) Here \( V \) is electric bias applied to the probe tip; \( U_f(x) \) is the surface displacement below the tip located at distance \( x \) from the plain domain wall located at \( x = a_0 \). The surface displacement \( U_3^{\text{step}}(x) \) of a steplike infinitely thin domain wall is derived in Ref. 33. Below we list the final close-form expression

\[
U_3^{\text{step}}(x) = V \left( \frac{x(1 + \nu) f_{313} - x f_{333}}{|x| + C_{333} z_o} \right) + \frac{x f_{351} d_{15}}{|x| + C_{351} z_o}.
\]

(4) Here \( d_{15} = d_{13}^{\text{bulk}} = d_{15}^{\text{bulk}} \) in the Vogt notation, \( \nu \) is the Poisson ratio. Characteristic distance \( z_o \) is determined by the parameters of the tip. In the effective point charge model it is the charge-surface separation. If we approximate the tip by the metallic disk of radius \( r \) in contact with surface, then \( z_o = 2r / \pi \). The expressions for material anisotropy constants \( f_{ijk} \) and \( C_{ijk} \) are given in Appendix A.

Using Eq. (4), we can derive a simple approximation for the effective width, \( \omega_{\text{PFM}} \) of infinitely thin domain wall (measured as distance between the points where the response is equal to \( \pm (1 - \eta) \) fraction of saturation polarization

\[
\omega_{\text{PFM}} = 2z_o \frac{1 - \eta [(1 + \nu) f_{313} C_{313} - f_{333} C_{333}] d_{31} + f_{333} C_{333} d_{33} + f_{351} C_{351} d_{15}}{[(1 + \nu) f_{313} - f_{333}] d_{31} + f_{333} d_{33} + f_{351} d_{15}}.
\]

(5) It should be noted that we have neglected the contribution of \( d_{22} \) and related terms, since their contribution far from the wall is exactly zero in the framework of the decoupling approximation model.\(^{37} \)
In the effective point charge approximation of the tip, electric field and dielectric anisotropy $\gamma = 1$, vertical piezoresponse $d_{33}^{eff}$ at a distance $x$ from the exponential domain wall profile $\beta(x, \omega_0) = [1 - \exp(-|x|/\omega_0)\text{sign}(x)]$ admits closed-form analytical representation:

$$d_{33}^{eff}(x, \omega_0, z_0) = \left[ -\left( \frac{1}{4} + \nu \right) d_3 + \frac{3}{4} d_3 + \frac{d_{15}}{4} \right] \beta(x, \omega_0) - \left[ -\left( \frac{1}{4} + \nu \right) d_3 + \frac{3}{4} d_3 + \frac{d_{15}}{4} \right] \frac{z_0}{8\omega_0} \left[\exp\left(\frac{|x|}{\omega_0}\right) F\left(\frac{z_0}{4\omega_0}\right) - F\left(\frac{|x|}{\omega_0} + \frac{z_0}{4\omega_0}\right)\right] \text{sgn}(x).$$

(6)

Here, $\omega_0$ is the intrinsic wall width for the wall profile described by $\beta(x, \omega_0)$, function $F(x) = \exp(-x)\text{Ei}(x) - \exp(x)\text{Ei}(-x)$, where $\text{Ei}(x) = \int_x^\infty \frac{\exp(-t)}{t} dt$ is the tabulated exponential integral function. An approximation $F(x) \approx [2x/(x^2 + c)] - [2x/(x^2 + c)]\ln[|x|/(|x| + 1)]$ (constant $c = 1/\Gamma(1-EulerGamma) \approx 2.365$) is valid with 3% accuracy for all $x$-range. The first term in Eq. (6) is the ideal image $\beta(x, \omega_0)$ of domain wall intrinsic profile. Near and far from the wall plane, the following expansions are valid:

$$d_{33}^{eff}(x) = \begin{cases} \frac{x}{\omega_0} \left[ -\left( \frac{1}{4} + \nu \right) d_3 + \frac{3}{4} d_3 \right] \left[ 1 + \frac{z_0}{4\omega_0} \text{Ei}\left(\frac{z_0}{4\omega_0}\right) \right] + \frac{d_{15}}{4} \left[ 1 + \frac{3z_0}{4\omega_0} \text{Ei}\left(\frac{3z_0}{4\omega_0}\right) \right], & |x| < \omega_0 \\
\text{sgn}(x) \left[ -\left( \frac{1}{4} + \nu \right) d_3 + \frac{3}{4} d_3 + \frac{d_{15}}{4} \right] \left[ \frac{3z_0}{4|x| + z_0} \right], & |x| \gg \omega_0, \end{cases}$$

(7)

B. Contribution of the conical part to the disk model for the tip

It is known that the conical part of the probe, as well as the tip-surface contact area contributions to the electrostatic potential broaden and diffuse the piezoresponse profile of the wall. To estimate the cone effects in PFM imaging, the conical part was modeled by a line charge,42 and the contact area by a disk touching the sample surface, as proposed elsewhere.42

Using electric field superposition principle, below we consider the probe electrostatic potential $\varphi(r, z)$ as the sum of effective line charge potential, $\varphi_L$, point charge potential $\varphi_q$, and disk potential $\varphi_D$:

$$\varphi(r, z) = \varphi_L(r, z) + \varphi_q(r, z) + \varphi_D(r, z).$$

(8)

Here the radius $r = \sqrt{x^2 + y^2}$. Normalization in Eq. (7) is such that $\varphi_L(0, 0) + \varphi_D(0, 0) + \varphi_q(0, 0) = V$, the applied potential to the tip. The conical part potential $\varphi_L$ is modeled by the linear charge of length $L$ with a constant charge density $\lambda_L = 4\pi\varepsilon_0 V \ln[(1 + \cos \theta)/(1 - \cos \theta)]$, where $\theta$ is the cone apex angle. Additional point charge potential $\varphi_q$ is chosen to reproduce the conductive tip surface as closely as possible by the isopotential surface $\varphi(r, z) = V$. The contact area potential is modeled by a disk of radius, $r$ (see Appendix B). Numerical calculations proved that the charge $q$ is located at the end of the line at a distance of approximately the disk radius $r$ from the surface, and that $q = 4\pi\varepsilon_0 V r$ for a wide range of cone angles $\theta$. It is clear from the Fig. 6 that for a chosen geometry, the isopotential surface $\varphi(r, z) = V$ reproduces the conductive tip shape in the vicinity of the surface for a wide range of cone angles $\theta$. Next we calculate domain wall profiles including different parts of the probe.

C. Diffused domain wall profile

Analytical theory predictions of the vertical PFM response near the single domain wall in LiNbO$_3$ are shown in Fig. 7. The influence of the tip radius itself on the wall profile is shown in Fig. 7(a) for a step-like wall (diffuseness $\omega_0 = 0$), clearly indicating the PFM wall width increase with radius $r$. The influence of domain wall diffuseness is shown in where the piezoelectric coefficient profile is $d_{33}^{eff}(x) = d_{33}^{bulk}\text{tanh}(x/\omega_0)$ [i.e., the intrinsic profile $\beta(x) = \text{tanh}(x/\omega_0)$]. This is chosen to mimic the polarization variation, $P_3$ across a 180°-domain wall, given by $P_3(x)$.
radii

significant nonlinearity to these curves for approximately tip series of theory plots in Fig. 4, along with experimental data

50, 70, 88, 110, 150, and 200 nm

LiNbO₃ as a function of the distance from the diffused wall with different away from the wall, where simulations show excellent

sample surface. The experiments, analytical theory, and FEM
differentially observed. Introducing an imaginary dielectric layer gap (air) of 2 nm (which is large) between the spherical tip and the surface increases the predicted \( \omega_{PFM} \), but still is considerably less than the experimentally measured widths. Only the disk-type tip model, including the conical section shows the best agreement with the experiments. In the context of the presented work, these results rule out the spherical text of the presented work, these results rule out the spherical

other. Within error bars, both experimental and simulated values of the maximum displacement \( U_z \) and the corresponding \( d_{33}^{eff} \) are relatively insensitive to the tip radius, and the presence of the cone. These agreements provide us confidence in our experimental and simulation methods.

Figure 8 shows a comparison of the \( \omega_{PFM} \) as a function of tip radius \( r \) for various tip models. It is clear from the comparisons that spherical tips with a point contact do not agree quantitatively with experimental results. The predicted PFM widths in this case are much smaller than those experimentally observed. Introducing an imaginary dielectric layer gap (air) of 2 nm (which is large) between the spherical tip and the surface increases the predicted \( \omega_{PFM} \), but still is considerably less than the experimentally measured widths. Only the disk-type tip model, including the conical section shows the best agreement with the experiments. In the context of the presented work, these results rule out the spherical tip models and the possibility of dielectric gaps. True contact with a disk-type tip and no dielectric gap therefore reflects the true nature of the PFM imaging presented here.

B. PFM wall widths versus intrinsic wall width

Finally, we pose the primary question we began with: what information can we extract about the intrinsic wall width of a ferroelectric using PFM? This question is naturally related with the question of what the resolution of the PFM technique is. FEM and analytical theory show that for a point contact of the tip, and in the absence of the conical part of the tip, the PFM wall width tends to zero. In other words, infinite resolution is, in principle, possible. However, this is not practical due to the presence of the cone. With the cone part of the tip, (20 \( \mu \)m long metallic coated silicon with a full cone angle of 30°), the linear extrapolation of the FEM

FIG. 8. (Color online) A comparison of different tip models with the experimental data for the \( \omega_{PFM} \) across a wall as a function of tip radius, \( r \). The experimental data are shown for sphere-type (tip set 1), and disk-type (tip set 2) tips. The different theory curves are as follows: (1) Analytical theory of a diffuse domain wall with \( \omega_0=100 \) nm using a disk-tip including cone section. (2) Analytical theory of a step domain wall with \( \omega_0=0 \) nm using a disk-tip, including cone section. (3) Analytical theory of a step domain wall with \( \omega_0=0 \) nm using a disk-tip, excluding the cone section. (4) FEM with \( \omega_0=0 \) nm using a disk-tip, including the cone section. (5) FEM with \( \omega_0=0 \) nm using a disk-tip, excluding the cone section. (6) FEM with spherical tip (excluding cone) removed at a distance of \( d=2 \) nm from the surface of the sample. (7) FEM with spherical tip including the cone, with \( d=0 \) nm. (8) FEM with spherical tip excluding the cone, with \( d=0 \) nm.

FIG. 7. (Color online) (a) Normalized theoretical PFM response profile near a steplike 180° domain wall (\( \omega_0=0 \)) in LiNbO₃ for disk radius \( r=17, 25, 36, 50, 70, 88, 110, 150, \) and 200 nm (curves 1–9, respectively), a cone length \( L=20 \) \( \mu \)m, \( \theta=15° \) for the PFM tip and an intrinsic half width \( \omega_0=20 \) nm. (b) Theoretical vertical PFM response near the single domain wall in LiNbO₃ as a function of the distance from the diffused wall with different half width values \( \omega_0=3, 30, 60, \) and 90 nm (curves 1, 2, 3, and 4, respectively); \( r=30 \) nm, \( L=20 \) \( \mu \)m, and \( \theta=15° \). The intrinsic wall diffuseness, \( d_{33}(x)\tan(x/\omega_0) \) is schematically shown in the inset

\[ d_{33}^{eff} = P_b^\text{bulk} \tanh(x/\omega_0), \]

since the piezoelectric coefficients and the polarization are linearly related by the electrostriction tensor. As expected, domain wall diffuseness broadens the PFM wall profile for a given tip radius \( r \). Similar results can be obtained for an exponential wall diffuseness profile by using Eqs. (6) and (7).

The combination of both a change in tip radius, \( r \) and a change in the wall diffuseness \( \omega_0 \) was previously shown in a series of theory plots in Fig. 4, along with experimental data points. The PFM wall width increases linearly with the tip radius \( r \) for a steplike wall. Domain wall diffuseness, \( \omega_0 \) adds significant nonlinearity to these curves for approximately tip radii \( r < \omega_0 \). The general quantitative agreement between the theory and experiments is excellent. It also suggests that there may be significant domain wall diffuseness in LiNbO₃ crystals. This issue is discussed in greater detail in Sec. V.

V. COMPARISON BETWEEN EXPERIMENTS, SIMULATION, AND THEORY

A. PFM amplitude and width

Figure 3 (shown earlier) plots the maximum effective piezoelectric coefficient, \( d_{33}^{eff}=U_z/V \) measured and simulated away from the wall, where \( V \) is the maximum voltage on the sample surface. The experiments, analytical theory, and FEM simulations show excellent quantitative agreement with each
predicted PFM width to zero tip contact radius is \( \sim 11 \pm 10 \) nm, which is statistically zero width. However, practical consideration of a finite tip contact radius, and abrasion of the tip while in contact with the sample results in experimentally measured PFM widths on the order of \( \sim 100 \) nm.

Nonetheless, if enough statistical data points are collected as in Fig. 4, one can begin to make some conclusions about intrinsic ferroelectric wall widths. Experimental results in Fig. 4 show a significant scatter in PFM widths up to 100 nm and more particularly in the small tip contact radius range. Does this reflect information regarding the intrinsic ferroelectric wall width at the surface?

To answer this, we first explore extrinsic factors such as tilted domain walls with respect to the surface normal. Cross-sectional polishing, etching, and imaging of domain walls reveal that within error of measurement, the domain walls in our samples were typically \(<0.1^o - 0.5^o\), and in some extreme cases, as much as 2.6° away from the surface normal. FEM simulations with tilted walls were performed, with no cone, and zero intrinsic domain wall width. The PFM wall width is apparently broadened by this tilt. For a 5° tilt, the extrapolated PFM wall width at zero tip contact radius was \( \sim 10 \) nm. For typical values of 0.1° tilt, the corresponding PFM width at zero tip contact radius was simulated to be <0.5 nm. Thus, one can reasonably say that domain wall tilts cannot account for full range of scatter of PFM widths (at zero tip contact radius) over 10 nm.

Finally, one can incorporate an intrinsic wall diffuseness, \( 2\omega_o \), in the analytical theory in terms of piezoelectric tensor distribution \( d_{ij}(x) = \rho_{ij}^{bulk} \operatorname{tanh}(x/\omega_o) \). (This was not possible with the ANSYS software; hence, FEM simulation was not performed.) Figure 4 shows the theoretical PFM width predictions for different values of intrinsic domain wall diffuseness. The PFM wall width versus tip contact radius becomes nonlinear for small tip radius, and reaches a saturation value equal to the intrinsic wall diffuseness in the limit the tip radius equals zero. The scatter of experimental data points fall below the \( 2\omega_o \sim 100 \) nm theory curve, suggesting a range of intrinsic wall diffuseness at the surface of congruent LiNbO₃. Figure 9(a) shows that for large tip radius \( (r = 200 \) nm), the match between experiments, FEM, and analytical theory is excellent, and \( \omega_o \) has little influence on the wall profile. However, as the tip radius \( r \) approaches \( \omega_o \), the simulation of a sharp (steplike) domain wall does not faithfully match the experimental line profile. Figure 9(b) shows that an excellent fit is obtained only when \( 2\omega_o = 60 \) nm for that particular line profile. This analysis was repeated for all the data points in Fig. 4, and \( 2\omega_o \) is found to vary from 20 to 100 nm.

One should also consider the possibility of the influence of moisture forming a water meniscus in the region of the PFM tip contacting the sample, and thus increasing the lateral extent of the tip itself. While such influences can be eliminated only by performing PFM experiments in controlled atmospheres, we believe that the observed wall broadening in this study has a dominant intrinsic component, for the following reason. Independent measurements of domain wall width in congruent LiNbO₃ using SNDM technique also show such widths.\(^{48}\) Cho et al.\(^{23,24}\) recently demonstrated imaging of the Si(111)7 × 7 surface atomic structure using similar second and third order capacitance terms in SNDM showing <0.5 nm resolution of SNDM. Surface domain wall widths of 20–150 nm have been measured in LiNbO₃ and LiTaO₃ crystals by this technique.\(^{48}\) Images in Ref. 22 reveal that the larger wall widths arise when large polar and dielectric defects exist adjacent to the wall. While SNDM has the resolution to reveal these defects, its signal is harder to interpret directly in terms of material properties. The PFM technique, in contrast, detects it as an effective broadening of the polarization profile across the domain wall. Similar SNDM studies in isostructural lithium tantalate,\(^{48}\) performed in cross-sectional, y-cut geometry of the crystal reveal that the wall width decreases from \( \sim 15 \) nm just below the surface to \( \sim 2.5–1 \) nm at a depth of \( \sim 50–100 \) nm from the \( z \)-surface of the crystal. This shows that surfaces also broaden domain walls. Thus, we conclude that dielectric/polar defects and surfaces can broaden antiparallel ferroelectric domain walls, and this broadening, on the scale of tens of nanometers is being detected in these PFM studies as broadening of the polarization profile.

VI. CONCLUSIONS

In conclusion, we have shown that PFM can be a quantitative tool for probing piezoelectric materials, and particu-
larly ferroelectric domains and domain walls. A PFM tip
with finite contact area and in true contact with the sample
surface gives the best agreement between PFM experiments,
analytical theory, and finite element modeling of the PFM
response across a domain wall. The PFM amplitude is in-
dependent of the tip radius. The PFM width across a sharp
domain wall is linear with tip contact radius, and is predicted
in theory to provide infinite resolution for a point contact.
However, practically, the presence of conical part of the tip,
slight tilts of the wall with respect to surface normal, and
importantly, the abrasion of the tip on contact with the sample
leads to finite resolution on the order of ∼10–20 nm. Theory predicts that walls with finite intrinsic
diffuseness will lead to a nonlinear relationship between
PFM width and tip contact radius, particularly for small tip
radii on the scale of wall diffuseness. Using a combination
of PFM experimental line profiles across 180° domain walls,
analytical theory, and FEM simulations, we conclude that
real domain walls on the surface of lithium niobate show
broadened walls on the scale of 2ω0 ∼ 20–100 nm, with
considerable scatter from location to location. The scatter
arises from the surface influence, as well as the presence of
dielectric and polar defects adjacent to walls, which have
been imaged by SNDM technique and reported in literature
in these materials.22,49 The PFM results show that these
defect-domain wall interactions lead to an effective broadening
of the walls in terms of polarization.

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| TABLE I. Relevant physical properties of LiNbO3 and LiTaO3. |
|-----------------|----------------|-----------------|-----------------|
| ϵ_{11} | ϵ_{33} | γ | d_{15} (pm/V) | d_{31} (pm/V) | d_{33} (pm/V) |
| LiNbO3 | 85 | 29 | 0.58 | 68 | -1 | 6 |
| LiTaO3 | 54 | 44 | 0.90 | 26 | -2 | 8 |

| TABLE II. Relevant PFM parameters in Eqs. (A1a)–(A1d) for LiNbO3 and LiTaO3. |
|-----------------|----------------|-----------------|-----------------|
| f_{331} | f_{333} | f_{351} | C_{311} | C_{333} | C_{351} |
| LiNbO3 | -1.26 | -0.86 | -0.14 | 0.24 | 0.21 | 0.68 |
| LiTaO3 | -1.05 | -0.775 | -0.225 | 0.25 | 0.24 | 0.74 |

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APPENDIX A: MATERIALS ANISOTROPY CONSTANTS, f_{ijk} and C_{ijk} in Section IV A

More rigorous consideration of disk part46 leads to the
substitution \( x_f 3_{ij} / (|x| + C_{3j} z_o) \rightarrow (2/\pi) f_{3ij} \arctan(x / (C_{3j} z_o)) \) in Eq. (4), valid for sharp domain walls.

Constants \( f_{ijk} \) and \( C_{ijk} \) depend only on the material di-
electric anisotropy factor \( \gamma \equiv \sqrt{\epsilon_{33} / \epsilon_{11}} \) as
\[
\begin{align*}
\gamma_{331} &= -\frac{\gamma^2}{(1 + \gamma)^2}, \\
\gamma_{333} &= -\frac{1 + 2\gamma}{(1 + \gamma)^2}, \\
\gamma_{351} &= -\frac{2}{1 + \gamma}. \\
\end{align*}
\]

APPENDIX B: CONTACT AREA POTENTIAL FOR

DISK-LIKE TIP

We consider the probe electrostatic potential \( \varphi(p, z) \) as
the sum of effective line charge potential, \( \varphi_{L} \), point charge
potential \( \varphi_{q} \), and disk potential \( \varphi_{D} \):
\[
\varphi(p, z) = \varphi_{L}(p, z) + \varphi_{q}(p, z) + \varphi_{D}(p, z),
\]

Here \( r = \sqrt{x^2 + y^2} \) is the radial coordinate. Under the condition \( \epsilon_{11,33} \gg 1 \) typically valid for the majority of ferroelectrics
in air, the following expressions for potential structure are valid:

\[
\begin{align*}
\varphi_{L}(p, z) &= \frac{V}{\ln\left(\frac{1 + \cos \theta}{1 - \cos \theta}\right)} \left\{ \begin{array}{ll}
\frac{2}{1 + \kappa} & \text{if } z > 0, \\
\frac{1 - \kappa}{1 + \kappa} & \text{if } z < 0,
\end{array} \right.
\end{align*}
\]

\[
\begin{align*}
\varphi_{q}(p, z) &= \frac{2}{1 + \kappa} \left( \frac{L + \Delta L + z + \sqrt{(L + \Delta L + z)^2 + p^2}}{\Delta L + z + \sqrt{(L + \Delta L + z)^2 + p^2}} \right), \\
\end{align*}
\]

\[
\begin{align*}
\varphi_{D}(p, z) &= -\frac{2}{1 + \kappa} \left( \frac{L + \Delta L - z + \sqrt{(L + \Delta L - z)^2 + p^2}}{\Delta L - z + \sqrt{(L - \Delta L - z)^2 + p^2}} \right),
\end{align*}
\]

\[
\begin{align*}
\varphi(p, z) &= \varphi_{L}(p, z) + \varphi_{q}(p, z) + \varphi_{D}(p, z),
\end{align*}
\]

\[
\begin{align*}
\varphi_{L}(p, z) &= \frac{V}{\ln\left(\frac{1 + \cos \theta}{1 - \cos \theta}\right)} \left\{ \begin{array}{ll}
\frac{2}{1 + \kappa} & \text{if } z > 0, \\
\frac{1 - \kappa}{1 + \kappa} & \text{if } z < 0,
\end{array} \right.
\end{align*}
\]

\[
\begin{align*}
\varphi_{q}(p, z) &= \frac{2}{1 + \kappa} \left( \frac{L + \Delta L + z + \sqrt{(L + \Delta L + z)^2 + p^2}}{\Delta L + z + \sqrt{(L + \Delta L + z)^2 + p^2}} \right), \\
\end{align*}
\]

\[
\begin{align*}
\varphi_{D}(p, z) &= -\frac{2}{1 + \kappa} \left( \frac{L + \Delta L - z + \sqrt{(L + \Delta L - z)^2 + p^2}}{\Delta L - z + \sqrt{(L - \Delta L - z)^2 + p^2}} \right),
\end{align*}
\]
Hereinafter, $\kappa = \sqrt{\varepsilon_{33} \varepsilon_{11}}$ is the effective dielectric constant and $\gamma = \sqrt{\varepsilon_{33} / \varepsilon_{11}}$ is the dielectric anisotropy factor. The conical part potential \( \varphi(q, z) \) is modeled by the linear charge of length $L$ with a constant charge density $q_L = 4 \pi \varepsilon_0 V / \ln[(1 + \cos \theta) / (1 - \cos \theta)]$, where $\theta$ is the cone apex angle. Additional point charge potential \( \varphi(0, z) \) is chosen to reproduce the conductive tip surface as closely as possible by the isopotential surface $\varphi(q, z) = V$. Our numerical calculations show that the charge $q$ is located at the end of the line; if that, the distance $\Delta L$ from the surface is approximately equal to the disk radius $r$ and $q = 4 \pi \varepsilon_0 V \Delta L$ for a typical range of cone angles $\theta$. Contact area potential \( \varphi(0, z) \) is modeled by the charged disk of radius $r$.

Using superposition (B1) we calculate the conical part of the probe electric field $E_z = -\partial \varphi / \partial x$, and then substitute it directly into Eq. (2).