The origins of electromechanical indentation size effect in ferroelectrics

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Metals exhibit a size-dependent hardening when subject to indentation. Mechanisms for this phenomenon have been intensely researched in recent times. Does such a size effect also exist in the electromechanical behavior of ferroelectrics?—if yes, what are the operative mechanisms? Our experiments on $BaTiO_3$ indeed suggest an elastic electromechanical size effect. We argue, through theoretical calculations and differential experiments on another nonferroelectric piezoelectric (quartz), that the phenomenon of flexoelectricity (as opposed to dislocation activity) is most likely responsible for our observations. Flexoelectricity is the coupling of strain gradients to polarization and exists in both ordinary and piezoelectric dielectrics. In particular, ferroelectrics exhibit an unusually large flexoelectric response. © *2009 American Institute of Physics*.
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The indentation size effect of hardness in metals is generally attributed to dislocation activities.[1–4] The model developed by Nix and Gao[3] argues the role of geometrically necessary dislocations associated with the strong strain gradient characteristically located below indenters. Nix and coworkers also conducted uniaxial compression experiments on micro-/nanopillars of metals, demonstrating the pillar size dependence of strength.[5–7] However, since no strain gradient is involved in these experiments, a different mechanism, dislocation starvation hardening, was proposed,[6] although the exact origins are still an active area of research.[8] In ferroelectrics also, increasing hardness with decreasing indenter radius has been observed for both Lead Zirconate Titanate as well as $BaTiO_3$.[9,10] Although Schneider and co-workers reported the elastic modulus to be independent of the indenter radius, the absence of contact stiffness versus contact radius curves for each indenter limits any direct comparison with our work. In the present work, we pay careful attention as to how the elastic behavior changes in ferroelectrics as a function of the indent size. Although the elastic properties of ordinary metals and ceramics[11] are nearly size independent down to a few nanometers, ferroelectrics[12] and certain amorphous materials[11] may prove exception to the rule.

The so-called *elastic* indentation size effect is nicely illustrated by our experiments on $BaTiO_3$ (001) oriented single crystals ($5\times5\times1$ mm^3). A series of nanoindentations with a Berkovich indenter provided the contact stiffness versus contact radius curve (*s-a* curve) for comparison with the theoretically computed *s-a* curve for a circular flat indenter of various indenter radii. Considering the geometry-independent stiffness and contact radius relationship in the case of purely mechanical loading, the *s-a* curve for Berkovich indenter can be experimentally obtained in a single experiment. Since it is difficult to manufacture and maintain a conical indenter with a sharp tip, the reliable data in the small scale cannot be obtained. Therefore, we adopted a sharp Berkovich indenter (three-sided pyramid, the tip radius is ~50 nm) at the expense of well-defined contact radius. The area function of the indenter tip, $A=f(h_c)$ was carefully calibrated using standard procedures,[13] where h_c is the contact depth. Although the projected contact area is not circular for the Berkovich indenter, the effective contact radius is calculated from the contact area by $\pi a^2=f(h_c)$ and this approximation is quite good for small depths.

On the theoretical side, Karapetian *et al.*,[14] provided a detailed model of piezoelectric indentation. Within the assumption of transverse isotropy and restriction of indenter shape to be a cylinder, they interrelated applied concentrated force P, concentrated charge Q, indentation depth w, and tip potential ψ_0,

$$P=\frac{2aC_1^*w}{\pi}+\frac{2aC_3^*\psi_0}{\pi},$$

$$Q=\frac{2aC_2^*w}{\pi}+\frac{2aC_4^*\psi_0}{\pi}. \quad (1)$$

The contact stiffness, under purely mechanical loading, is $s=2(C_1^*/\pi)a$.

We note here that C_1^* is not just the elastic modulus but a combination of elasticity, piezoelectric, and dielectric tensor components. The important aspect to keep in mind is that contact stiffness varies linearly with a or, alternatively, the ratio of contact stiffness to contact radius is a size-independent "constant." We note that a similar relation is obtained for indentation on elastically isotropic half spaces,[13,15] C_1^* is πE_r, where E_r is the reduced elastic modulus. This stiffness relation was derived for an axisymmetric indenter (circular contacts); however, it has been shown that it works well even for the nonaxisymmetric shapes provided a small correction factor is used.[13,15]

In Fig. 1 we plot both our experimental results as well as the results from the aforementioned model based on classical piezoelectricity. From Fig. 1 two points are well evident: (i) our experiments suggest a strong indentation size effect and (ii) classical piezoelectricity, as anticipated from the model based on classical piezoelectricity,[14] fails to capture this. We may be tempted to resort to dislocations based arguments to explain this size effect. Our theoretical analysis (to follow),

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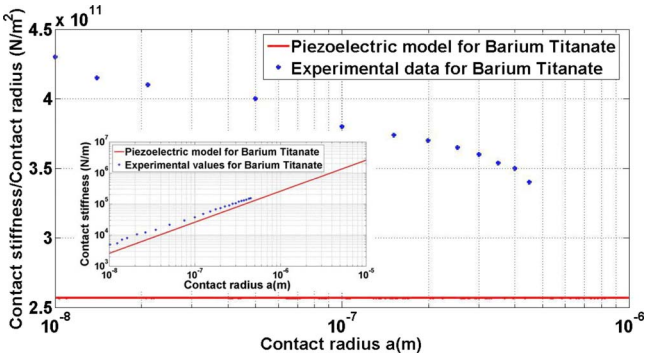

FIG. 1. (Color online) Variation in the ratio of the contact stiffness and contact radius with respect to the contact radius a for $BaTiO_3$. The inset graph plots the contact stiffness vs radius.

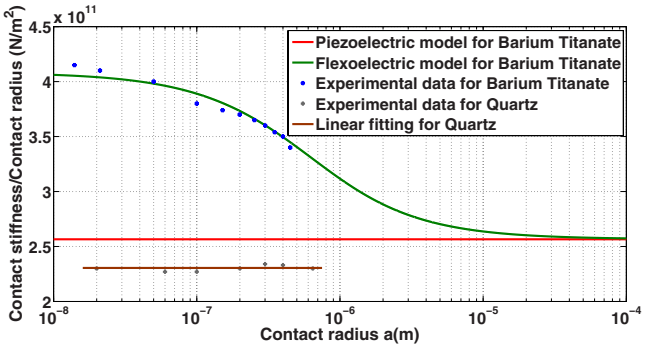

FIG. 2. (Color online) Variation in the ratio of the contact stiffness and contact radius as a function of contact radius. Experimental results for both $BaTiO_3$ and Quartz are plotted along with the results from the flexoelectricity and classical piezoelectricity based models.

however, hints toward another explanation, namely, *flexoelectricity*.

Piezoelectricity requires that the crystalline unit cell lack centrosymmetry (for example, NaCl is not piezoelectric, while $BaTiO_3$ is). An underappreciated fact is that in the presence of inhomogeneous strain, inversion symmetry can be broken, leading to the development of polarization even in nonpiezoelectric materials,

$$(P)_i = (d)_{ijk}(\varepsilon)_{jk} + (f)_{ijkl}\nabla_l(\varepsilon)_{jk}, \tag{2}$$

where d is the third order piezoelectric tensor and f is the fourth order flexoelectric tensor. This is well illustrated for graphene through *ab initio* simulation under bending (which is manifestly nonpiezoelectric)—e.g., Ref. 16.

Recently one of us has clarified some of the basic mechanisms behind flexoelectricity as well as evaluated flexoelectric properties through atomistic calculations.[17] Other very interesting works have also appeared. Experiments on finding flexoelectric properties were pioneered by Ma and Cross[18] who have established that flexoelectric constants are three orders of magnitude larger than ordinary dielectrics. Recently, Zubko[19] published the experimental characterization of the complete flexoelectric tensor of $SrTiO_3$. The two papers by Catalan and co-workers[20,21] describe the impact of flexoelectricity on properties of ferroelectric thin films, while a more recent letter[22] provides some interesting insights into the role of intrinsic strain gradients invariably present in ferroelectric nanostructures (e.g., nanoparticles). Recently, we have shown the prospects of enhanced piezoelectricity in nanostructures[12] due to flexoelectricity, its role in the origins of the dead layer in ferroelectric based nanocapacitors[23] and underscored Cross's idea[24] of the possibility of creating apparently piezoelectric materials without using piezoelectric materials.[25]

In prior work we have presented a mathematical formulation of the theory of flexoelectricity.[26] The equations are quite complicated even for an isotropic continuum, let alone an anisotropic crystal, which also exhibits direct piezoelectricity (as is the case for $BaTiO_3$). Nevertheless, we, employing a perturbation approach coupled with guidance from some partial numerical calculations, have been successful in generating closed form expression for the effect of flexoelectricity on indentation. Details of the model itself will be presented elsewhere.[27,28] To summarize, we find the following (for purely mechanical loading):

$$P = \frac{2a}{\pi}C_1^* w - \frac{2}{\pi a}f_1^* w \frac{\varepsilon}{(A^i)^2}(\varepsilon e^{-\frac{A^i}{\varepsilon}a} - \varepsilon + A^i a). \tag{3}$$

The ratio of the contact stiffness to the contact radius is then

$$\frac{s}{a} = \frac{1}{a}\frac{\partial P}{\partial w} = \frac{2}{\pi}C_1^* - \underbrace{\frac{2f_1^*}{\pi a^2}\frac{\varepsilon}{(A^i)^2}(\varepsilon e^{-\frac{A^i}{\varepsilon}a} - \varepsilon + A^i a)}_{\text{size effect}}, \tag{4}$$

where A^i and f_1^* are constants depending on the material properties and ε is the approximate value of flexoelectric and piezoelectric ratio. Equation (4) shows the presence of a size effect due to flexoelectricity (underlined terms). The results embodied in Eqs. (3) and (4) ignore some of the intrinsic polarization gradient effects alluded to by Catalan and co-workers[20,21] and Eliseev *et al.*[22] Given the large strain gradients caused by the indentation process relative to the intrinsic mechanisms, this approximation is justified in the present case (although certainly future work should explore the correction if any that would result from incorporating that effect).

Experiments of Ma and Cross[18] indicate that flexoelectric coefficients are quite large for $BaTiO_3$ and thus we anticipate flexoelectricity to contribute significantly. However, can other mechanisms such as dislocation hardening be ruled out? While the latter is a complex problem, two simple steps (one qualitative argument and the other a simple differential experiment) can help provide some insight. Quartz is not expected to exhibit a *widely* different dislocation activity from $BaTiO_3$; on the other hand, its flexoelectric properties are nearly three orders of magnitude lower than that of $BaTiO_3$. Accordingly, we also carried out an identical set of indentation experiments on quartz following essentially the same procedure as that for $BaTiO_3$. Comparisons of our flexoelectricity based model with both our experiments are shown in Fig. 2.

As well evident from Fig. 2, the agreement between our model and experiments is quite close—remarkably since there is no "fitting or calibration" performed between our theoretical/computational model and experiments. Quartz shows no size effect in the experiments and is clearly anticipated by our model since the flexoelectric constants are quite small for this material [i.e., the underlined term in Eq. (4) is essentially zero in the range of contact sizes shown in Fig. 2].

The role of mechanisms, such as domain wall activity, dislocation based mechanisms, among others, to explain the observed electromechanical size effect cannot be conclusively ruled out based solely on the work presented here. Certainly domain activities are absent in quartz. However, the argument that quartz has low flexoelectricity and coupled with the fact that we are emphasizing *elastic* behavior as well as the close agreement of our model with experiments indicates that flexoelectricity is most likely the dominant mechanism behind the observed size effect. Further, recent experiments by Luk'yanchuk *et al.*,[29] suggest a change in surface hardness as well which could very well be related to the present study.

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[1]N. A. Stelmashenko, M. G. Walls, L. M. Brown, and Y. V. Milman, Acta Metall. Mater. **41**, 2855 (1993).
[2]Q. Ma and D. R. Clarke, J. Mater. Res. **10**, 853 (1995).
[3]W. D. Nix and H. J. Gao, J. Mech. Phys. Solids **46**, 411 (1998).
[4]J. G. Swadener, E. P. George, and G. M. Pharr, J. Mech. Phys. Solids **50**, 681 (2002).
[5]M. D. Uchic, D. M. Dimiduk, J. N. Florando, and W. D. Nix, Science **305**, 986 (2004).
[6]J. R. Greer, W. C. Oliver, and W. D. Nix, Acta Mater. **53**, 1821 (2005).
[7]J. R. Greer and W. D. Nix, Phys. Rev. B **73**, 245410 (2006).
[8]J. R. Greer, C. R. Weinberger, and W. Cai, Mater. Sci. Eng., A **493**, 21 (2008).
[9]T. Scholz, J. Muñoz-Saldaña, M. V. Swain, and G. A. Schneider, Appl. Phys. Lett. **88**, 091908 (2006).
[10]A. Hurtado-Macias, J. Muñoz-Saldaña, F. J. Espinoza-Beltran, T. Scholz, M. V. Swain, and G. A. Schneider, J. Phys. D: Appl. Phys. **41**, 035407 (2008).
[11]R. Maranganti and P. Sharma, Phys. Rev. Lett. **98**, 195504 (2007).
[12]M. S. Majdoub, P. Sharma, and T. Cagin, Phys. Rev. B **77**, 125424 (2008); M. S. Majdoub, P. Sharma, and T. Cagin, Phys. Rev. B **79**, 119904(E) (2009).
[13]W. C. Oliver and G. M. Pharr, J. Mater. Res. **7**, 1564 (1992).
[14]E. Karapetian, M. Kachanov, and S. V. Kalinin, Philos. Mag. **85**, 1017 (2005).
[15]G. M. Pharr, W. C. Oliver, and F. R. Brotzen, J. Mater. Res. **7**, 613 (1992).
[16]T. Dumitrica, C. M. Landis, and B. I. Yakobson, Chem. Phys. Lett. **360**, 182 (2002).
[17]R. Maranganti and P. Sharma, Phys. Rev. B **80**, 054109 (2009).
[18]W. Ma and L. E. Cross, Appl. Phys. Lett. **88**, 232902 (2006).
[19]P. Zubko, G. Catalan, P. R. L. Welche, A. Buckley, and J. F. Scott, Phys. Rev. Lett. **99**, 167601 (2007).
[20]G. Catalan, L. J. Sinnamon, and J. M. Gregg, J. Phys.: Condens. Matter **16**, 2253 (2004).
[21]G. Catalan, B. Noheda, J. McAneney, L. J. Sinnamon, and J. M. Gregg, Phys. Rev. B **72**, 020102(R) (2005).
[22]E. A. Eliseev, A. N. Morozovska, M. D. Glinchuk, and R. Blinc, Phys. Rev. B **79**, 165433 (2009).
[23]M. S. Majdoub, R. Maranganti, and P. Sharma, Phys. Rev. B **79**, 115412 (2009).
[24]J. Fousek, L. E. Cross, and D. B. Litvin, Mater. Lett. **39**, 287 (1999).
[25]N. D. Sharma, R. Maranganti, and P. Sharma, J. Mech. Phys. Solids **55**, 2328 (2007).
[26]R. Maranganti, N. D. Sharma, and P. Sharma, Phys. Rev. B **74**, 014110 (2006).
[27]M. Gharbi, Z. H. Sun, P. Sharma, K. White, and S. El-Borgi (unpublished).
[28]See EPAPS supplementary material at http://dx.doi.org/10.1063/1.3231442 for details of derivation of the flexoelectric model.
[29]I. A. Luk'yanchuk, A. Schilling, J. M. Gregg, G. Catalan, and J. F. Scott, Phys. Rev. B **79**, 144111 (2009).