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Analysis of shape effects on the piezoresponse in ferroelectric nanograins with and without adsorbates

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Using $BaTiO_3$ as a piezoelectric model system we compare a finite element model with experimental data to demonstrate the impact of grain topography on the in-plane piezoelectric response at the perimeter. Our findings emphasize the need for a careful consideration of both electric field and piezoelectric tensor orientation. An analysis is given showing that the in-plane piezoresponse is a function of two directions of the electric field, whereas the out-of-plane response is a function of all three directions of the applied field. The effect of an adsorbate layer on the piezoelectric response is quantified with typical material parameters. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2010603]

Piezoresponse force microscopy (PFM) is the method of choice to investigate piezoactivity as a necessary condition for ferroelectricity on a nanometer scale.[1,2] In a previous letter we have shown that a $BaTiO_3$ single crystal perovskite under atmospheric conditions is covered by an adsorbate layer,[3] leading to a voltage drop across it. As a result the electric field applied to the perovskite is overestimated and misleading piezoelectric constants are calculated. All the above also applies to small grains.

In this letter we quantify the effect of these adsorbates on the electric potential distribution as well as the in-plane and out-of-plane piezoresponse. We simulate the effect of the contamination in the case of a nanograin for different tip positions on the grain. The results show a large influence of the grain shape on the detectable in-plane piezoresponse.

Figure 1 shows a profile of a 115-nm-high, 300-nm-wide $BaTiO_3$ grain modeled with ANSYS. An anisotropic dielectric permittivity of $\varepsilon_{11}=1500$ and $\varepsilon_{33}=75$[4,5] ($\tan\delta=0$) and the following piezoelectric constants are used:[4]

$$d_{33}=85.6\ \text{pm/V},$$

$$d_{31}=d_{32}=-34.5\ \text{pm/V},$$

$$d_{15}=d_{24}=392\ \text{pm/V}.$$

We assume a *c*-axis oriented sample, i.e., a polarization perpendicular to the bottom electrode.

In our model both the bottom electrode and the cantilever are made of Pt. The round tip with a diameter of 40 nm is approximated by a polygon. The insulating adsorbate layer is modeled with vertical thickness of 2 nm and $\varepsilon=6$.[6] A constant voltage of −1 V is applied to the cantilever.

We only model a cross section of $BaTiO_3$ which is possible without loss of generality due to the tetragonal symmetry (4 mm). These two-dimensional (2D) finite element simulation results are given in Figs. 2(a)–2(f). On the left [(a), (c) and (e)] we show the case without an adsorbate layer, while the right parts [(b), (d) and (f)] are calculated with an adsorbate layer. These images illustrate the steady state after the potential has been applied. A drastic influence of the adsorbate is visible in the potential distribution [parts (a) and (b)]. In the case of direct contact between the tip and $BaTiO_3$, the voltage drops over large parts of the grain. Due to the curvature of the tip, the voltage drop is highest directly underneath the tip.[7] In Fig. 2(b) the potential drops almost completely across the adsorbate layer so that the actual voltage applied to the grain is about one order of magnitude less than the voltage applied to the tip. This effect of an increasing thickness fraction of adsorbates on the field applied to the sample becomes evident in Fig. 3: The out-of-plane signal with adsorbates follows the topography. In the in-plane piezoresponse [parts (c) and (d) of Fig. 2] as well as the out-of-plane piezoresponse [parts (e) and (f)] the maximum contraction is nearly two orders of magnitude smaller than in the case of a clean surface. As the piezoresponse is directly proportional to the applied voltage, this confirms the expectation that the piezoresponse decreases dramatically in the case of present adsorbates.

Figures 2(c) and 2(d) indicate that the in-plane response is effectively zero on a flat (001) surface. This finding becomes clear if we recall the signal detection process. We are only sensitive to the deflection of the beam reflected from the cantilever, i.e., all we see is a somehow moving tip. In some

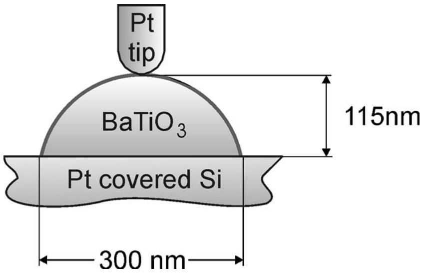

FIG. 1. Sketch of the $BaTiO_3$ nanograin used for the simulation.

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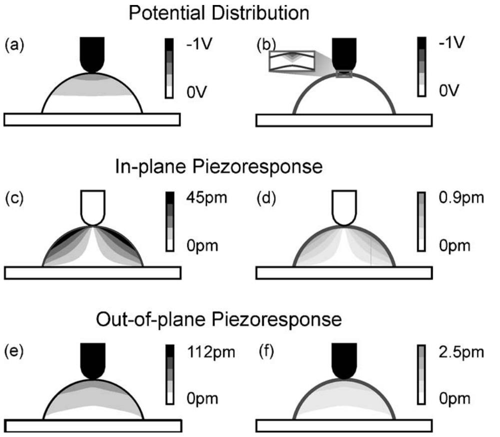

FIG. 2. Simulation of the potential distribution [(a) and (b)], the in-plane piezoresponse [(c) and (d)] and the out-of-plane piezoresponse [(e) and (f)] for an adsorbate free nanograin (left) as well as for an adsorbate covered nanograin (right).

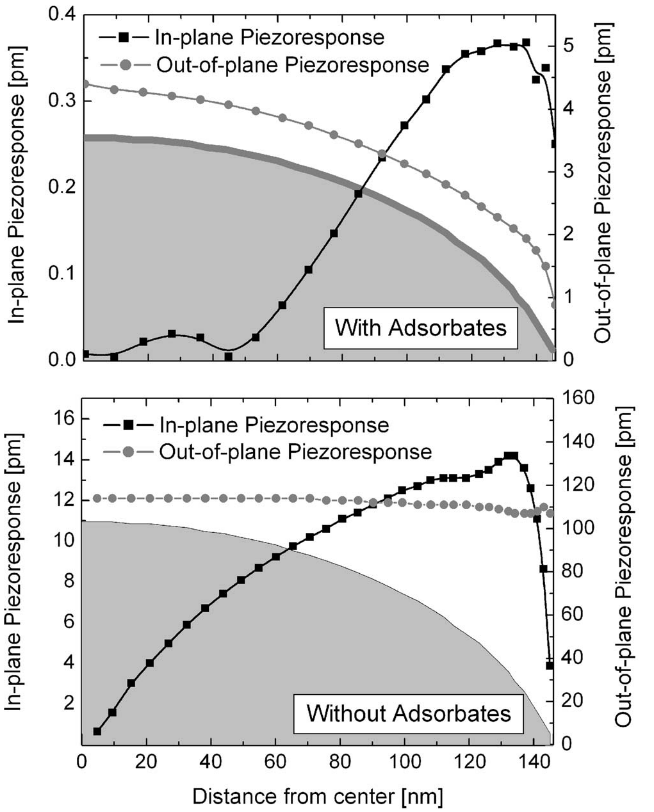

FIG. 3. Simulated in-plane and out-of-plane piezoresponse (absolute values) as a function of the distance from the center of the nanograin. In both clean and contaminated surfaces the in-plane response changes drastically. The out-of-plane activity decreases at the edge in the case with adsorbates due to an increasing thickness fraction of the adsorbates leading to a reduced voltage applied to the $BaTiO_3$. The lines connecting the simulated points are a guide to the eye.

cases this movement cancels out for symmetry reasons. This is exactly the case for the in-plane response on a flat surface of a (001) oriented sample with 4 mm symmetry.

We now move the tip off center whereby it is modeled as a point contact. The results are given in Fig. 3. An in-plane signal cannot be detected in a symmetric arrangement (as can also be seen in Figs. 2(c) and 2(d) where the in-plane response is 0 in the middle of the grain). The increase of the in-plane signal close to the perimeter is due to the broken radial symmetry underneath the tip. Note that for tetragonal symmetry no shearing is related to fields along the polar axis. In the presence of the adsorbate layer the in-plane piezoresponse near the edge is smaller compared to the case of a clean surface. The out-of-plane response without adsorbates is essentially thickness independent as the increasing field is cancelled out by the decreasing amount of expanding material. In the presence of adsorbates the out-of-plane response is dominated by the steadily growing thickness fraction of the adsorbates as we approach the perimeter.

We confirm these simulations in a dedicated piezoelectric system. Measuring these effects (constant piezoresponse in the out-of-plane direction and enhancement in the in-plane direction) is challenging as the polarization of the ferroelectric material needs to be uniform in the direction perpendicular to the substrate. Figure 4 shows the topography and piezoresponse of a $BaTiO_3$ grain prepared by pulsed laser deposition on a $SrRuO_3$ (50 nm) covered (100) $SrTiO_3$ single crystal. Our original out-of-plane PFM data show a background piezoresponse signal that is removed in Fig. 4 (center image) to provide zero response for the electrode. According to Refs. 8,9 this offset is a measuring artifact due to an electrostatic interaction between the cantilever and the electrode.

For a constant voltage the electric field is inversely proportional to the thickness of the grain. Therefore the electric field at the perimeter may become sufficiently large to cause significant electrostriction.[10] In this case a simultaneous increase of both in- and out-of-plane piezoresponse would be detected near the edge in contrast to our observation. Depending on the radius of the tip and the form of the grain, this region may be inaccessible to measurements.

To sketch the physics of our simple system (most situations will be more complex), the applied electric field as well as the piezoelectric coefficients in all directions have to be taken into account. Figure 5 depicts the electric field for the case of a voltage applied to points A and B. The components of the electrical field distribution in direction 1 are different for the two points (i.e., component in direction 1 of E_A and E_B). As a consequence **E** and **P** are no longer parallel and shear deformation (d_{15}) occurs.

For constant temperature and with no additional mechanical stress the strain tensor is given as[11]

$$\epsilon_{jk} = d_{ijk}E_i.$$

For crystals like $BaTiO_3$ with 4 mm symmetry the piezoelectric tensor d_{ijk} can be written in the Voigt notation as

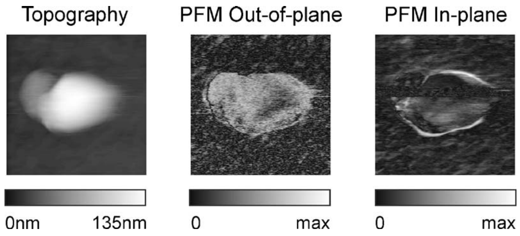

FIG. 4. Topography (500 nm × 500 nm), amplitudes of out-of-plane and in-plane piezoresponse of a $BaTiO_3$ grain. The out-of-plane response is relatively constant over the total grain, whereas the in-plane response is very small in the middle and high at the perimeter.

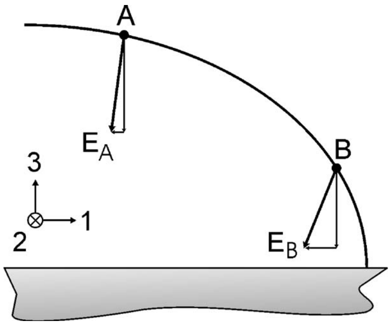

FIG. 5. Electric field magnitude and direction at Points A and B where a voltage of 1 V is applied. Note the difference of the component in direction 1 between E_A and E_B.

$$d_{ij} = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix} \text{ with } \begin{matrix} d_{31} = d_{32} \\ d_{15} = d_{24} \end{matrix}.$$

Considering the field distribution we obtain the following elements of the strain tensor:

$$\epsilon_{11} = d_{311}E_3,$$

$$\epsilon_{22} = d_{322}E_3,$$

$$\epsilon_{33} = d_{333}E_3,$$

$$\epsilon_{13} = d_{113}E_1 = \epsilon_{31} = d_{131}E_1,$$

$$\epsilon_{23} = d_{223}E_2 = \epsilon_{32} = d_{232}E_2.$$

The PFM setup is sensitive to a contraction or expansion of the piezoelectric material. This length change is dependent on the strain tensor and on the distance from the origin. These changes are in our case given as

$$\Delta\ell_1 = \epsilon_{11}\ell_1 + \epsilon_{13}\ell_3 = d_{311}E_3\ell_1 + d_{113}E_1\ell_3,$$

$$\Delta\ell_2 = \epsilon_{22}\ell_2 + \epsilon_{23}\ell_3 = d_{322}E_3\ell_2 + d_{223}E_2\ell_3,$$

$$\begin{aligned}\Delta\ell_3 &= \epsilon_{31}\ell_1 + \epsilon_{32}\ell_2 + \epsilon_{33}\ell_3 \\ &= d_{131}E_1\ell_1 + d_{232}E_2\ell_2 + d_{333}E_3\ell_3.\end{aligned}$$

We have compared our experimental data and finite element analysis of piezoelectricity in ferroelectric $BaTiO_3$ nanograins and find good agreement. We emphasize that PFM is very sensitive to the morphology of the sample. Even in single crystalline material we observe that the out-of-plane piezoresponse is a function of the electric field in *all three* directions and that the in-plane response is a function of the electric field in directions 1 and 3.

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