<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Quantitative determination of tip parameters in piezoresponse force microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Authors(s)</strong></td>
<td>Kalinin, S. V.; Jesse, S.; Rodriguez, Brian J.; et al.</td>
</tr>
<tr>
<td><strong>Publication date</strong></td>
<td>2007-05-24</td>
</tr>
<tr>
<td><strong>Publication information</strong></td>
<td>Applied Physics Letters, 90 (21): 212905-212905</td>
</tr>
<tr>
<td><strong>Publisher</strong></td>
<td>American Institute of Physics</td>
</tr>
<tr>
<td><strong>Item record/more information</strong></td>
<td><a href="http://hdl.handle.net/10197/5475">http://hdl.handle.net/10197/5475</a></td>
</tr>
<tr>
<td><strong>Publisher's statement</strong></td>
<td>The following article appeared in Applied Physics Letters, 90 (21) : 113105-113105 and may be found at <a href="http://link.aip.org/link/doi/10.1063/1.2200400">http://link.aip.org/link/doi/10.1063/1.2200400</a>. The article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.</td>
</tr>
<tr>
<td><strong>Publisher's version (DOI)</strong></td>
<td>10.1063/1.2742900</td>
</tr>
</tbody>
</table>

Downloaded 2018-12-15T03:05:12Z

The UCD community has made this article openly available. Please share how this access benefits you. Your story matters! (@ucd_oa)

Some rights reserved. For more information, please see the item record link above.
Quantitative determination of tip parameters in piezoresponse force microscopy

Sergei V. Kalinin, Stephen Jesse, and Brian J. Rodriguez
Materials Sciences and Technology Division and the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennesse 37831

Eugene A. Eliseev
Institute for Problems of Materials Science, National Academy of Science of Ukraine, 3 Krijianovskogo, 03142 Kiev, Ukraine

Venkatraman Gopalan
Department of Materials Science and Engineering and Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802

Anna N. Morozovska
V. Lashkaryov Institute of Semiconductor Physics, National Academy of Science of Ukraine, 41, Prospect Nauki, 03028 Kiev, Ukraine

(Received 19 January 2007; accepted 1 May 2007; published online 24 May 2007)

One of the key limiting factors in the quantitative interpretation of piezoresponse force microscopy (PFM) is the lack of knowledge on the effective tip geometry. Here the authors derive analytical expressions for a 180° domain wall profile in PFM for the point charge, sphere plane, and disk electrode models of the tip. An approach for the determination of the effective tip parameters from the wall profile is suggested and illustrated for several ferroelectric materials. The calculated tip parameters can be used self-consistently for the interpretation of PFM resolution and spectroscopy data, i.e., linear imaging processes. © 2007 American Institute of Physics. [DOI: 10.1063/1.2742900]
above the surface, as illustrated in Fig. 1(a). The domain wall profile, i.e., the vertical surface displacement \( u_3(s) \) at position \( a \) relative to the domain wall at position \( a_0 \) produced by a single charge \( Q \) at distance \( d \) from the surface [Fig. 1(b)] is

\[
\begin{align*}
  u_3(s) &= \frac{Q}{d} \tilde{u}_3(s) = \frac{1}{2 \pi e_0 (e_s + \kappa)} \frac{Q}{g_{331}(s, \gamma, \nu)} d_{s1} \\
  &+ g_{351}(s, \gamma) d_{15} + g_{333}(s, \gamma) d_{33},
\end{align*}
\]

(1)

where \( s = (a - a_0)/d \) is the coordinate along the domain wall normalized by charge-surface separation, \( e_s \) is the dielectric constant of the medium \( (e_s = 1 \) for air and \( e_s = 80 \) for water), \( \kappa = \sqrt{\epsilon_{11} \epsilon_{33}} \) is the effective dielectric constant of material, \( \gamma = \sqrt{\epsilon_{33} / \epsilon_{11}} \) is dielectric anisotropy factor, and \( \nu = 0.35 \) is Poisson modulus. The functions \( g_{ijk}(s, \gamma) \) are

\[
\begin{align*}
  g_{351}(s, \gamma) &= - \frac{s^2}{(1 + \gamma)^2 |s| + C_{351}(\gamma)^2}, \\
  g_{333}(s, \gamma) &= - \frac{1 + 2 \gamma s}{(1 + \gamma)^2 |s| + C_{333}(\gamma)}, \\
  g_{313}(s, \gamma, \nu) &= \frac{1 + 2 \gamma s}{(1 + \gamma)^2 |s| + C_{333}(\gamma)} \\
  &- \frac{2 + \nu s}{1 + \gamma |s| + C_{313}(\gamma)}. \\
\end{align*}
\]

(2a)

(2b)

(2c)

The constants \( C_{ijk}(\gamma) \) depend only on the dielectric anisotropy of the material and, in particular, for \( \gamma = 1 \) the corresponding values are \( \{C_{351}, C_{333}, C_{313}\} = \{0.75, 0.25, 0.25\} \). For the case of a single point charge, the domain wall profile for \( \gamma = 1 \) can be simplified as

\[
\begin{align*}
  d_{33}^\text{eff} &= d_{03} + \left[ \frac{3}{4} d_{33} + \frac{1}{3} d_{31} \right] \frac{s}{|s| + 1/4} \\
  &+ \frac{1}{4} d_{15} \frac{s}{|s| + 3/4}. \\
\end{align*}
\]

(3)

Here, we use Eq. (1) to establish an approach for tip calibration in a PFM experiment, i.e., the derivation of the parameters of image charge(s) representing the tip, \( \{Q_i, d_{im}\}_N \), from experimental data.

PFM measurements were performed on a commercial scanning probe microscopy system (Veeco MultiMode NS-III) equipped with additional function generators and lock-in amplifiers (DS 345 and SRS 830, Stanford Research Instruments, and model 7280, Signal Recovery), as described elsewhere. Measurements were performed using Pt and Au coated tips (NSC-12 C, Micromash, \( l = 130 \mu m \), resonant frequency of \( \sim 150 \) kHz, spring constant \( k \sim 4.5 \) N/m). The samples used were BaTiO$_3$ single crystals, switched domains in LiNbO$_3$, epitaxial lead zirconate titanate (PZT) thin films, and PZT ceramics.

The domain wall profile data acquired at multiple scan sizes (i.e., 30 nm, 100 nm, 300 nm, 1 \( \mu m \), and 3 \( \mu m \)) were exported to ASCII files. To determine tip parameters from experimental data, a MATLAB program was developed. Briefly, the functional

\[
F[u_3] = \left( \frac{1}{2 \pi e_0 (e_s + \kappa)} \sum_{m=0}^{N} \frac{Q_m}{d_m} \tilde{u}_3(s_m) \right)^2 da
\]

(4)

is minimized with respect to the set of image charges \( \{Q_i, d_{im}\}_N \) representing the tip. Here \( PR(a) \) is the measured piezoresponse and integration is performed over all available values. The number of images charges, \( N \), is predefined. The dielectric constant of the medium can be fixed to the value of free air \( (e_s = 1) \) or water in the tip-surface junction or imaging in liquid \( (e_s = 80) \). The output of the fitting process is the set of reduced charges \( q_i = Q_i / 2 \pi e_0 \) and their charge-surface separations \( d_i \). Note that the charges and the dielectric constants cannot be determined independently, since only \( Q_m / (e_s + \kappa) \) ratios enter Eqs. (1)–(4).

Shown in Fig. 2 is the example of a domain wall profile and the corresponding fit by Eq. (4) with \( N = 1 \) for LiNbO$_3$. The corresponding image charge parameters are summarized in Table I. Note that while functions in Eq. (1) allow the correct description of the functional behavior of the piezoresponse in the vicinity of the domain wall, the fit quality is significantly reduced for long-distance tails due to different statistical weightings of the regions close to and far away from the center of domain wall. The use of equally spaced data points leads to a better quality fit, as shown in Fig. 2(d). The fit in the vicinity of the domain wall is shown in Fig. 2(e). To improve the fit quality, more complex fitting functions with \( N = 2 \) and \( N = 3 \) were attempted. However, in-
dependent of the choice of the initial values of the image charge, the fit converged to a single image charge, i.e., \( d_1 = d \) and \( \sum Q_i = Q \).

Similar behavior was observed for other domain walls studied here, as summarized in Table I. The effective charge-surface separations are compared to the domain wall width determined using a standard Boltzmann fit. Note that for imaging in ambient and using the same tip, the charge-surface separations are comparable. In all cases, only a single image charge can be determined and fits with \( N = 2 \) or \( 3 \) result in a convergence of image charges to a single position independently of initial values. Careful inspection of the existing data sets has illustrated that in nearly all cases, the domain wall is asymmetric, i.e., domain wall profiles differ in positive and negative domains. This asymmetry can be due to tip-shape effects and may negatively affect the fitting procedure. To verify this assumption, we attempted fits of a symmetrized domain wall profile, \( u_3(a) = (u_3(a-a_0) + u_3(a_0-a))/2 \). However, in this case, the single point-charge fit provides a good description of the data as well.

This analysis suggests that the electrostatic field produced by the tip is consistent with a single point charge positioned at a relatively large separation from the surface, contrary to the behavior anticipated in contact mode imaging. To complement the simple point-charge model, we have extended the analysis to the case of a sphere-plane model (radius of curvature \( R_{\text{s}} \)) and disk-plane (radius \( R_{\text{d}} \)) model. In these cases, the domain wall profile can be approximated by Eq. (1), where effective charge value \( Q^* \) and distance \( d^* \) are

\[
Q^* = \begin{cases} 
4\pi e_0 e_\varepsilon \frac{\kappa + e_\varepsilon}{\kappa - e_\varepsilon} \ln \left( \frac{e_\varepsilon + \kappa}{2 e_\varepsilon} \right) R_0 U, & \text{sphere plane} \\
4e_0 (\kappa + e_\varepsilon) R_0 U, & \text{disk}
\end{cases}
\]

and

\[
d^* = \begin{cases} 
\frac{2 e_\varepsilon}{\kappa - e_\varepsilon} \ln \left( \frac{e_\varepsilon + \kappa}{2 e_\varepsilon} \right) R_0, & \text{sphere plane} \\
2R_{\text{d}} \pi, & \text{disk}.
\end{cases}
\]

Thus determined parameters are given in Table I. The sphere parameters are calculated both for ambient and water environments to account for possible capillary condensation effects. From the data, it is clear that the use of the sphere/air model leads to implausibly large radii. Hence, experimental data are consistent either with the presence of a capillary water film in the sphere model or conductive disk model. Note that previously developed formalisms\(^{14-16} \) for the polarization switching and spectroscopy in the point-charge model can be directly applied to the sphere model (image charges on one line), but not for the disk model.

To summarize, here we derive a closed-form expression for a domain wall profile in PFM of a 180° domain wall. An approach for determining the effective tip parameters from the wall profile is suggested and illustrated for several ferroelectric materials. Because of the limitations of available experimental data, only the single image charge can be determined reliably, corresponding to sphere/liquid or disk models for the tip. Because of the highly linear behavior of PFM imaging,\(^{18} \) the calculated image charge parameters can be used self-consistently for the interpretation of PFM resolution and spectroscopic data. Modeling of switching phenomena will require improved estimates of tip geometry.

Research supported by Division of Materials Science and Engineering, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725. VG would like to acknowledge support from NSF-DMR Grant Nos. 0507146, 0512165, 2132623 and 0602986.


\(^17\)A. Wu, P. M. Vilarinho, V. V. Shvartsman, G. Suchaneck, and A. L. Kholkin, Nanotechnology 16, 2587 (2005).


<table>
<thead>
<tr>
<th>Material</th>
<th>( e_\varepsilon )</th>
<th>Wall width (nm)</th>
<th>Point charge</th>
<th>Disc ( R_d ) (nm)</th>
<th>Sphere plane ( R_s ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNbO(_3)</td>
<td>1</td>
<td>96</td>
<td>1000</td>
<td>92</td>
<td>58.6</td>
</tr>
<tr>
<td>Epitaxial</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.8</td>
</tr>
<tr>
<td>PZT</td>
<td>1</td>
<td>107</td>
<td>2550</td>
<td>125</td>
<td>79.6</td>
</tr>
<tr>
<td>PZT in air</td>
<td>1</td>
<td>58</td>
<td>723</td>
<td>86.5</td>
<td>55.1</td>
</tr>
<tr>
<td>PZT in liquid</td>
<td>80</td>
<td>6</td>
<td>104</td>
<td>11.8</td>
<td>7.5 N/A</td>
</tr>
<tr>
<td>Sphere</td>
<td>( e_\varepsilon = 1 ) (( \mu )m)</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plane</td>
<td>( e_\varepsilon = 80 ) (nm)</td>
<td>75</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>