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Mesoscopic Dielectrics*

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Abstract

This paper describes four unsolved theoretical problems in ferroelectrics and related dielectrics with high permittivities: (1) finite size effects in thin films and small particles, and their relationship to depolarisation fields; (2) nucleation and growth kinetics, and especially the recently discovered coherent nucleation of small domains in front of advancing walls; (3) low-temperature quantum effects in ferroelectrics and the process of ‘freeze-out’, in which domain wall mobilities suddenly drop to zero; (4) self-patterning of nanoscale assemblies on the surfaces of substrates, and the consideration of lateral finite size effects.

1. Introduction

Dielectrics have had a small group of devotees studying them for the past seventy years, in comparison with other areas of condensed matter physics, such as superconductivity, magnetism and conventional semiconductors. In large measure this has been due to the fact that they were regarded as classical systems in which the long-range Coulomb forces eliminated true (fluctuation-dominated) critical phenomena, and free-energy models devoid of explicit quantum mechanics could explain most observed properties. Moreover, despite their large-scale commercial use in capacitors, they had produced no compelling reasons for examining the fundamental limits of their performance: What is the ultimate switching speed of a ferroelectric? What is the ultimate (minimum) electric coercive field? What are the exact mechanisms of nucleation and growth of domains? What is the quantum-mechanical mechanism of domain wall ‘freeze-out’ (domain wall mobility reaching zero at cryogenic temperatures)? Why are magnetic domains sometimes supersonic but ferroelectric domains apparently not? The parallels between ferroelectric and ferromagnetic domains have been largely unexplored except in a superficial way: for example, are there ferroelectric analogs (Scott *et al.* 1993) to both Bloch walls and Neel walls?

In this paper I present a brief outline of four unsolved theoretical problems in this area, together with the appropriate references. The work has a new impetus brought on by the commercial utilisation of nanoscale films of high dielectric

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constant in both ferroelectric random access memories (FeRAMs; Scott and Araujo 1989), in which the memory bits are stored intrinsically in the ferroelectric (+ polarisation designating a '1' and –polarisation a '0' in the usual Boolean algebra), and conventional silicon dynamic random access memories (DRAMs; Tasch and Parker 1989), in which the dielectrics merely form a thin-film capacitor (ca. 15–50 nm thick). Since this device market is worth approximately \$15 billion per year, it will become increasingly important to understand the fundamental limits of dielectric performance, particularly regarding lateral size and thickness for nanoscale, gigabit memory cells, as illustrated in the 200-nm strontium bismuth tantalate e-beam patterned array shown in Fig. 1 (Alexe 1998).

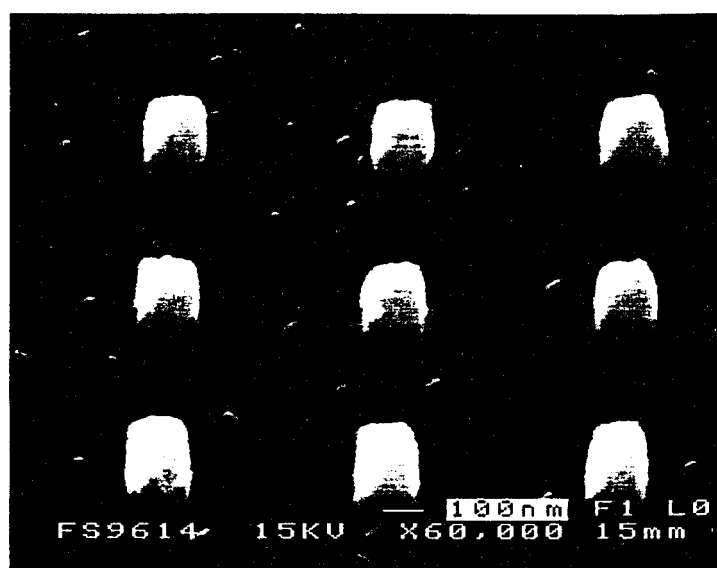


Fig. 1. Array of 120-nm-wide ferroelectric memory cells, cut out using electron-beam lithography (Alexe 1998).

2. Finite Size Effects

The physics of finite size effects has been of great interest in superconductors, magnets, semiconductors and metal clusters recently, and of at least passing interest in ferroelectrics for three decades. In each case there is an intrinsic length scale against which lengths are relative. In superconductivity this may be the distance between Cooper pairs; in semiconductors, the radius of an exciton. But in ferroelectrics, it has been the penetration depth of depolarisation fields. In fact the question is more subtle in ferroelectrics, because the parameters of greatest interest are switching times and coercive switching fields, and these can be measured only by putting electrodes on opposing surfaces. Thus one has the profound complication that the parameters are characteristic not of the dielectric *per se*, but of a system including two electrodes. Ferroelectrics, particularly the common oxides, are generally p-type semiconductors of moderately wide bandgaps (3–4 eV), so one cannot treat them as perfect insulators [as has been done in most textbooks since the early work (Landau 1937; Devonshire 1949)], but

must also include the usual metal–semiconductor interface physics. More recent treatments (Batra and Silverman 1972) assume that the characteristic length in the problem is the Thomas–Fermi screening length in the (metal) electrode, and derive expressions for the Curie temperature as a function of film thickness or particle diameter $T_C(d)$ and the polarisation as a function of depth into the film (or particle) $P(z)$, via Euler–Lagrange equations:

$$F = b \int \{ \xi^2 (dP/dz)^2 + (1 + T/T_C) P^2 - 2P^4 + P^6 \} dz + [c\xi/2d](P_+^2 + P_-^2). \quad (1)$$

Here F is the free energy, ξ the correlation length in bulk, P the spontaneous polarisation, z the direction normal to the film, d the film thickness, and P_{\pm} the charge at the surface. The key term is the gradient term in polarisation (which also turns up in free energies for incommensurate ferroelectrics). Integration by parts yields $P(z)$.

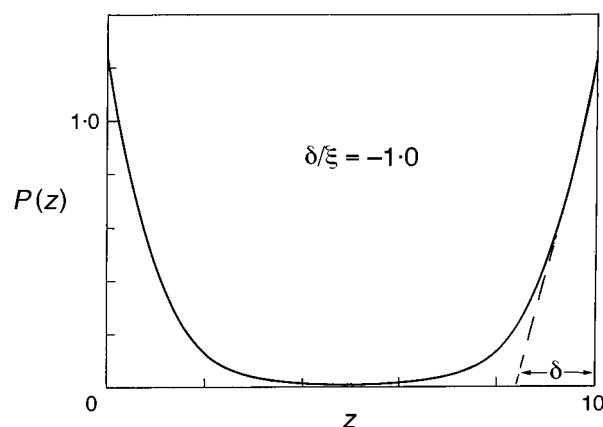


Fig. 2. Spontaneous polarisation P versus depth z in a ferroelectric thin film (Scott *et al.* 1988). The extrapolation length δ is the distance beyond the film surface at which the polarisation linearly extrapolates to zero. It is a phenomenological parameter related to the Thomas–Fermi screening length in the metal electrode. Shown as negative (into the film) in the figure, it is positive in most films [$P(z)$ curves downward as the surface is approached from the interior].

The latter parameter, $P(z)$, illustrated in Fig. 2 (after Tilley 1993), can bend up or down as the metal interface is approached. The extrapolation length δ is related to the coherence length in the film and the Thomas–Fermi screening length in the electrode, but in the phenomenological theory (Tilley and Zeks 1984) is a purely empirical parameter whose sign and magnitude are both undeterminable from microscopic theory. If $P(z)$ decreases at the surfaces, the Curie temperature $T_C(d)$ decreases with decreasing film thickness d approximately as

$$T_C(\text{bulk}) - T_C(d) = bd^{-1}, \quad (2)$$

where b is a positive constant.

The first limitation of this theory is that it is time-independent. It would be important to know whether the ferroelectricity experimentally observed in thin films is metastable on a timescale of years or microseconds. A detailed application of Landau–Ginzburg theory to ferroelectric films, following the well known route for superconducting films, would seem in order. Second, there is a complication of domain instability in thin films due to strain (no depolarisation fields). As first outlined by Roytburd (1976) and developed in recent years (Erbil *et al.* 1994; Pompe *et al.* 1998), the domain wall width w that minimises the classical free energy in thin films varies approximately as $d^{1/2}$, the square root of the film thickness. Experimentally it can be difficult and ambiguous to subtract off secondary, extrinsic size effects (such as surface strain and porosity) from intrinsic size effects due to depolarisation fields. As a result, most of the early work on mesoscopic dielectrics (e.g. Uchino *et al.* 1982, 1989; Ishikawa *et al.* 1966) was misinterpreted quantitatively. On the basis of work in three different groups in 1998 (Payne 1999; Cao and Randall 1996; Randall *et al.* 1999; Tanaka and Makino 1998; see Fig. 3), we now believe that intrinsic finite size effects in ferroelectric particles do not occur until ca. 14 nm and certainly not at the much larger particle sizes (120 nm) studied by Uchino *et al.*

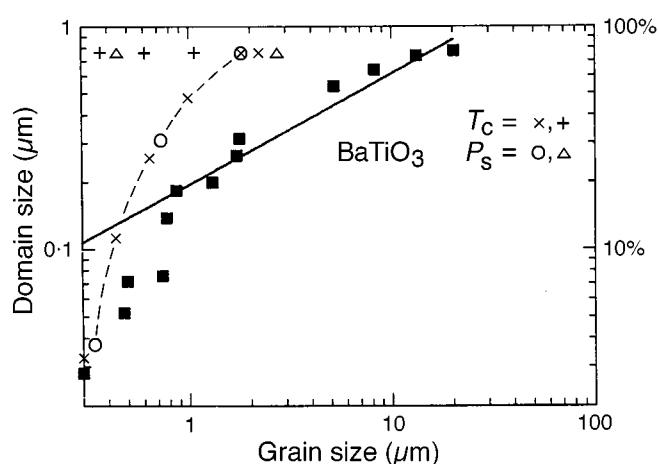


Fig. 3. Schematic diagram of finite size effects in ferroelectrics, with the original relationship for domain size and grain size, due to Roytburd (1976), drawn as the theoretical line (Arlt 1990).

The discussion above emphasises work on finite-sized (spherical) particles, but the situation with regard to thin films is as controversial as that for small spherical particles (which can be prepared nicely now via colloidal precipitation). The most recent theories estimate a minimum film thickness of ca. 50 nm for ferroelectric switching on metal electrodes (limited by the electrode Thomas–Fermi screening length) and 400 nm on semiconducting electrodes, but in 1998 complete switching in polyvinylidene fluoride copolymer films from 0.9 to 35 nm in thickness was reported (Bune *et al.* 1998; Fridkin *et al.* 1999). There are three unsolved

theoretical sub-problems relating to these data. First, we remind readers that in Landau theory one can calculate exactly the coercive field required to switch a ferroelectric from $+$ to $-$ polarisation. Typically this value is approximately 1000 times larger than the measured coercive field. The reason is that Landau theory includes no domain walls; rather, it is the field requisite for simultaneous switching of every atomic cell from $+$ to $-$. But real switching can occur at much lower applied electric fields via movement (usually sideways) of domain walls. Fridkin (1999) has pointed out that the large coercive fields they measure for their thicker (*ca.* 30 nm) films match those calculated from Landau theory and thus imply domain-free switching via simultaneous reversal of polarity in each crystallographic unit cell. If correct, this would imply that the domain walls may be constrained by the thin-film geometry and have no mobility.

Fridkin makes a further assertion that the ultrathin films (*ca.* 1 nm) are true [2D] ferroelectrics (and not thin [3D] ferroelectrics). I regard this as the second unresolved theoretical problem of their work, and will not discuss this argument here but refer readers to their original *Nature* paper (Bune *et al.* 1998). The authors have, however, carefully eliminated a purely electric interpretation of their data (polarising of charged defects) by showing that their specimens exhibit a distinct Curie temperature.

The third and most important theoretical puzzle of the Bune–Ducharme–Fridkin work is that the switching time observed diverges (approximately exponentially) as $1/d$, the reciprocal film thickness, from a ‘normal’ value of *ca.* microseconds at $d = 35$ nm, to an amazing 5 s at $d = 1$ nm. This cannot be accounted for in simple Landau theory. Landau–Ginzburg theory has not yet been applied to the problem, but does not qualitatively suggest an interpretation. It has been suggested (Watanabe *et al.* 1996) that the presence of surface traps on such thin films will stabilise their polarisation at thicknesses much less than those estimated from metal electrode screening lengths, but at the cost of greatly longer switching times and switching polarity asymmetries (longer $+$ to $-$ than $-$ to $+$). No tests of switching asymmetry have been yet reported for these ultrathin films.

I can offer two new suggestions here that might provide additional mechanisms for ultrathin film stability not previously considered. We know experimentally and theoretically (de Wette 1997) that although perovskite oxides do not undergo surface reconstruction (unlike silicon), they do manifest significant surface relaxation, with shrinkage of order 0.01 nm along the direction perpendicular to the surface. Since Ti–O bond lengths are of order 0.1 nm, this is a large (10%) effect. Such shrinkage can have two effects. First, it may mechanically stabilise an ultrathin film that would otherwise be unstable to depolarisation fields. Second, and perhaps more important, since all ferroelectrics are necessarily piezoelectric, it can produce a large piezoelectric electric field that will compensate for the depolarisation field, thus stabilising ferroelectric thin films beyond the thinness expected from standard theories.

3. Nucleation and Growth of Domains

It is generally stated in texts that a ferroelectric, initially in a single-domain $+$ polarisation state and subject to a large external electric field downward,

will switch via either of two processes: (a) inhomogeneous nucleation at defect sites, primarily at the cathode or anode, followed by needle-like subsonic growth to the opposite electrode and subsequent sideways growth; or (b) homogeneous nucleation throughout the interior of the dielectric. Because it is difficult to distinguish these processes via real-time observation, there has remained for several decades a controversy concerning supersonic domain wall motion. It is clear that the charge is switched in a time faster than that given by d/v , where d is the film thickness and v the sound velocity, but this can occur through process (b) above in the absence of supersonic domain walls. [We note parenthetically that supersonic magnetic domain walls are well known from the work in Moscow (Democritov *et al.* 1988); in this case magnon–phonon interaction produces Cerenkov-like bow waves of acoustic phonons, but the existence of supersonic ferroelectric domain walls has not yet been demonstrated in the same way.] To complicate things, we now know experimentally that mechanisms (a) and (b) above are not the only switching mechanisms in ferroelectrics, and may not be even the dominant mechanisms. As Shur *et al.* (1992; see Fig. 4) have shown in lead germanate via pulsed nitrogen laser illumination of domains with variable time delay after an electrical switching pulse is applied, small domains nucleate in front of large advancing domain walls. This creates a snowplough effect such that the phase velocity and the group velocity of the wall are quite different (one may be supersonic!). Keep in mind (Janovec 1983) that ferroelectric domain walls, unlike magnetic domain walls, are generally charged, so that this process is presumably induced by the advancing Coulombic field.

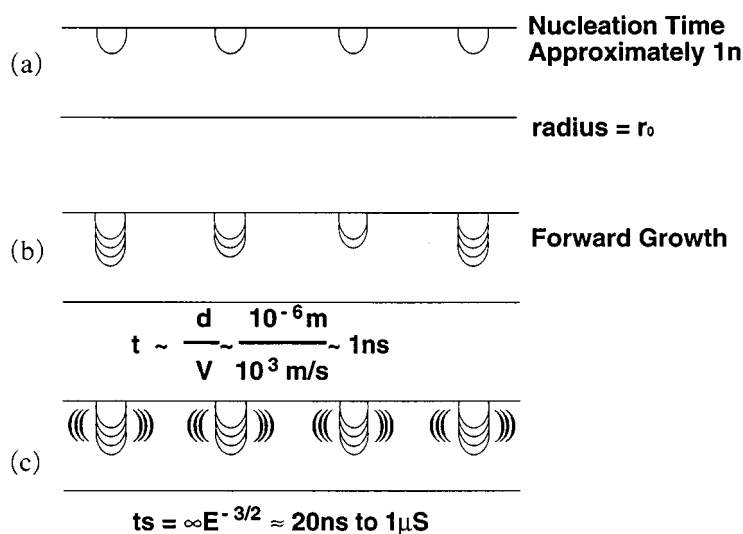


Fig. 4. Micro-domains nucleating in front of a (charged) advancing domain in ferroelectric lead germanate (Shur *et al.* 1992).

There is no theoretical model in the literature for this coherent nucleation process. Moreover, even the semiclassical inhomogeneous nucleation process is not

understood in detail. The process is thought to be analogous to the breaking of a soap bubble (initiation of a microscopic void; fluctuation, growth and shrinkage of this void, including occasional disappearance without rupture; reaching of a critical radius, above which rapid, exponential growth of the void occurs; rupture of the bubble). The critical size r required for a nanodomain to begin exponential growth has been estimated numerically (Godfrey *et al.* 1986; Araujo *et al.* 1986) for KNO_3 as 1 nm, and the time to reach this size, 1 ns (Scott 1998). However, no quantum-mechanical model of this process has been published, and as a result the fluctuating stage is poorly understood. In the context of the present paper, the pertinent question is: What happens when the lateral size of the ferroelectric is a few nm and comparable to the size of the fluctuating nanodomain? Will the confinement suppress the fluctuations and slow down the nucleation process? If so, by how much?

4. Domain Freeze-out

At cryogenic temperatures the mobility of domain walls in most ferroelectrics or ferroelastics drops abruptly to zero (Bornarel 1972; Gridnev 1990; Fedosov and Sidorkhin 1977; Baski *et al.* 1987; Huang *et al.* 1997). For example, in SrTiO_3 this phenomenon occurs at 37 K (Salje *et al.* 1998*a*, 1998*b*; Balashkova *et al.* 1996). There is no quantum-mechanical model for this process. In many aspects ‘quantum ferroelectrics’ (Samara 1971, 1988) can be described accurately by simply restoring to its exact form the Bose factor $n(T, \omega)$ that has been expressed as $kT/h\omega$ in the semiclassical approximation. However, several questions remain: Does the saturation of the order parameter in systems like strontium titanate arise simply from the third law of thermodynamics (Kozlov *et al.* 1983; Fox *et al.* 1980), or does it require an additional term in the free energy assumed (Salje *et al.* 1991; Thomas 1997)?* How does one modify the classical model of thermally activated domain wall motion to account for domain wall freeze-out in quantum ferroelectrics? Are the results explicitly dependent upon grain size in a fine-grained ceramic or upon film thickness d in a thin film?

In the case of strontium titanate, the known domain wall freeze-out near 37 K (Balashkova *et al.* 1995; Balashkova and Lemanov 1997; Salje *et al.* 1998*a*, 1998*b*) may have been misinterpreted as manifestations of second sound (Courten *et al.* 1993, 1996, 1997; Gurevich and Tagantsev 1988; Hehlen *et al.* 1995, 1997; Vacher *et al.* 1992) or of some exotic but unspecified form of macroscopic coherence (Mueller *et al.* 1991; Scott and Ledbetter 1997; Chen *et al.* 1999). Can domain wall freeze-out be mistaken for a ‘type-zero’ (non-symmetry-breaking) phase transition (Cowley 1967)? Domain wall freeze-out is not a thermodynamic phase transition (since domain walls do not usually exist in the thermodynamic ground state but are merely metastable), but it may mimic many of the type-zero predictions, including a discontinuous change in c/a ratio (Neumann *et al.* 1995*a*, 1995*b*).†

* Thomas (1997) expressed the view that the high-temperature order-parameter saturation model of Salje *et al.* (1991) applies also to SrTiO_3 below 105 K. The present author disagrees.

† Personal communication from these authors subsequently revealed that any c/a discontinuity is *not* reproducible, however.

5. Self-patterning of [2D] Ferroelectric Arrays

Like many other materials, ferroelectrics can sometimes spontaneously generate nanoscale patterning on their surfaces (Alexe *et al.* 1998; Scott *et al.* 1998). In the case of Bi in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ or $\text{SrBi}_2\text{Ti}_4\text{O}_{15}$ the [2D] surface structures are *ca.* 100 nm in diameter and are thought to come from ‘surface droplet epitaxy’ (Scott 1999), a process known to arise in Si:Ag or Si:Au (Wakayama and Tanaka 1998) and which requires an endothermic eutectic transition for the metal-in-semiconductor solution. In other dielectrics such as Bi_2O_3 , nanopatterning of 5 nm islands has been reported (Yu *et al.* 1997), at which scale confinement energies become significant (a few hundred meV). Although we understand now that such lateral sizes are possible for ferroelectrics, we do not know what finite size effects will be important for such systems (the prior studies cited in Section 2 above relate only to [3D] spherical particles and to thin films of infinite lateral dimensions). What finite size effects are expected and what depolarisation effects anticipated for a thin film of 5 nm lateral dimension? Although such a film will resemble a small box, whose aspect ratio may be nearly unity, it is not so easy to solve this problem. The main interest is in switching time, and although Laplace’s equation can be solved for the box, it is not valid in the time-dependent switching problem. Moreover, minor details, such as having interfaces (silicon nitride?) at the sidewalls of the ferroelectric quite different from those at the top and bottom (electroded), complicate the calculations for real systems.

6. Summary

In this paper I have tried to lay out four problems of theoretical interest in ferroelectrics. Each has in common with the others that the problems are exacerbated in mesoscopic (nanoscale) systems and probably require a non-classical solution. Readers may find in work not known to the author that these problems have indeed been solved; but in my judgment, if that is the case, the solutions are not well known. The present level of development of submicron ferroelectric cells for nonvolatile memory applications makes it imperative that we achieve a deeper level of understanding of these problems. In the future, since a 100×100 nm ferroelectric capacitor cell delivers only *ca.* 200 electrons of switched charge, the need to limit noise in the sense amplifier READ operation of multi-gigabit memories may dictate operation at cryogenic temperatures (77 K) to minimise thermal noise. In this case a non-classical description of phenomena such as domain wall freeze-out, nucleation and growth of domains during switching, and finite lateral size effects would also be useful.

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