Stress and strain in ferroelectrics

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Ferroelectrics are being integrated into many structures, both large and small. Various innovations have once again brought the fundamentals of ferroelectricity into focus. Advances have been made in understanding stress and strain effects, especially on phenomena at small size scales. These phenomena include depoling and cracking in actuators, and properties of small free particles, fine grain ceramics and thin films.

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Abbreviations

BST	$Ba_xSr_{1-x}TiO_3$
PZT	$PbZr_{1-y}Ti_yO_3$

Introduction

Barium titanate ($BaTiO_3$) undergoes a phase transition at ~120°C. Above the transition temperature, the crystal has a cubic lattice. At room temperature, the crystal has a tetragonal lattice structure and a spontaneous polarization; that is, an applied electric field can switch the polarization from one direction to another. The high temperature phase is paraelectric and the room temperature phase is ferroelectric. Commercial uses of $BaTiO_3$ and related materials have largely been in the form of bulk ceramics [1]. Paraelectric $Ba_xSr_{1-x}TiO_3$ (BST) capacitors can store a large amount of electric charge per unit weight. Ferroelectric $PbZr_{1-y}Ti_yO_3$ (PZT) ceramics are ubiquitous as sensors and actuators. Some single crystals of ferroelectric materials can have large actuation strains and small hysteresis, and are being investigated for ultrasonic transducers [2••]. The past decade has seen intense research into thin films, motivated by the potential of integrating ferroelectrics onto silicon chips [3]. Applications of such materials include high-permittivity capacitors in dynamic random access memories, bistable media in nonvolatile memories and active parts in micromachines.

Drawing mainly upon work published since 1997, this article reviews stress and strain effects in ferroelectrics, and their relations to theoretical models at several length scales. Phenomenological constitutive laws, together with the field equations in mechanics and electrostatics, determine various fields in bulk structures. Domain dynamics underlie bulk behavior and are even more important to understanding thin films. Atomistic descriptions are needed for ultrathin films where interfaces dominate material behavior.

Paraelectric behavior

Due to their high permittivities, paraelectric BST ceramic films are being developed for dynamic random access memories. The capacitance of BST films, however, is lower than that anticipated from the bulk permittivity. Causes for this difference include interfacial capacitance, residual stress, and a fine grain structure. Experimental data have been fitted to an empirical relation [4••]:

$$\frac{1}{c}=\frac{1}{c_i}+\frac{t}{\varepsilon_f} \qquad (1)$$

Here c is the capacitance per unit film area and t the film thickness; c_i and ε_f are fitting parameters. The data are interpreted as follows [5•]; in a BST film, near a film-electrode interface, thin layers (thickness of approximately a few lattice constants) are 'dead', equivalent to a capacitor of a low-permittivity material. An applied voltage drops across the interfacial layers and the film in series. Consequently, c_i and ε_f are interpreted as the interfacial capacitance and the film permittivity, respectively. For a film thinner than 50 nm, c_i significantly limits the overall capacitance. The use of oxide, rather than metallic electrodes can increase the capacitance [6,7].

If a film was to be free-standing, a voltage applied across the thickness would cause it to contract in its plane by an electrostrictive strain $Q_{12}D^2$, where Q_{12} is the electrostrictive coefficient and D the electric displacement [8•]. A BST film on a silicon substrate, however, is often under a tensile residual stress, σ, as a result of the deposition process and a thermal expansion misfit. The Devonshire theory predicts a change in permittivity [9]:

$$\frac{1}{\varepsilon_f}=\frac{1}{\varepsilon_u}-4Q_{12}\sigma \qquad (2)$$

where ε_f is the permittivity of the stressed film and ε_u the permittivity of the unstressed film. Because $Q_{12} < 0$, a residual tension in the film reduces the permittivity. This above formula is valid for all dielectrics. For BST films, the change in permittivity can be pronounced because ε_u and σ are large. In an experiment (TM Shaw, Z Suo, M Huang, unpublished data), the residual stress was determined by a wafer curvature method, and Q_{12} by the capacitance change as the wafer was bent by a known mechanical load. The value of Q_{12} was found to be comparable with that of bulk BST.

Another cause for the permittivity reduction is the small grain size in the films. For $Ba_xSr_{1-x}TiO_3$ the composition x is often chosen such that the bulk crystal undergoes the cubic–tetragonal transition near room temperature, where permittivity peaks. For thin films of the same composition, x, the permittivity-temperature curve has no peak and the material remains paraelectric down to very low temperatures. This grain size effect will be discussed later in this review.

The residual stress in BST films can be in the gigaPascal range; this raises the question as to whether a ceramic film can sustain such a large tensile stress without cracking. The answer depends on the film thickness. The formation of a crack reduces elastic energy, but increases surface energy. As the film becomes thinner, the volume-to-surface ratio decreases, and the elastic energy reduction cannot compensate for the increase in surface energy, such that the crack cannot form. This energetic condition is expressed by

$$\beta t\sigma^2/Y<\gamma \qquad (3)$$

where t is the film thickness, σ the residual stress in the film, Y is Young's modulus, γ the surface energy, and β a dimensionless number of order unity. Consequently, a very thin film can sustain a large stress without cracking. This well established energetic approach has recently been applied to integrated microstructures [9].

Large stresses can also be generated by an electric field. In a multilayer actuator, around an internal electrode edge, the electric field is nonuniform and intense. Consequently, a stress field arises, which may cause the ceramic to crack. The problem causes a dilemma in developing new materials. On the one hand, materials capable of large strains are desired for actuators; on the other hand, the large strains make the devices prone to cracking near field concentration sites. There have been anecdotal observations that, as the device feature size miniaturizes, cracking may be averted. The trend can be understood in terms of the energetic consideration outlined above [10–12]. So far, no systematic experimental demonstration has been made. Note that the electric field is very high around an electrode edge. A constitutive law that captures the high field effects in electrostrictive materials has been implemented into finite element codes to analyze realistic device structures [11,12,13•].

Ferroelectric behavior

A ceramic must be poled by a strong electric field to exhibit overall piezoelectricity. Used as an actuator, the ceramic deforms under an electric field against a mechanical force. The compressive stress so generated may depole the material, leaving it nonpiezoelectric. An order of magnitude estimate of the depoling stress is given by,

$$E\Delta P\approx\sigma\Delta\gamma \qquad (4)$$

Here E is the electric field needed to pole a sample under no stress, σ is the stress needed to depole the sample under no electric field; and ΔP and $\Delta\gamma$, respectively, are the changes in polarization and strain associated with the poling. Several types of measurements can quantify depoling [14,15].

Ferroelectricity has several effects on the fracture in bulk ceramics. Stress-induced switching is a toughening mechanism that leads to the fracture resistance curve behavior [16]. Tests using Vickers indenters have shown that poling of a ferroelectric ceramic increases toughness in the poling direction, and decreases it in the direction perpendicular to the poling direction. Toughness also depends on whether or not an electric field is applied and in what direction it is applied. A cyclic electric field causes a crack to grow stably by a certain amount per cycle. All such effects have been analyzed using micromechanics models ([17–20]; T Zhu, W Yang, personal communication). There are no generally accepted constitutive laws for ferroelectrics, although earlier attempts to formulate such laws have been revived ([21,22]; M Kamlah, C Tsakmakis, personal communication; RM McMeeking, ACF Cocks, personal communication), their usefulness in modeling field concentration and fracture remains to be established.

At room temperature, bulk $BaTiO_3$ is in the tetragonal phase. With submicron free particles, as the particle size decreases, the degree of tetragonality decreases and below a critical size, the particles are all in the cubic phase. A common explanation for this particle size effect is as follows [23,24•,25]. For a ferroelectric particle, spontaneous polarization gives rise to electric charges on the surfaces of the two poles. The charges may be compensated for by drawing free charges from the environment, an external circuit, or the particle itself. If not compensated, however, spontaneous polarization causes electric energy. In a large particle, domains form a pattern to reduce this electric energy. As the particle size decreases, however, the surface-to-volume ratio increases, and the reduction in the electric energy cannot compensate for the increase in wall energy, such that the domain size scales down disproportionally. In a small particle, the electric energy can be large enough to destabilize the tetragonal phase in favor of the cubic phase. In an experiment by Liu *et al.* [26•], particles were coated with a copper layer, allowing an electric charge to flow from one pole to the other to compensate the spontaneous polarization and thereby stabilizing the tetragonal phase.

In a dense ceramic, elastic energy, as well as electric energy, plays a similar role in destabilizing the ferroelectric phase. Domains in each grain select their polar directions among a set of crystalline directions. Consequently, neighboring grains suffer misfits in both spontaneous polarization and spontaneous strain; these misfits may be partially compensated by charges and dislocations, respectively. In large grain ceramics, the formation of a domain pattern reduces the misfit energy. In fine grain ceramics, just as in small free particles, domains cannot be refined proportionally, such that the misfit energy can be large enough to destabilize the ferroelectric phase. As stated before, thin BST films are paraelectric even at very low temperatures, and their permittivities are lower than those of bulk BST [4••]. In some large grain PZT ceramics, over half of the piezoelectric response comes from domain wall motion. This contribution is eliminated from fine grain ceramics [27,28••]. If, however, neighboring grains have similar crystalline orientations, the texture should have two effects: a reduction in the misfit energy and more cooperative domain switching among neighboring grains, both of which tend to reduce the size effects.

In addition to being fine grained, a thin film is constrained by the substrate. In the limit where a film is much thinner than the substrate, when a voltage is applied across the film thickness no net strain can occur in the plane of the film. That is, any strain caused by non-180° switching must be compensated for by an elastic strain. The latter corresponds to a stress that resists the switching. It should be pointed out that the substrate constraint persists even for large grains and thick films, so long as the film is much thinner than the substrate. Ideally one should distinguish the grain size effect from the substrate constraint effect. This is difficult in practice because the grain size in a film is often comparable to the film thickness. Even for thick PZT films (12 μm), dielectric and piezoelectric properties are still lower than bulk values [29]. This seems to suggest that the substrate constraint should have some effect on non-180° domain wall motion. In thin PZT films, non-180° domain wall motion is limited and makes little contribution to dielectric and piezoelectric responses [30••]. Furthermore, such responses do not change significantly under an applied stress of the order of 100 MPa, tension or compression, in the plane of the film.

A single crystal ferroelectric film may grow epitaxially on a substrate of a similar crystal structure. If the lattice constants of the film and the substrate are different, the film may be stressed to match the lattice constant of the substrate. Alternatively, the film may form a domain pattern to reduce the elastic energy (see [31,32] for recent work; N Sridhar, JM Rickman, DJ Srolovitz, personal communication). The effect of substrate constraint on the paraelectric–ferroelectric transition has also been considered [33••]. Furthermore, calculations have shown that, when a polydomain film is subject to a small electric field, non-180° domain walls can move, contributing to dielectric and piezoelectric responses [34,35••].

Two approaches have been developed to simulate ferroelectric domain dynamics. One approach is an extension of the classical grain growth model [36,37••]; it treats a domain wall as a sharp surface. Each domain is piezoelectric, straining and polarizing in the vicinity of a spontaneous state. The free energy includes both field energy and domain wall energy. A kinetic law relates the domain wall velocity to the free energy reduction associated with the domain wall motion, for which intrinsic length and time scales have been identified [36]. The second approach is an extension of the Landau–Ginsburg model [38,39••]. The domain wall is modeled as a diffuse interface by adding polarization gradient terms to the free energy. A kinetic law relates the rate of polarization change to the reduction in the free energy. This model has been implemented with electric and elastic effects, together with a domain nucleation condition. Further progress may benefit from concepts developed in the strain gradient theory [40].

Conclusions

Multiple energetics underlie diverse ferroelectric effects, particularly in small or constrained objects. Many such effects are understood individually in principle. Further quantitative experiments and computations are needed to weigh their relative significance. Substantial work is needed to elucidate ferroelectricity at interfaces, as they begin to dominate the response of thin films as most materials in use are traditional ones optimized for bulk applications. Insight into small object behaviors should lead to novel materials for thin film applications.

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