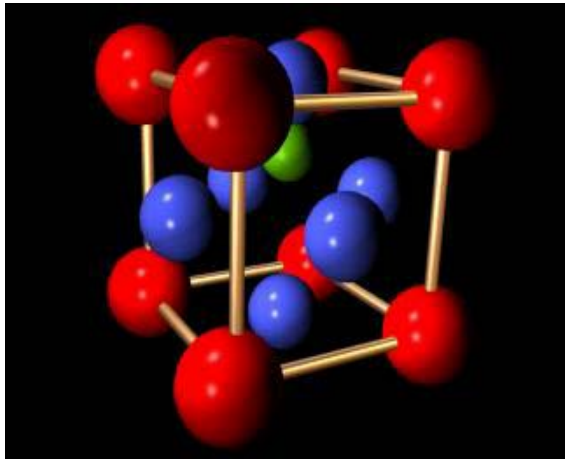
Nanoscale Ferroelectrics: where size really does matter

Marty Gregg
Queen's University Belfast

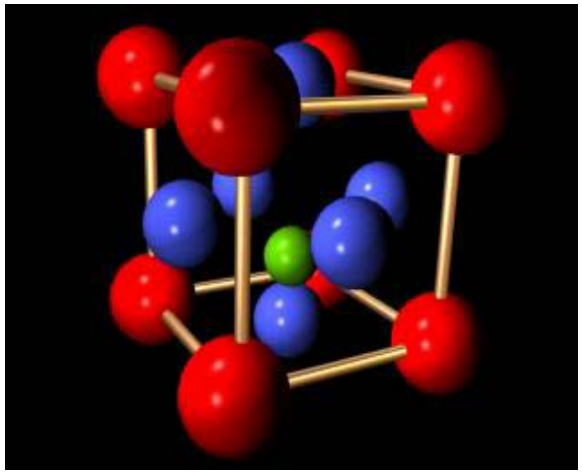
Outline:

- Basics of ferroelectricity
- Influence of boundaries I: strain coupling
- Influence of boundaries II: depolarising fields
- Strain and depolarisation effects on ferroelectric domains
- Size effects on *dynamics* of ferroelectrics

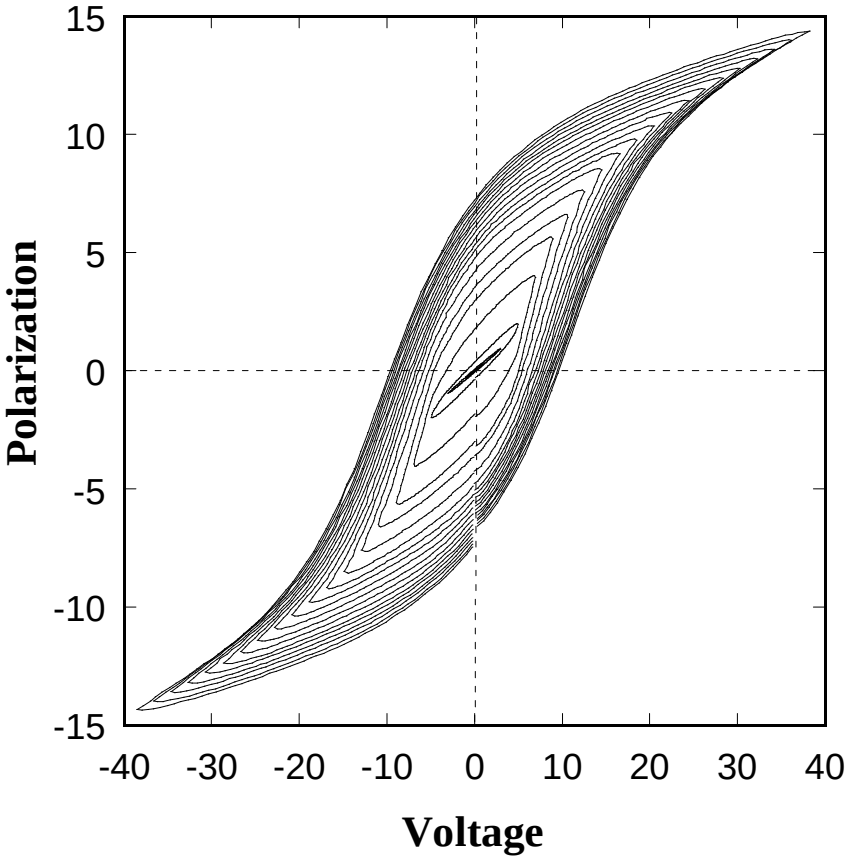
Ferroelectrics develop reversible electrical polarisation when electric field is applied



Field Up



Field Down



Important fundamental features which point to a strong sensitivity to size:

- Ferroelectricity traditionally described as a cooperative effect – below a ‘critical volume’ ferroelectricity is not thought to be sustained – expect ferroelectricity to be destabilised as size is reduced;

- Development of polarisation involves, in most cases, physical distortion of the unit cell – strain and polarisation are therefore coupled. Surface / interfacial strain and strain clamping has a major influence;

- Dipolar nature means that discontinuities / boundaries / surfaces can be charged – the field between charged surfaces opposes the dipole formation – depolarising fields increase when surfaces are close together.

Influence of boundaries I: Strain coupling

$$\Delta G = \tfrac{1}{2}\alpha P^2 + \tfrac{1}{4}\beta P^4 - \tfrac{1}{2}s_{ij}X_iX_j - Q_{ij}X_iP^2$$

Inherent importance of strain coupling is undeniable – manifested in bulk through shape-conserving twins / 90° domains, BUT…..in thin film geometries, particularly those in which misfit strain between film and substrate is small and film thicknesses are less than needed to form misfit dislocations, strain coupling to substrates becomes extremely important. This recognised in classic phenomenological work by N. A. Pertsev *et al.*

VOLUME 80, NUMBER 9 PHYSICAL REVIEW LETTERS 2 MARCH 1998

Effect of Mechanical Boundary Conditions on Phase Diagrams of Epitaxial Ferroelectric Thin Films

N. A. Pertsev,[1] A. G. Zembilgotov,[2] and A. K. Tagantsev[3]
[1]*A. F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia*
[2]*State Technical University of St. Petersburg, 195251 St. Petersburg, Russia*
[3]*Laboratoire de Céramique, Ecole Polytechnique Fédérale de Lausanne, Lausanne CH 1015, Switzerland*
(Received 1 May 1997; revised manuscript received 14 January 1998)

A phenomenological thermodynamic theory of ferroelectric thin films epitaxially grown on cubic substrates is developed using a new form of the thermodynamic potential, which corresponds to the actual mechanical boundary conditions of the problem. For single-domain $BaTiO_3$ and $PbTiO_3$ films, the "misfit-temperature" phase diagrams are constructed. It is found that the 2D clamping of the films, apart from a shift of the temperature of the ferroelectric transition, results in a change of its order. A change of the sequence of the phases and the appearance of phases forbidden in the bulk crystals are predicted. [S0031-9007(98)05421-0]

PACS numbers: 77.55.+f, 77.22.Ch, 77.80.Dj

Pertsev Phase Diagrams

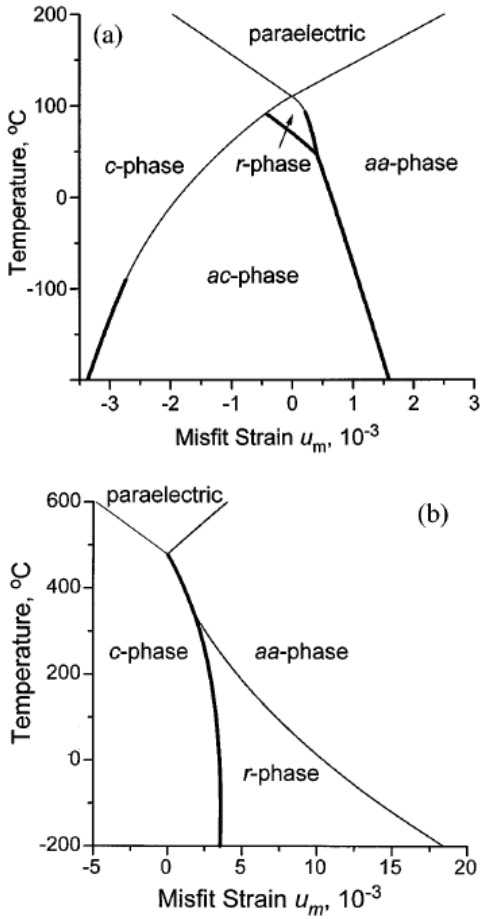


FIG. 1. Phase diagrams of (001) single-domain $BaTiO_3$ (a) and $PbTiO_3$ (b) thin films epitaxially grown on different cubic substrates providing various misfit strains u_m in the heterostructures. The second- and first-order phase transitions are shown by thin and thick lines, respectively. The quadruple and triple points at $u_m = 0$ correspond to the Curie-Weiss temperatures of these materials in the bulk form.

Pertsev and co-workers suggest new phase diagrams for epitaxial thin film ferroelectrics that are clamped to single crystal substrates.

Work progressed by others involved in Landau-Ginzburg-Devonshire free energy descriptions of ferroelectrics *e.g.* Ban and Alpay JAP (2002) / (2003). Also atomistic simulations contribution to the strain clamped alterations in phase diagrams (mostly Vanderbilt and co-workers).

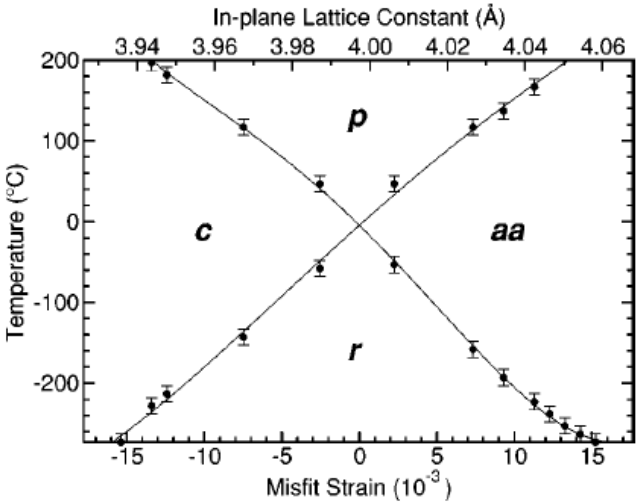


FIG. 4. Phase diagram of epitaxial $BaTiO_3$ obtained using the effective Hamiltonian of Zhong, Vanderbilt and Rabe (see Ref. 19).

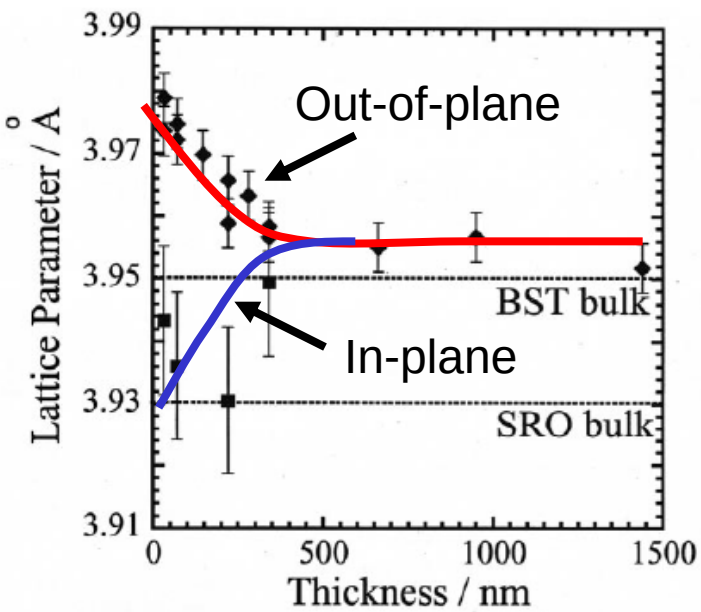
Experimental testing of Pertsev ideas

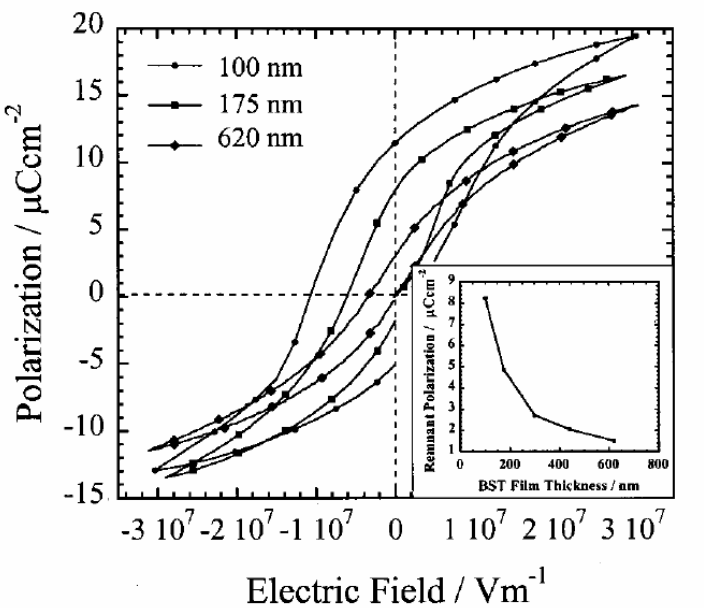
Substrates and thin film electrode systems which induce compressive epitaxial strain relatively easy to make. Some early reports of strain-coupled stabilisation of c-phase (consistent with Pertsev) *e.g.* Sinnamon *et al* APL (2002),

APPLIED PHYSICS LETTERS VOLUME 81, NUMBER 5 29 JULY 2002

Thickness-induced stabilization of ferroelectricity in $SrRuO_3/Ba_{0.5}Sr_{0.5}TiO_3/Au$ thin film capacitors

L. J. Sinnamon, R. M. Bowman, and J. M. Gregg[a)]
Department of Pure and Applied Physics, Queen's University Belfast, Belfast BT7 1NN, United Kingdom

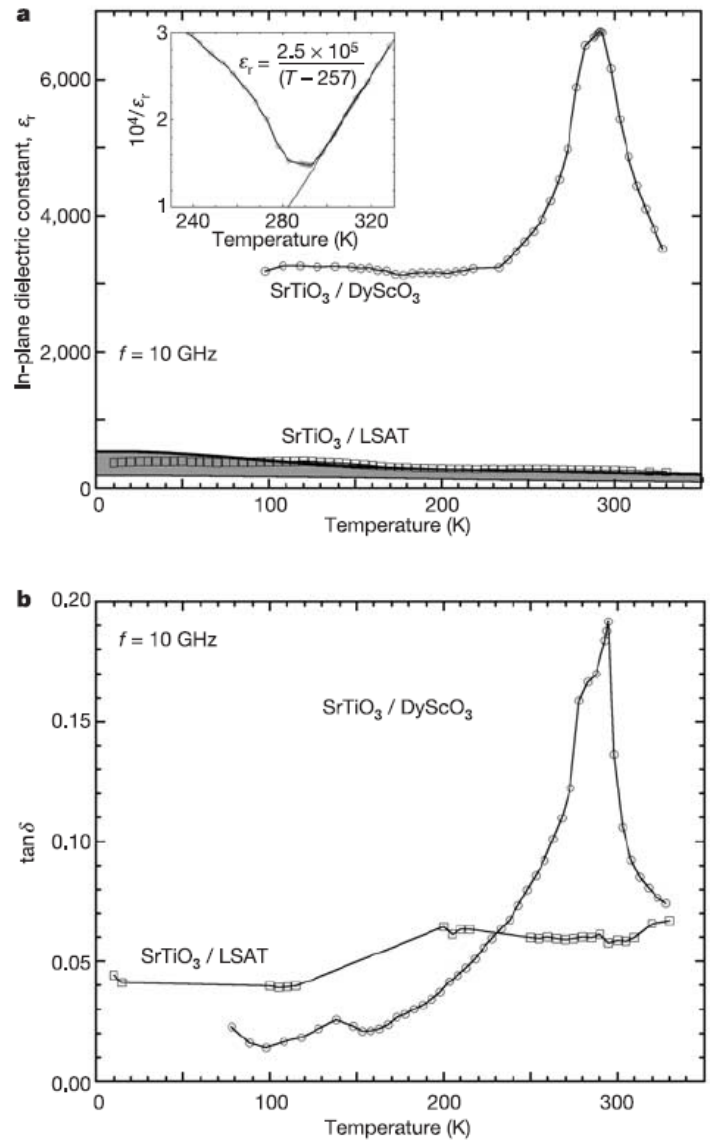




Room-temperature ferroelectricity in strained $SrTiO_3$

J. H. Haeni[1], P. Irvin[2], W. Chang[3], R. Uecker[4], P. Reiche[4], Y. L. Li[1], S. Choudhury[1], W. Tian[5], M. E. Hawley[6], B. Craigo[7], A. K. Tagantsev[8], X. Q. Pan[5], S. K. Streiffer[9], L. Q. Chen[1], S. W. Kirchoefer[3], J. Levy[2] & D. G. Schlom[1]

Most impressive experimental observation of compressive strain coupling by Haeni et al. Nature (2004):
$SrTiO_3$ film grown coherently onto $DyScO_3$ – in-plane compression sufficient to not only raise Curie temperature, but to change incipient ferroelectric into genuine ferroelectric.



Under tensile strain ?

PRL **96,** 127602 (2006) PHYSICAL REVIEW LETTERS week ending 31 MARCH 2006

Polar Domains in Lead Titanate Films under Tensile Strain

G. Catalan,[1,*] A. Janssens,[2] G. Rispens,[1] S. Csiszar,[1] O. Seeck,[3] G. Rijnders,[2] D. H. A. Blank,[2] and B. Noheda[1,†]

[1]*Materials Science Centre, University of Groningen, Groningen 9747AG, The Netherlands*
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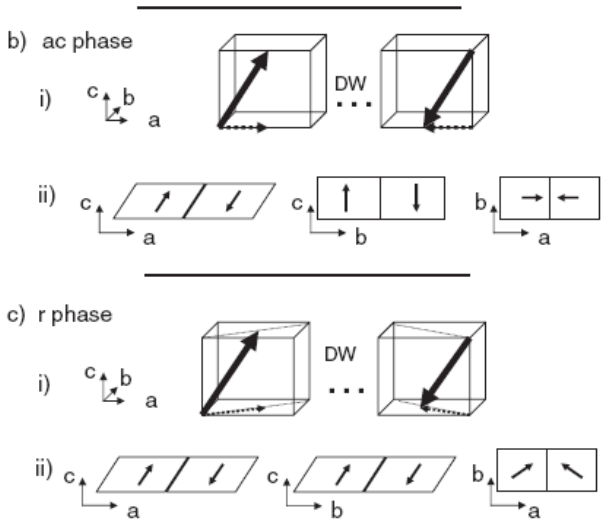
(Received 25 December 2005; published 31 March 2006)

Thin films of $PbTiO_3$, a classical ferroelectric, have been grown under tensile strain on single-crystal substrates of $DyScO_3$. The films, of only 5 nm thickness, grow fully coherent with the substrate, as evidenced by synchrotron x-ray diffraction. A mapping of the reciprocal space reveals intensity modulations (satellites) due to regularly spaced polar domains in which the polarization appears rotated away from the substrate normal, characterizing a low-symmetry phase not observed in the bulk material. This could have important practical implications since these phases are known to be responsible for ultrahigh piezoelectric responses in complex systems.

DOI: 10.1103/PhysRevLett.96.127602 PACS numbers: 77.55.+f, 61.10.−i, 68.55.−a, 77.80.−e



Central idea that strain clamping / strain coupling causes alterations in phase transition behaviour very evident in recent work.

Strain coupled transition behaviour in nanoscale systems with many interfaces – ferroelectric superlattices

FIRST-PRINCIPLES STUDY OF SYMMETRY LOWERING…

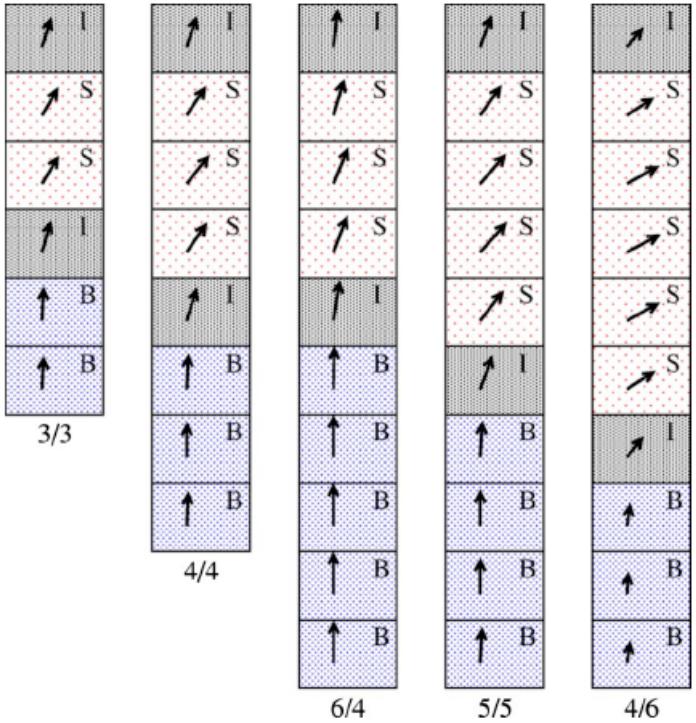


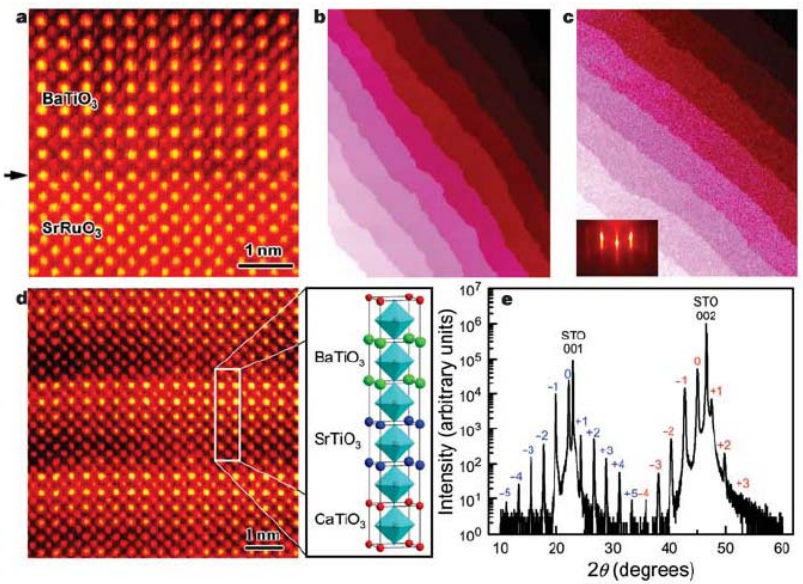
FIG. 1. (Color online) Magnitude of P_{local} in the [110] and [001] directions. $SrTiO_3$, $BaTiO_3$, and interface cells are labeled as S, B, and I, respectively.

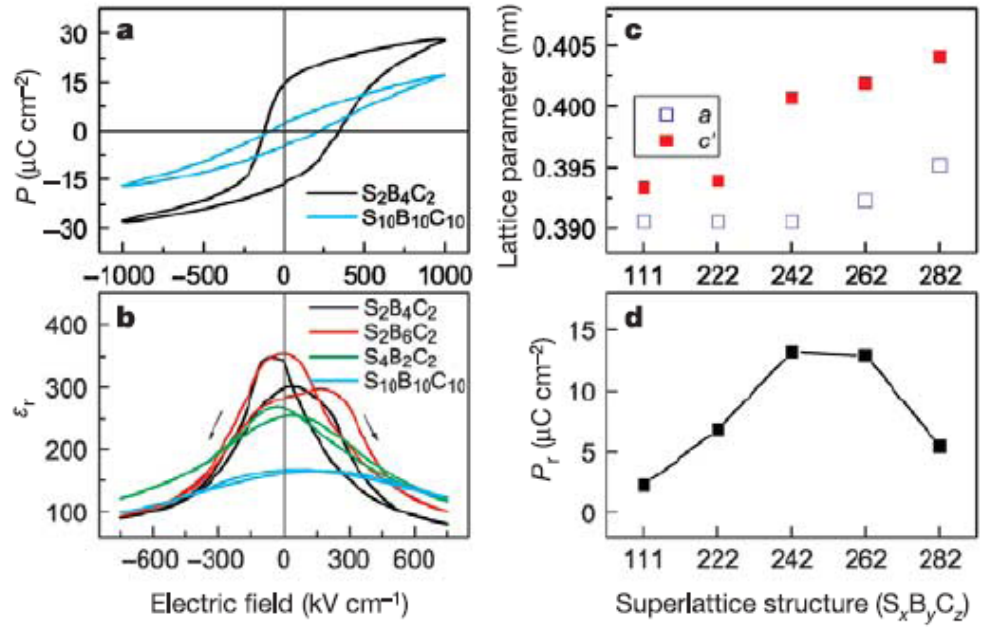
Strain coupling in BTO / STO superlattices responsible for development of in-plane polarisation in STO at room temperature seen by Rios *et al.* JPCM (2003), and rationalised by atomistic simulations by Johnston *et al* PRB (2005)

Strain coupled enhanced polarisation in superlattices

Strong polarization enhancement in asymmetric three-component ferroelectric superlattices

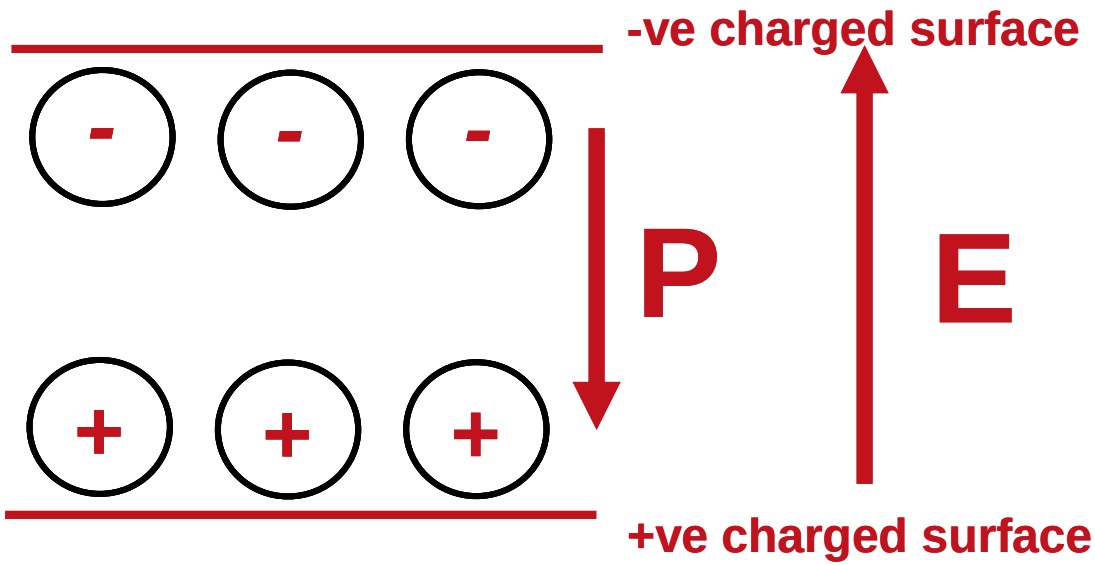
Ho Nyung Lee, Hans M. Christen, Matthew F. Chisholm, Christopher M. Rouleau & Douglas H. Lowndes





Also watch for work by Dawber and Triscone on superlattice coupling effects

Influence of boundaries II: depolarising fields



Existence of surfaces which do not offer any charge compensation create voltage and field which opposes the polarisation responsible for the charge in the first place. As distances between surfaces decreases the charge density on the faces is largely unchanged – hence depolarisation field dramatically increases in nanoscale objects.

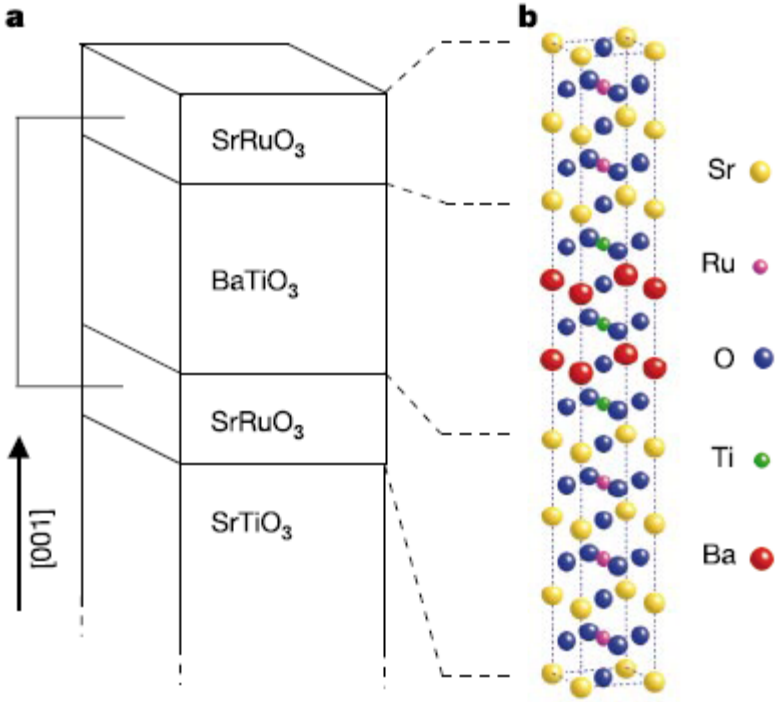
Suspected effects of the depolarising field

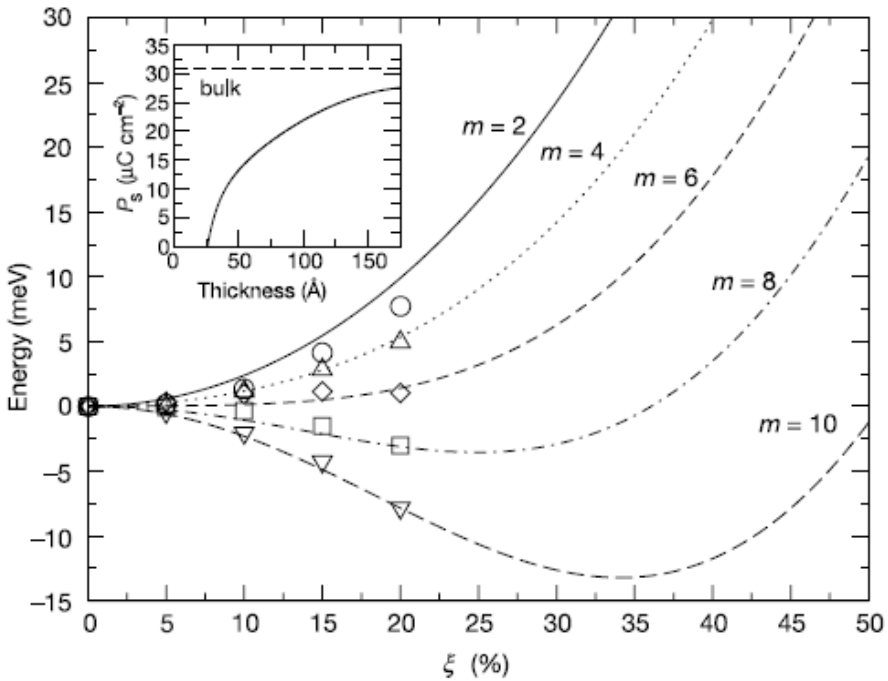
- Progressive loss of ferroelectricity (if no domain formation considered)

letters to nature

Critical thickness for ferroelectricity in perovskite ultrathin films

Javier Junquera & Philippe Ghosez





Equivalent modelling with acknowledgement of surface effects

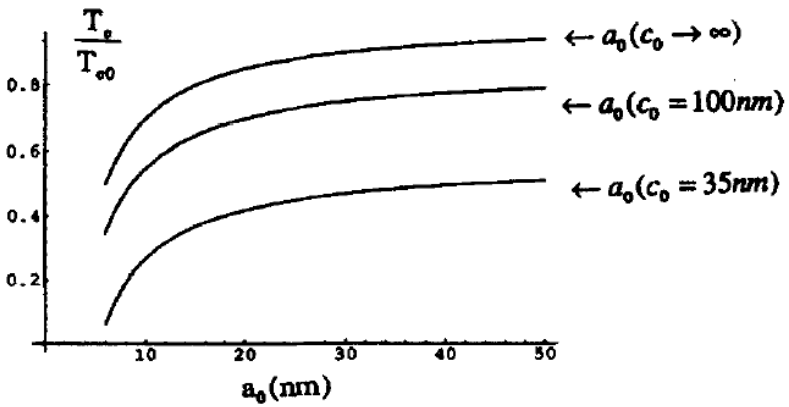


Fig. 1. T_c dependence of lateral sizes for several different thick-

Shaoping Li *et al.* Phys. Lett. A **212** (1996)

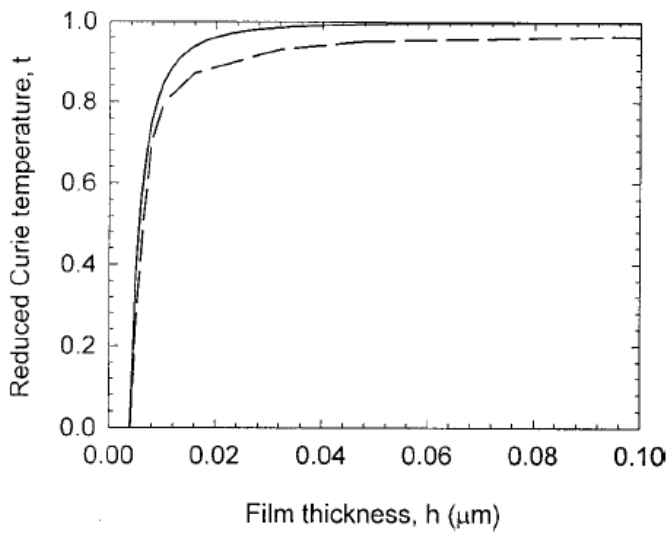


FIG. 3. Reduced Curie temperature of a thin film $Ba_xSr_{1-x}TiO_3$ ($x=0.5$). Solid line was simulated by Eq. (22), dotted line was taken from Ref. 23.

Vendik and Zubko JAP (2000)

What about suppression of ferroelectricity in experiment ?

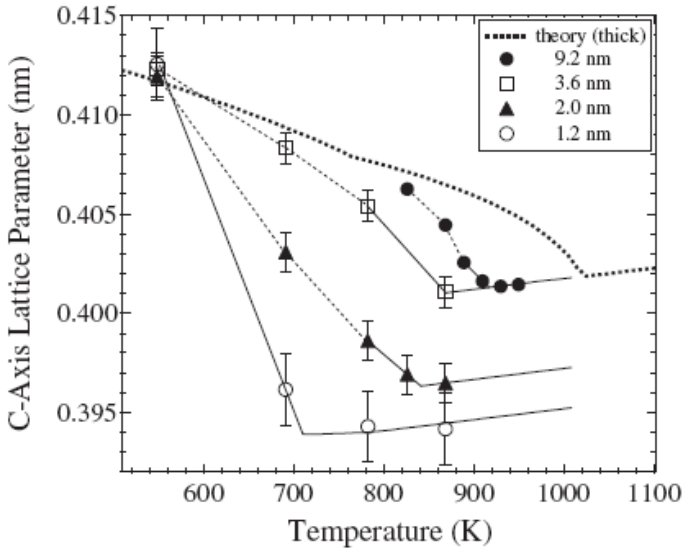
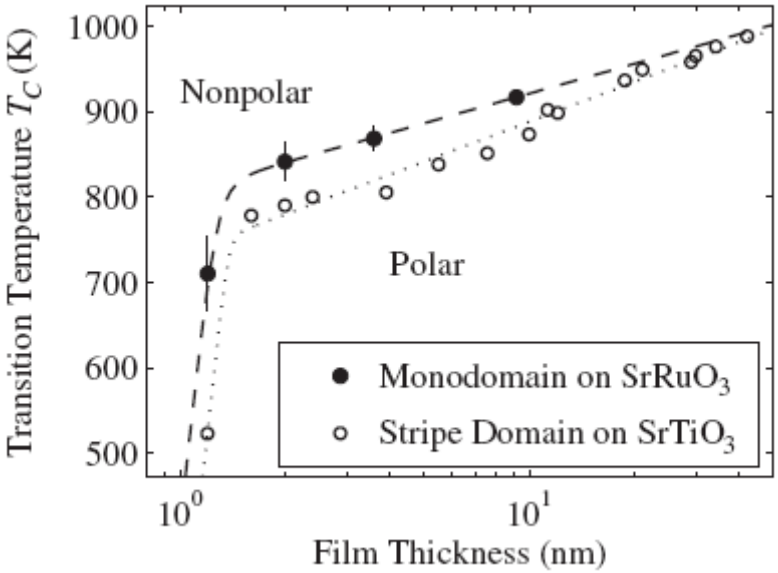
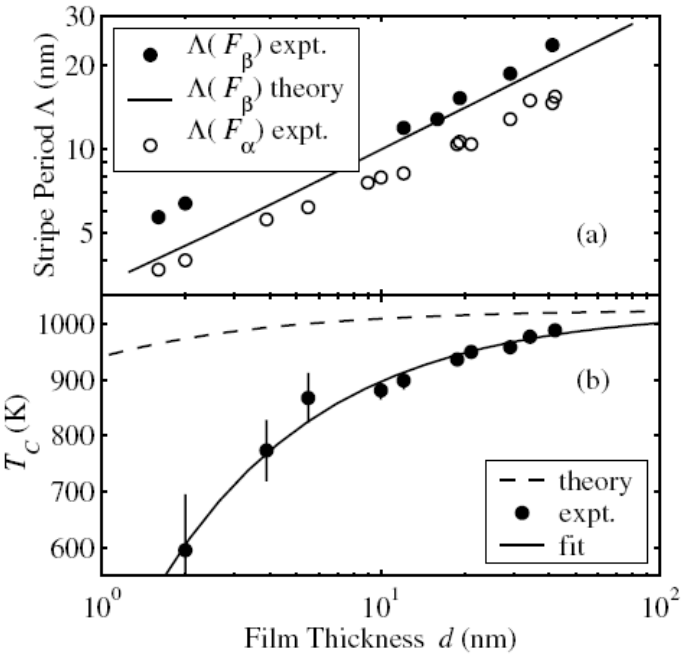


FIG. 2. The c lattice parameter vs T for each film, with solid lines showing the break in slope used to estimate T_C. The upper curve is the Landau theory prediction for thick $PbTiO_3$ on $SrTiO_3$ [2].



In thin films of $PbTiO_3$, while Tc is progressively suppressed with reduced thickness – ferroelectricity persists. Above figure (Fong *et al.* PRL 2006) relates to compensating surfaces, but similar in non-compensating conditions with formation of domains holding stability of ferroelectricity (see next overhead).

Other experimental observations – thin films and nanowires



Streiffer *et al.* PRL (2002) – thin film $PbTiO_3$ – Tc suppressed, but RT ferroelectricity remains. Depolarisation field effects negated by 180º domains

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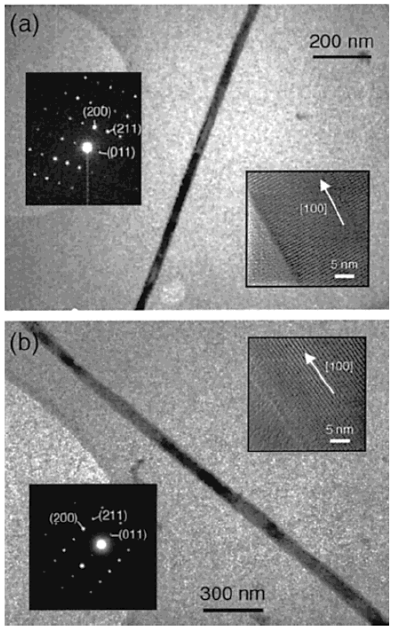
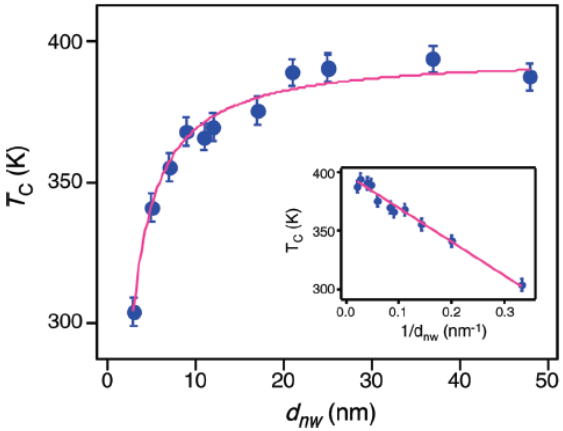
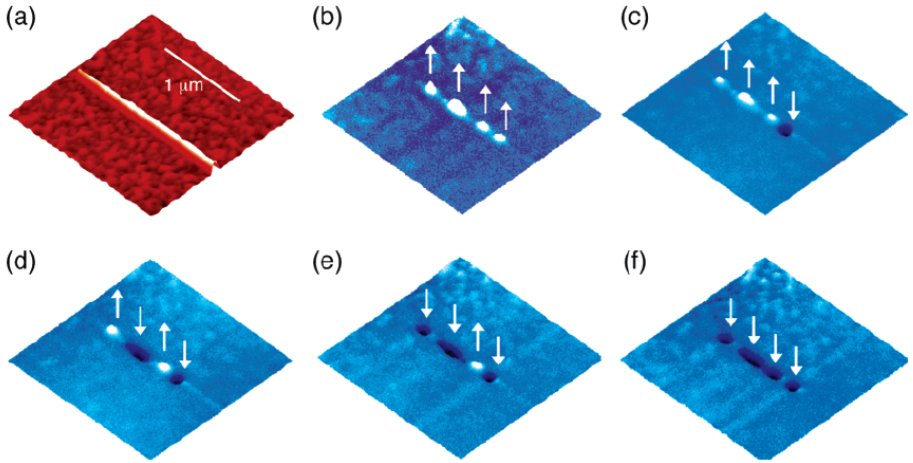
Ferroelectric Phase Transition in Individual Single-Crystalline $BaTiO_3$ Nanowires

Jonathan E. Spanier,[†,§,∥] Alexie M. Kolpak,[†,⊥] Jeffrey J. Urban,[§] Ilya Grinberg,[⊥] Lian Ouyang,[§] Wan Soo Yun,[‡,§] Andrew M. Rappe,[*,⊥] and Hongkun Park[*,§]

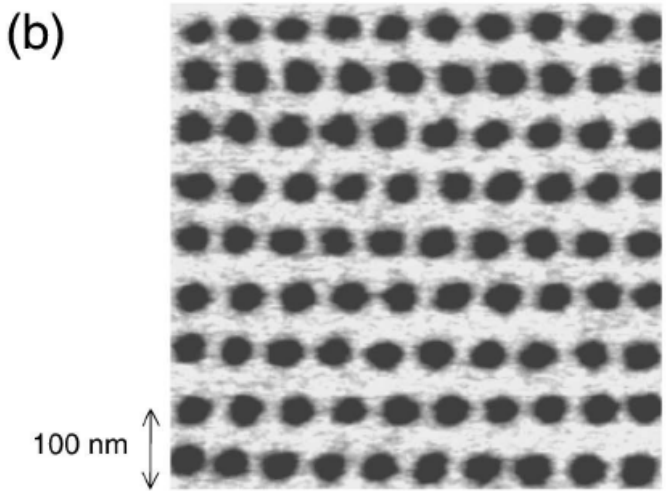




SPM-written ‘bits’ surprisingly stable when very small indeed in nanowires and thin film media

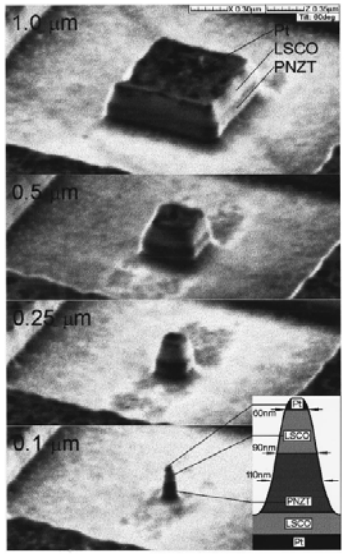


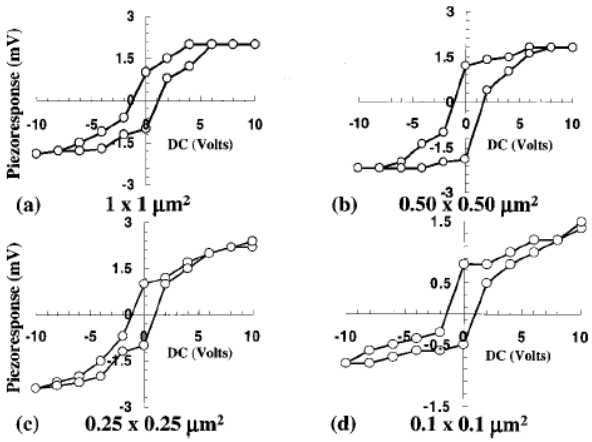
Yun *et al.* Nanoletters (2002) non-axial remanent polarisation stable at RT on 12nm single crystal $BaTiO_3$ nanowire



Tybell *et al.* PRL (2002) – SPM out-of-plane switching in thin film PZT

FE stability down to ultrananoscale in isolated islands is less clear





Islands cut from thin films by FIB (Ganpule *et al.* APL 1999) show ferroelectric response down to ~100nm diameter

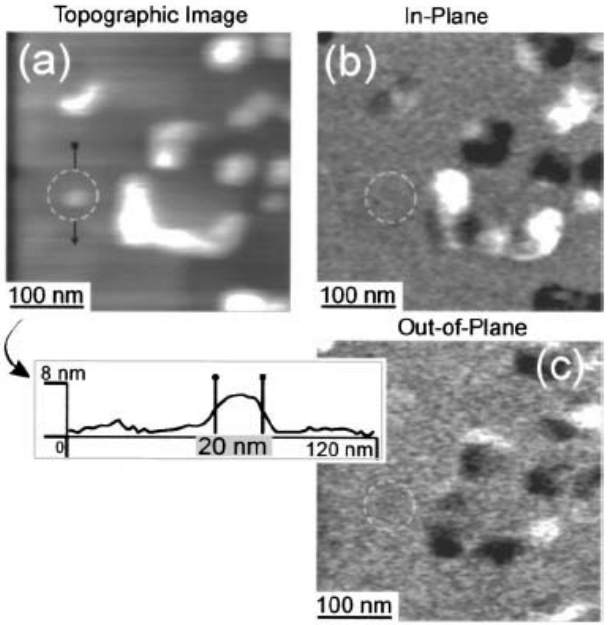
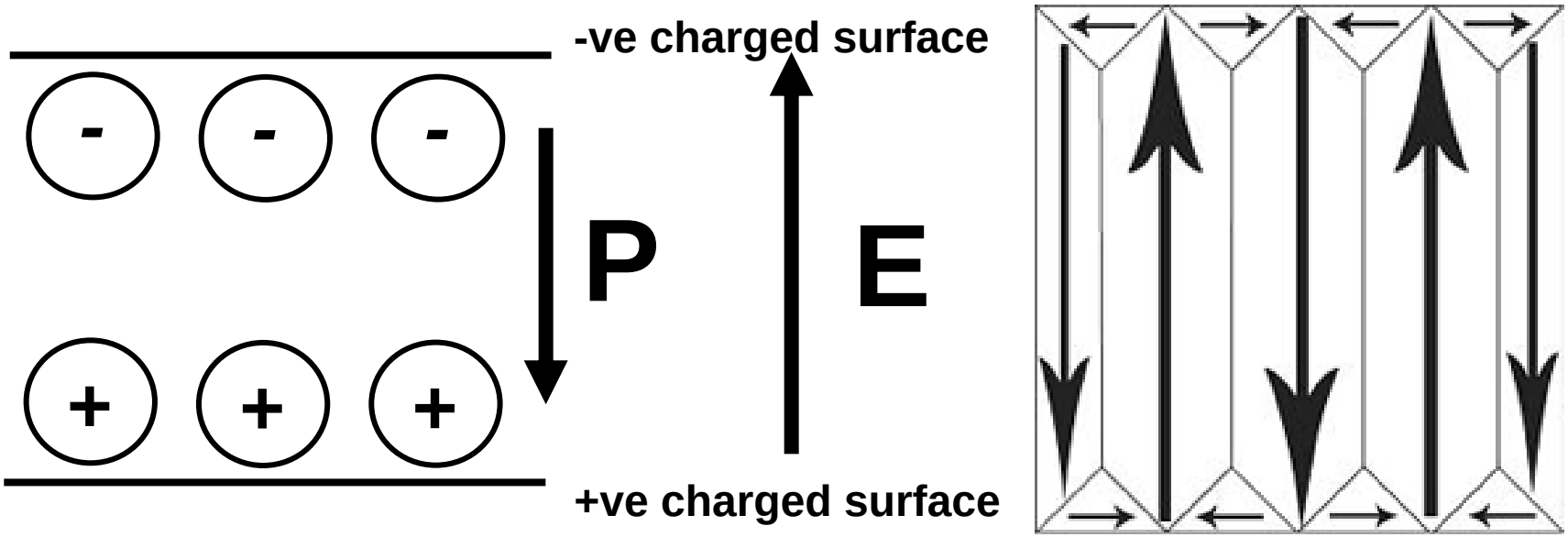


FIG. 4. The topographic image (a) shows 11 PTO grains of sizes between 100 down to 20 nm indicated by the circles. In the line scan over the grain denoted with an arrow, shown at the bottom, the size of the grains can be determined. In the PFM images (b) in-plane and (c) out-of-plane piezoresponse the grain of the size of 20 nm is not visible leading to the assumption they do not have any permanent polarization.

Islands examined by Roelofs *et al.* APL (2002) suggest loss of ferroelectricity below diameter ~20nm

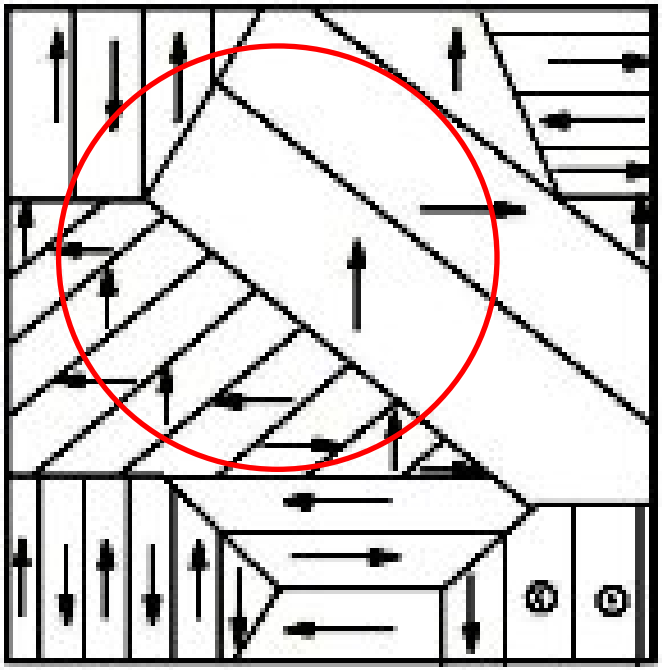
Strain and depolarisation effects on ferroelectric domains



Domains minimise the macroscopic manifestation of the depolarising field

Shape contraint at surfaces and boundaries induces 90° domain formation

Domains can also form in order to accommodate macroscopic shape constraints – shape compensating domains



Basic phenomenological physics for domain periodicities variation with size

Electrostatic energy associated with free surface

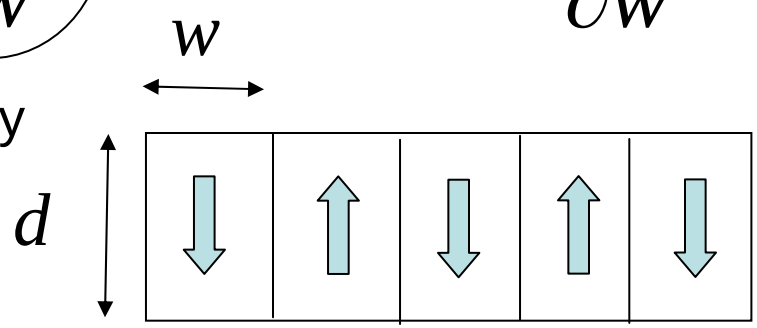
$$F = Uw + \gamma \frac{d}{w}$$

Total domain wall energy

Under equilibrium:

$$\frac{\partial F}{\partial w} = 0 = U - \gamma \frac{d}{w^2}$$

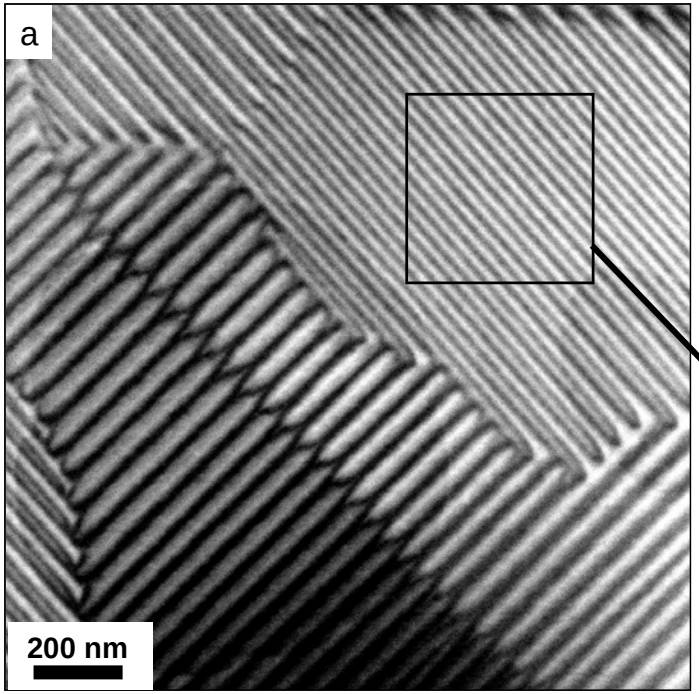
$$w^2 = \gamma \frac{d}{U}$$

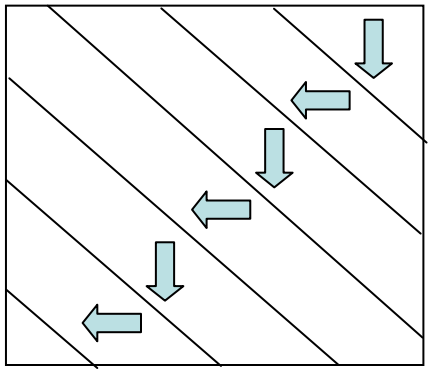


180º domains

Kittel, *Phys. Rev.* **70**, 965 (1946); Zhirnov, *Sov. Phys. JETP* **35**, 822 (1959); Mitsui & Furuichi, *Phys. Rev.* **90**, 193 (1953); Roytburd, *Phys. Status Solidi A* **37**, 329 (1976).

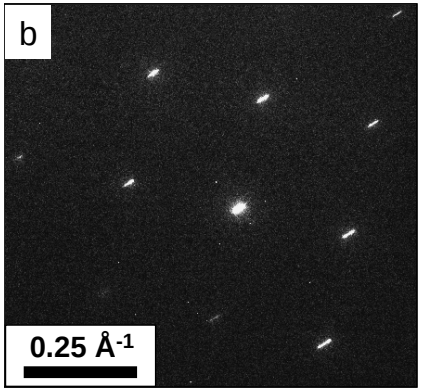
Study domains imaged by STEM in $BaTiO_3$ slabs of controlled thickness (cut with FIB)

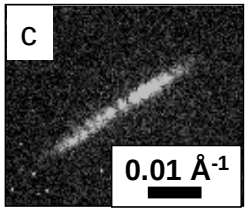




90º domains

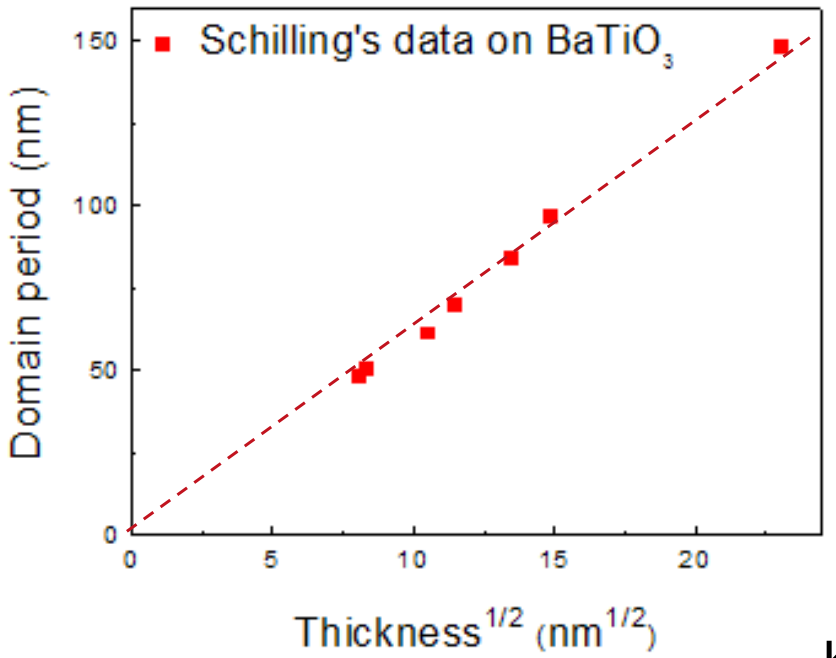
Region for selected area diffraction



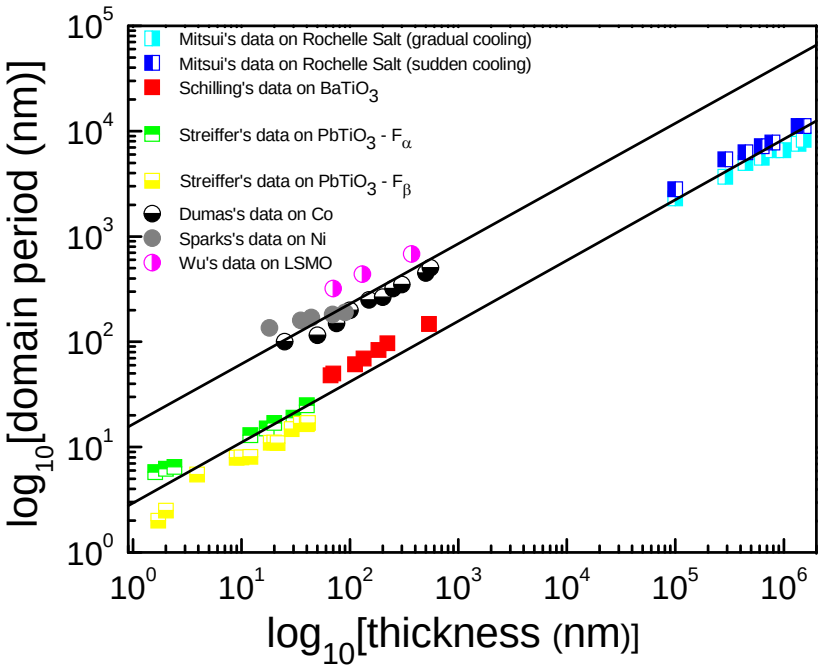


{110} domain walls,
Period in this case ~50nm from both real space and reciprocal space measurements

Find Kittel's law obeyed across 6 orders of magnitude



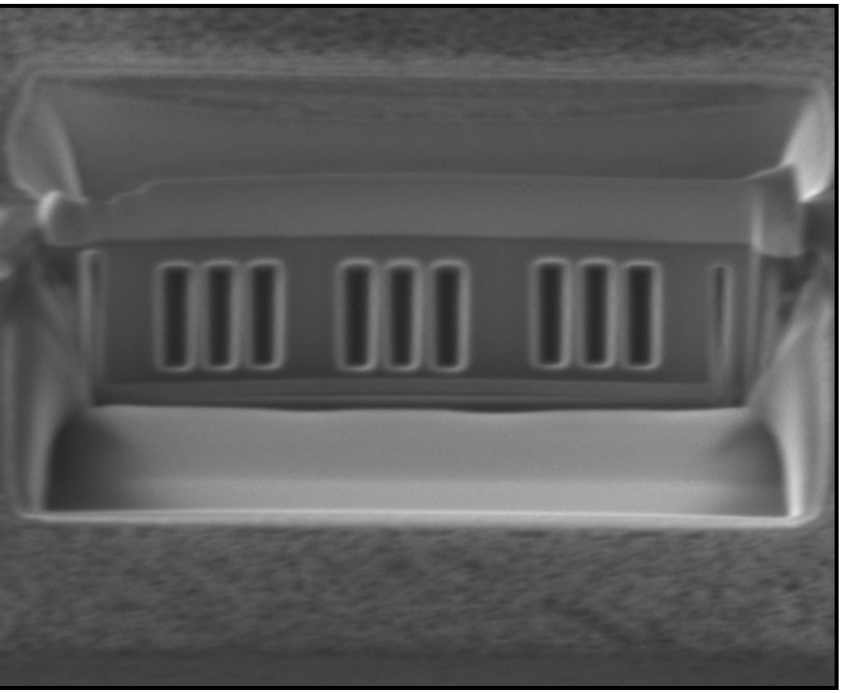
Schilling *et al.*, PRB (2006)



Kittel's law

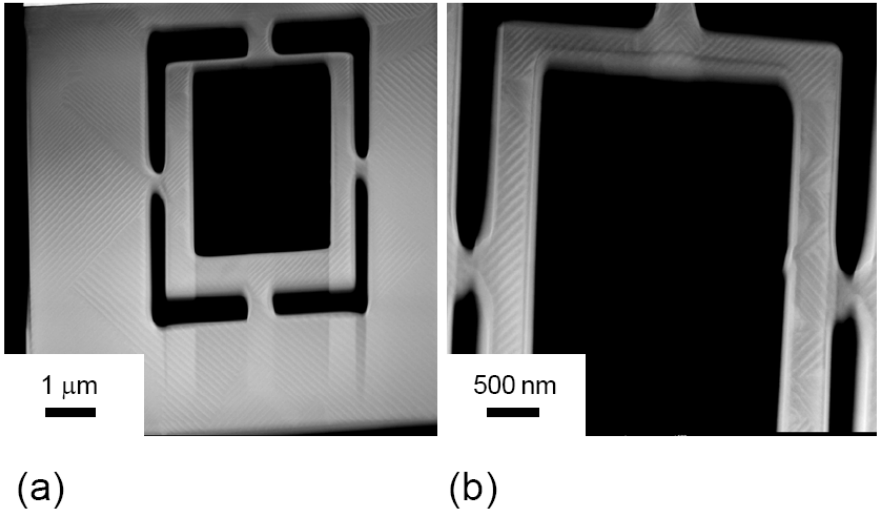
$W=kd^{1/2}$ holds for ferroics across 6 orders of mag.

Constant of proportionality similar within each ferroic subgroup.

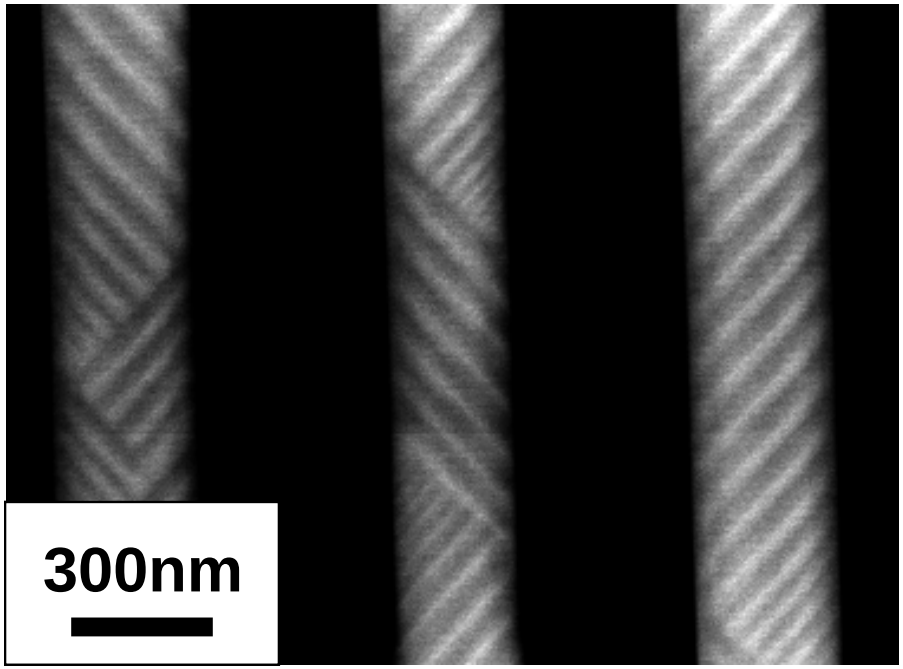


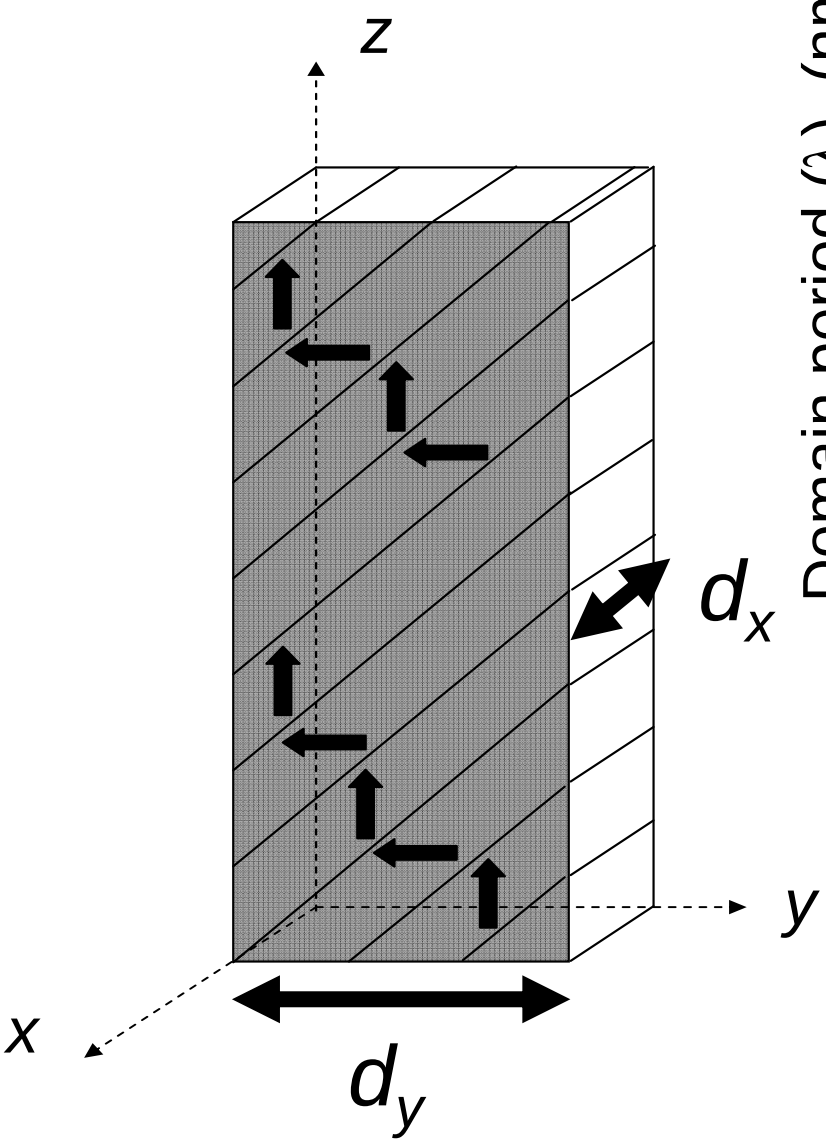
Ferroelectric columns / wires / picture frames

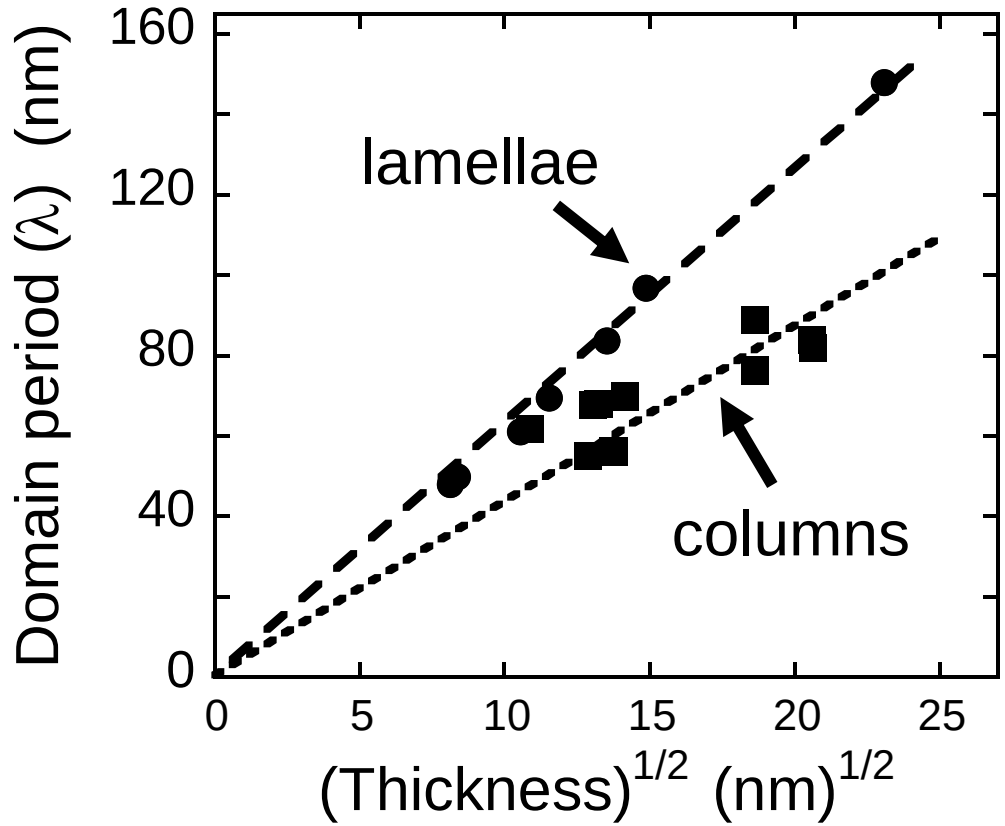
Stripe domains;
Domain periodicity response sensitive to additional size constraint (being thin in more than one dimension)



Schilling *et al*., APL (2006)





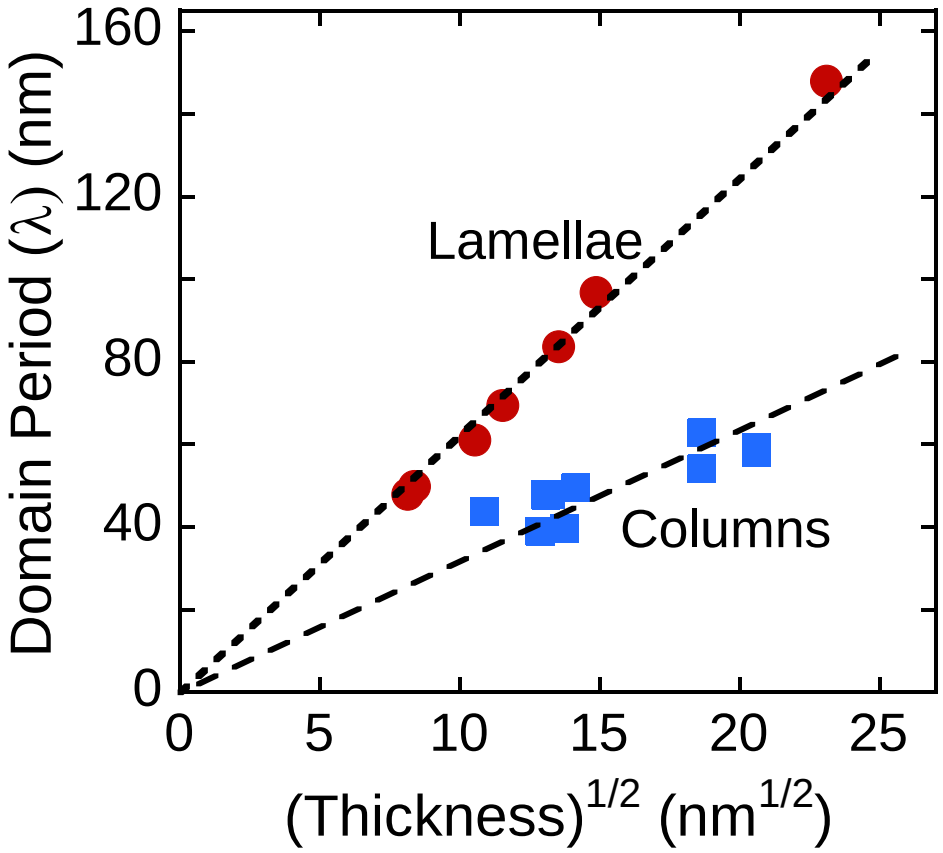


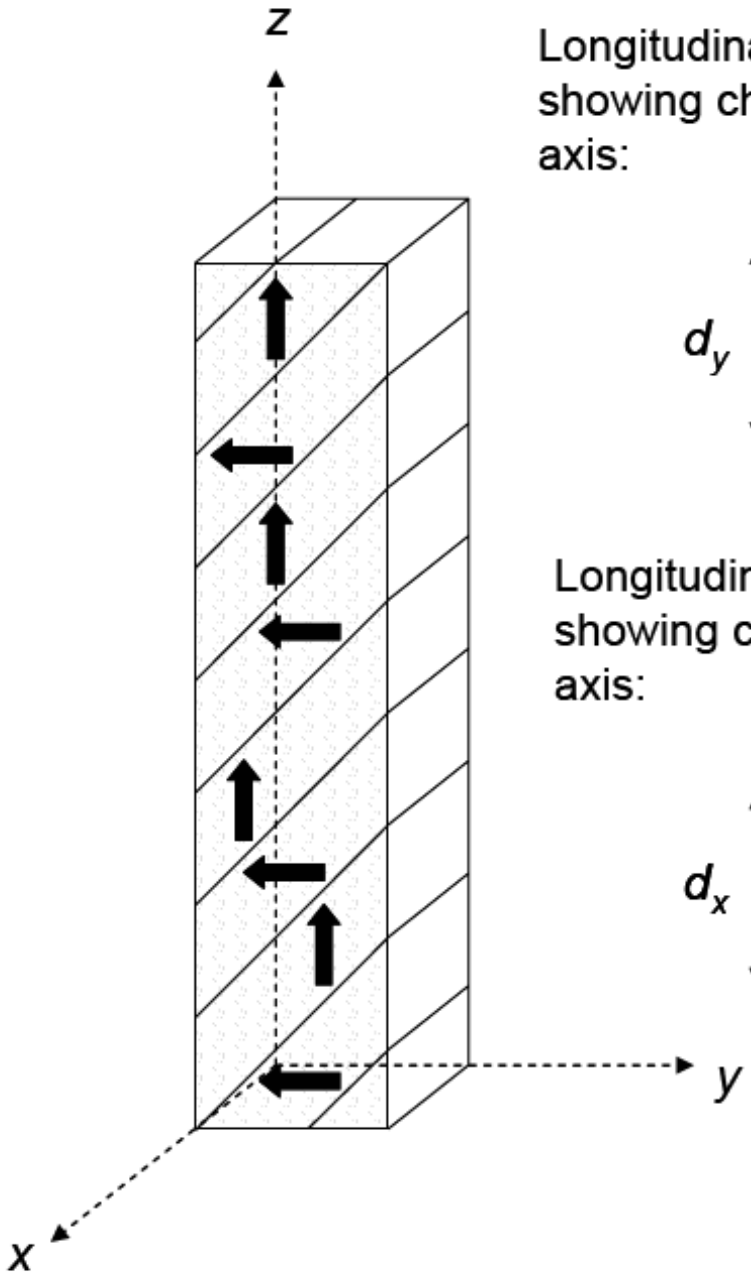
Kittel:

$$w = \left(\frac{\gamma}{U}\right)^{1/2} d^{1/2}$$

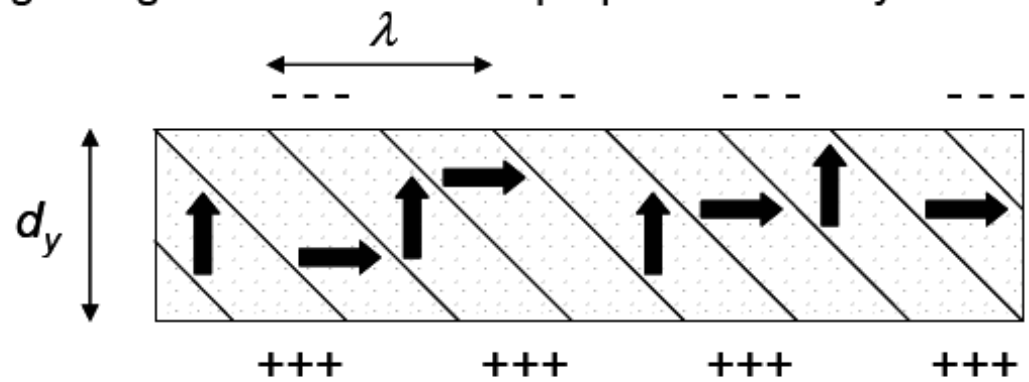
Gradient of plot $\propto \dfrac{1}{\sqrt{U}}$

In fact gradient difference is larger than in previous slides – we measured periodicity parallel to column axis, rather than perpendicular to domain wall – hence factor root two correction. Leads to more obvious surface energy differences (unpublished):

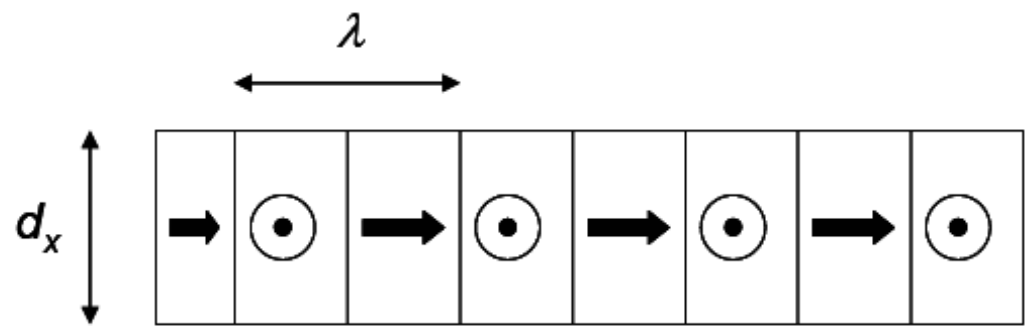




Longitudinal-section (1) perpendicular to x-axis showing charge state on surface perpendicular to y-axis:



Longitudinal-section (2) perpendicular to y-axis showing charge state on surface perpendicular to x-axis:



Full treatment of Kittel for 2D constraint

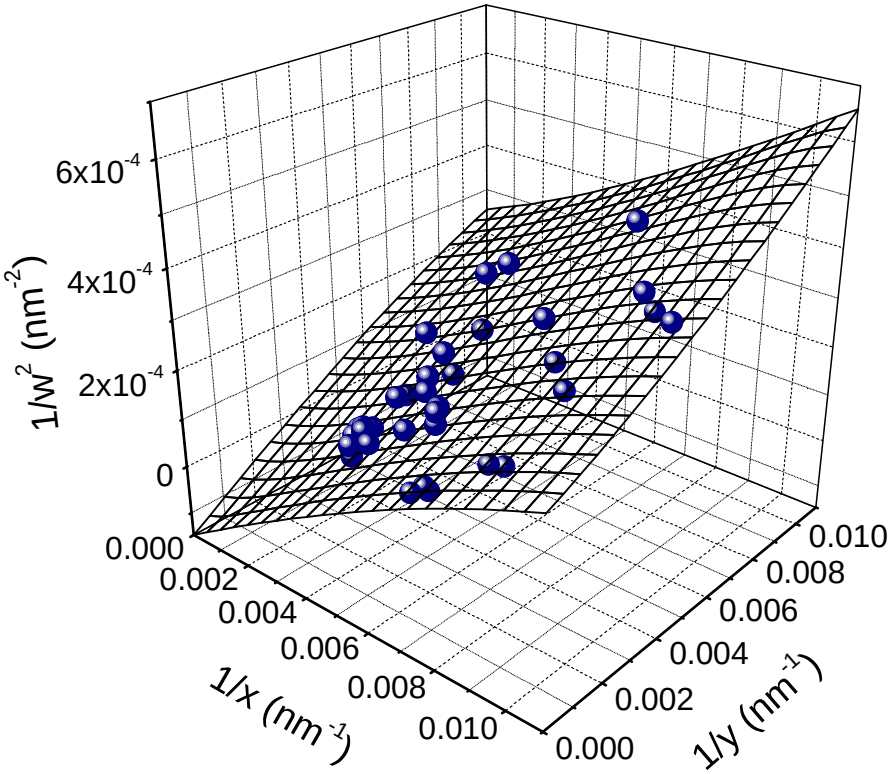
$$w^2 = \frac{\sqrt{2}}{2} \frac{\sigma}{\frac{U_x}{d_x} + \frac{U_y}{d_y}}$$

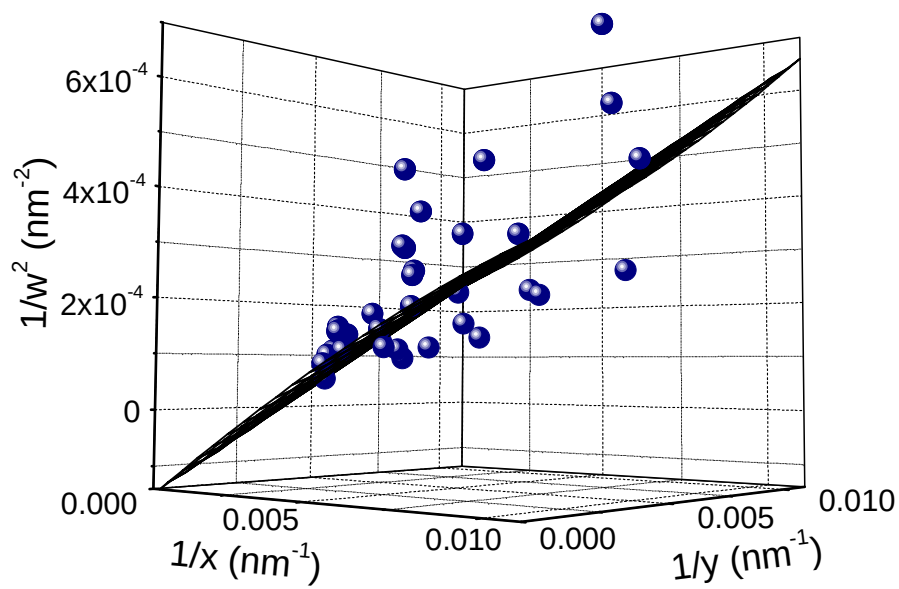
Rewritten:

$$w^{-2} = \left(2\sqrt{2}\sigma\right)^{-1} \left(\frac{U_x}{d_x} + \frac{U_y}{d_y} \right)$$

This defines a plane for w^{-2} vs d_x^{-1} and d_y^{-1}.

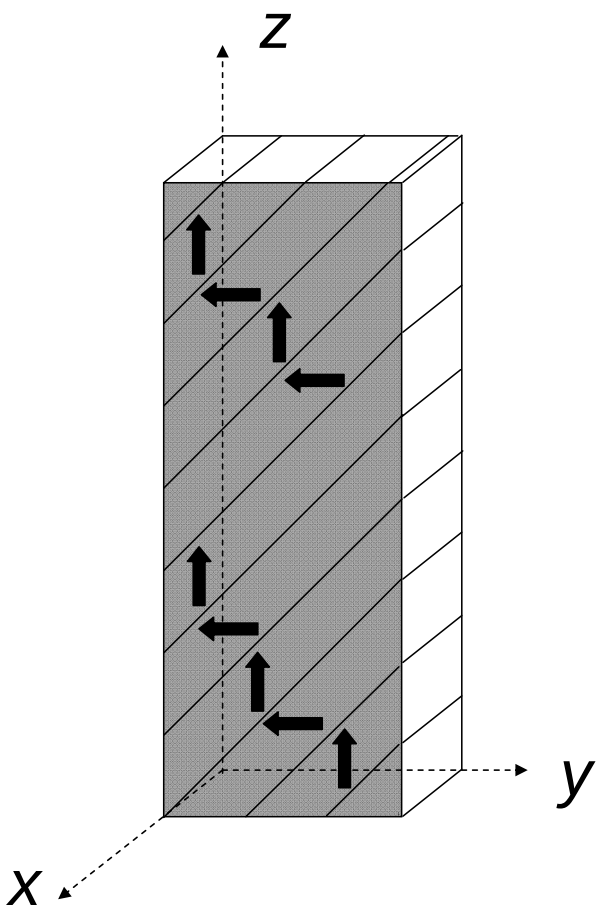
Catalan *et al. JPCM (2007)*





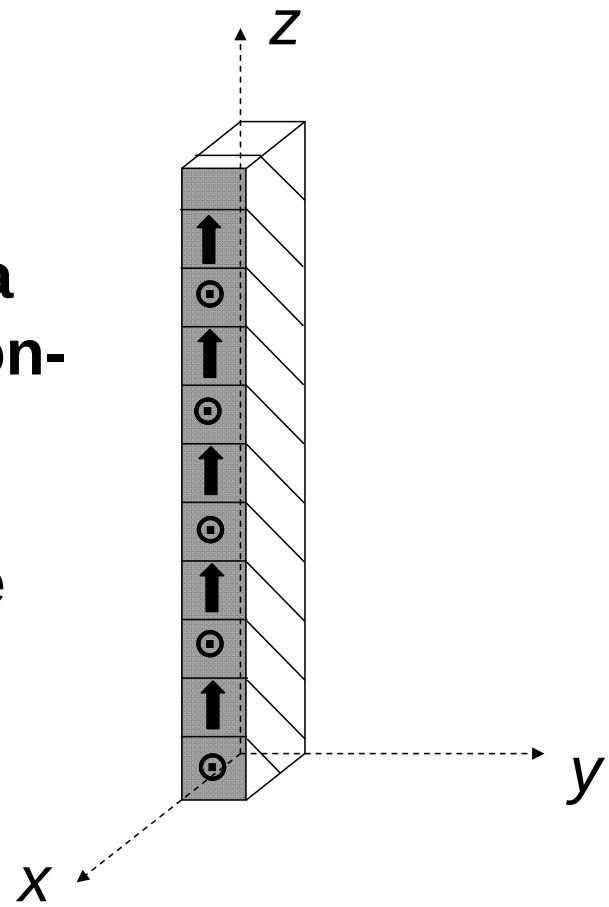
Column energy study suggests:

If $d_y > d_x$ then expect:

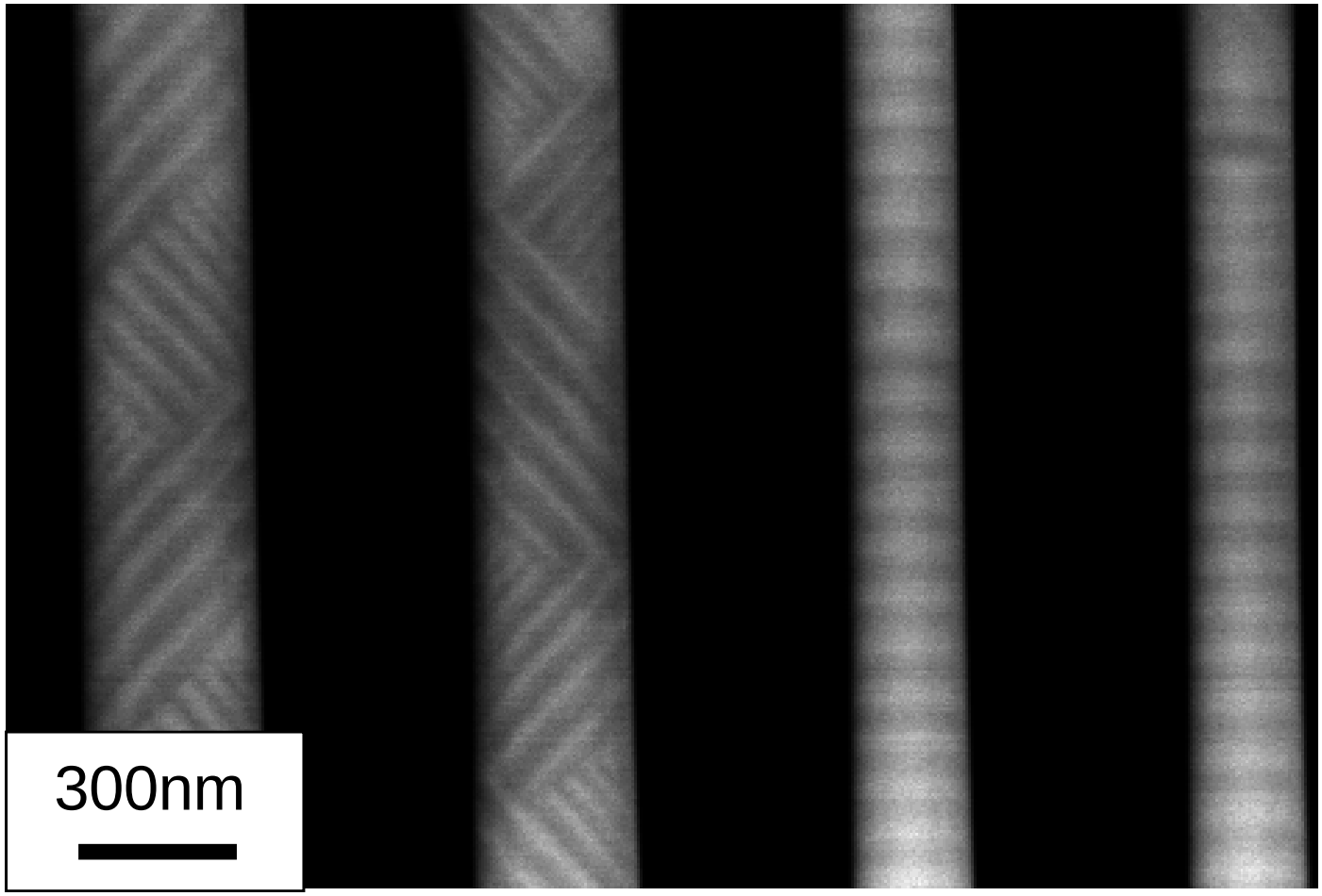


Smaller surface area supports non-axial polarisation out-of-plane

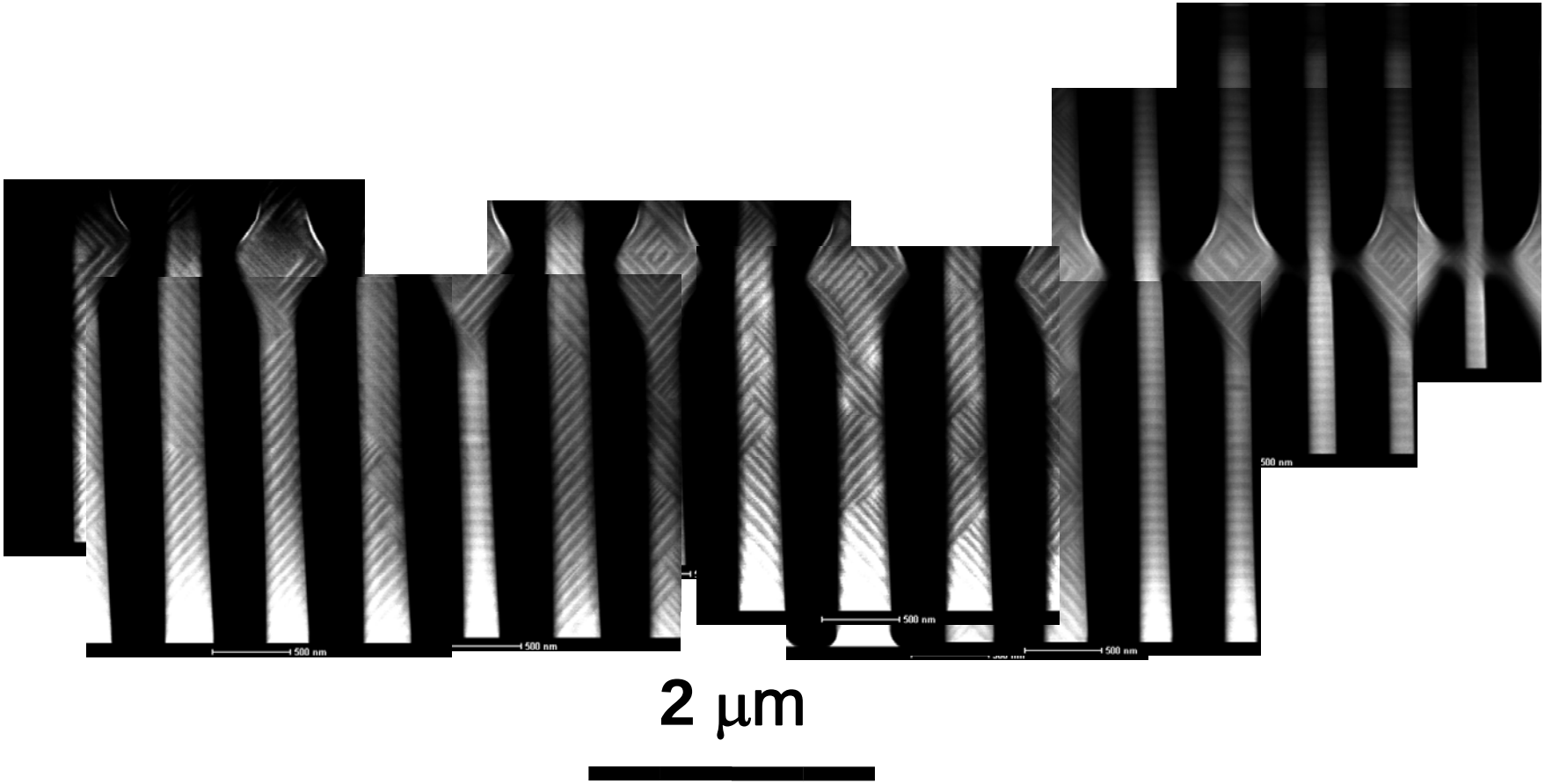
If $d_y < d_x$ then expect:

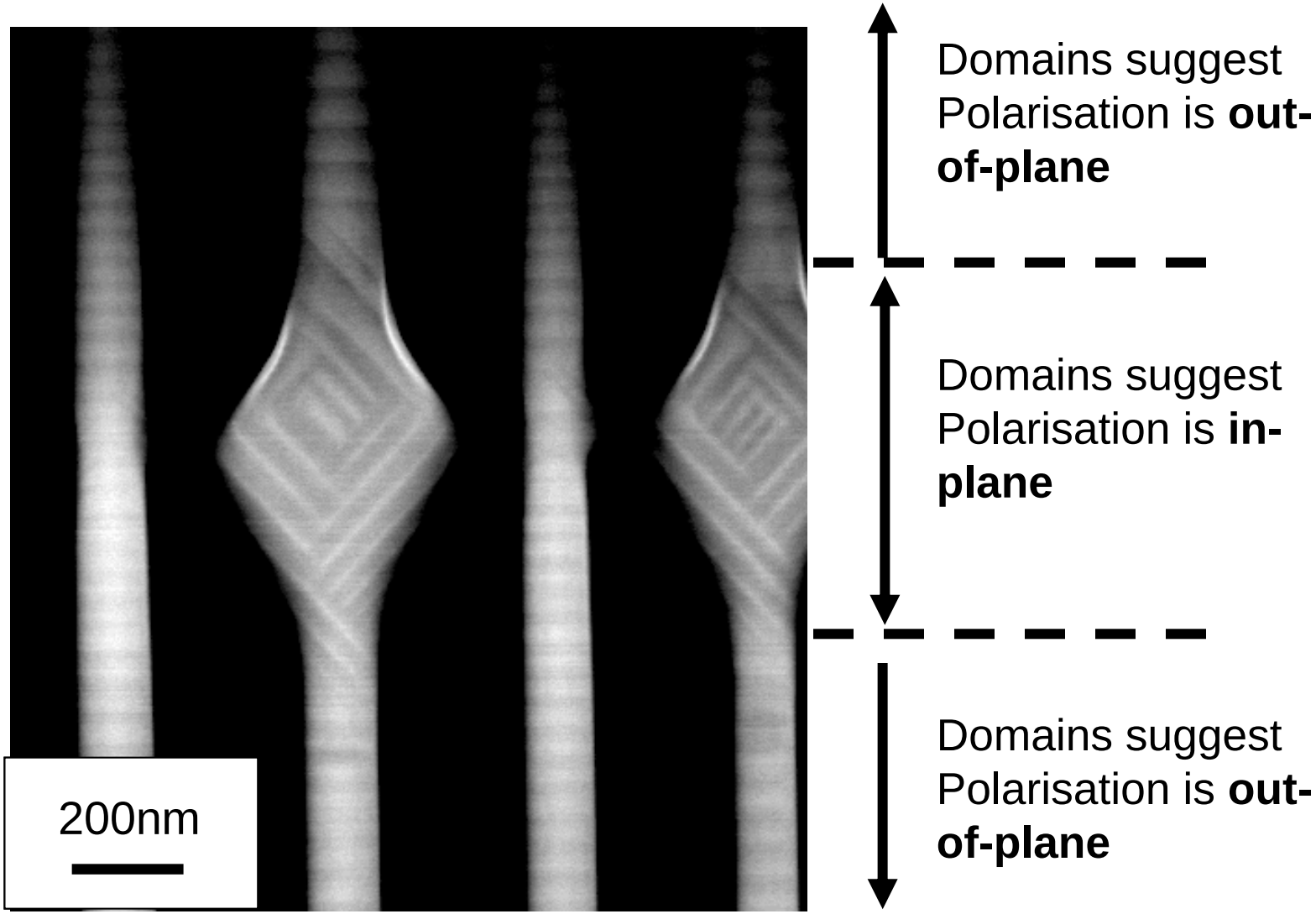


Progression from d_y~350nm to ~150nm (d_x ~ 200nm)



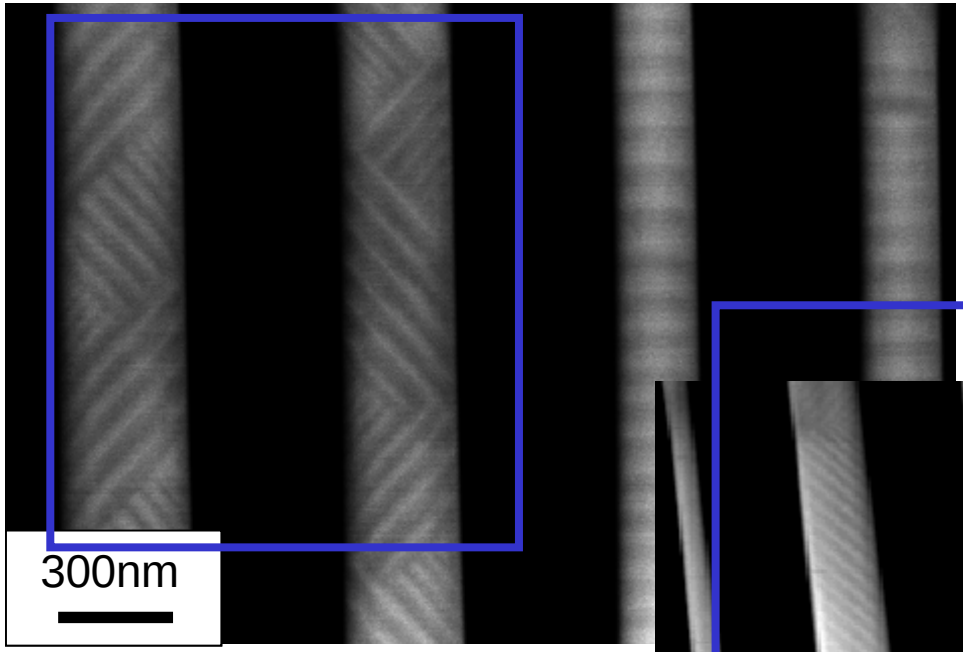
Alina Schilling sculptures on FIB a series of complex nanowire samples – STEM montage of one below:



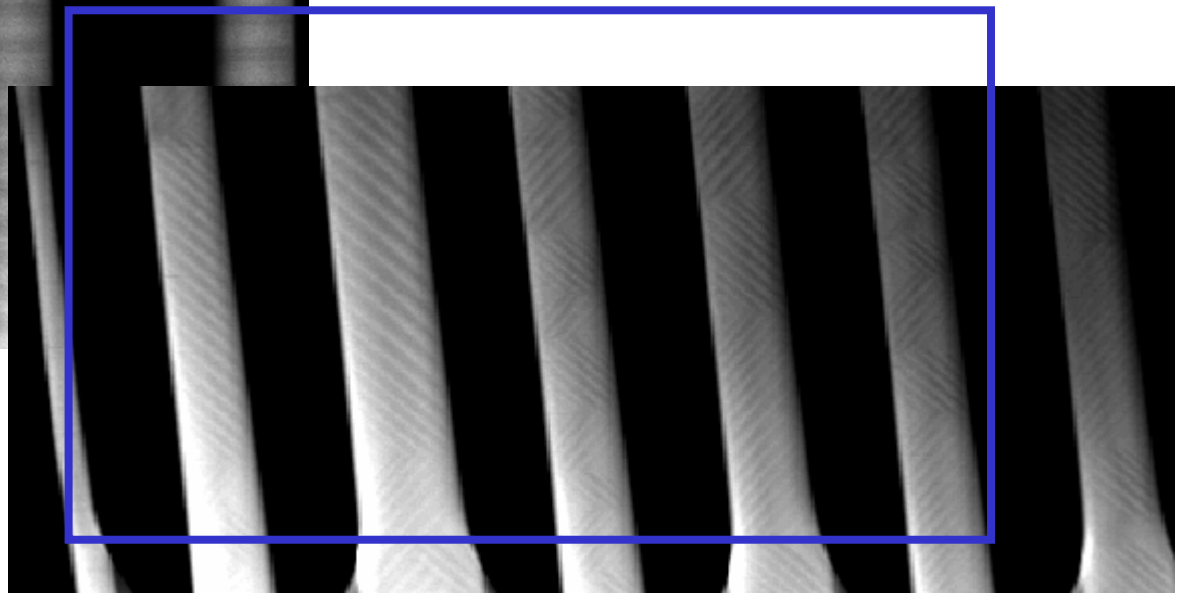


Morphological control of polar orientation

Other interesting domain configurations not completely rationalised

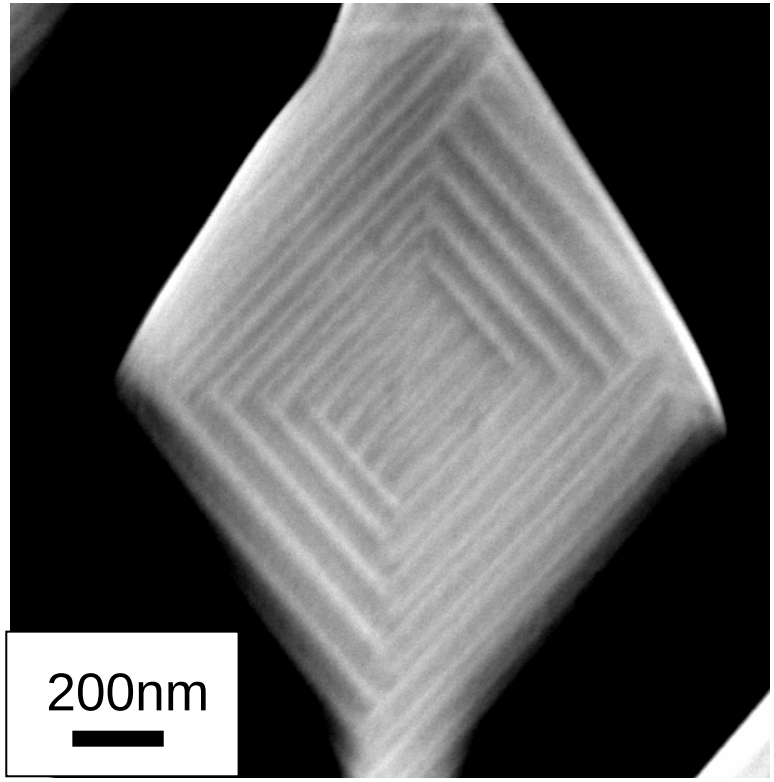


Formation of domain ‘superperiods’ as a further mechanism for minimising depolarisation field

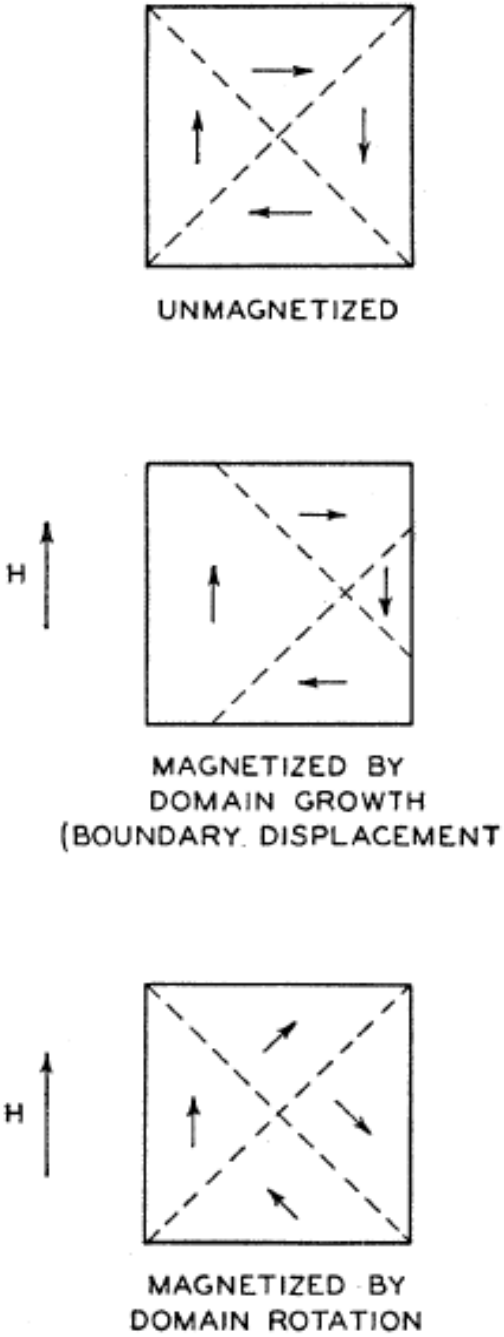


Subtle domain periodicity changes at more complex domain boundaries

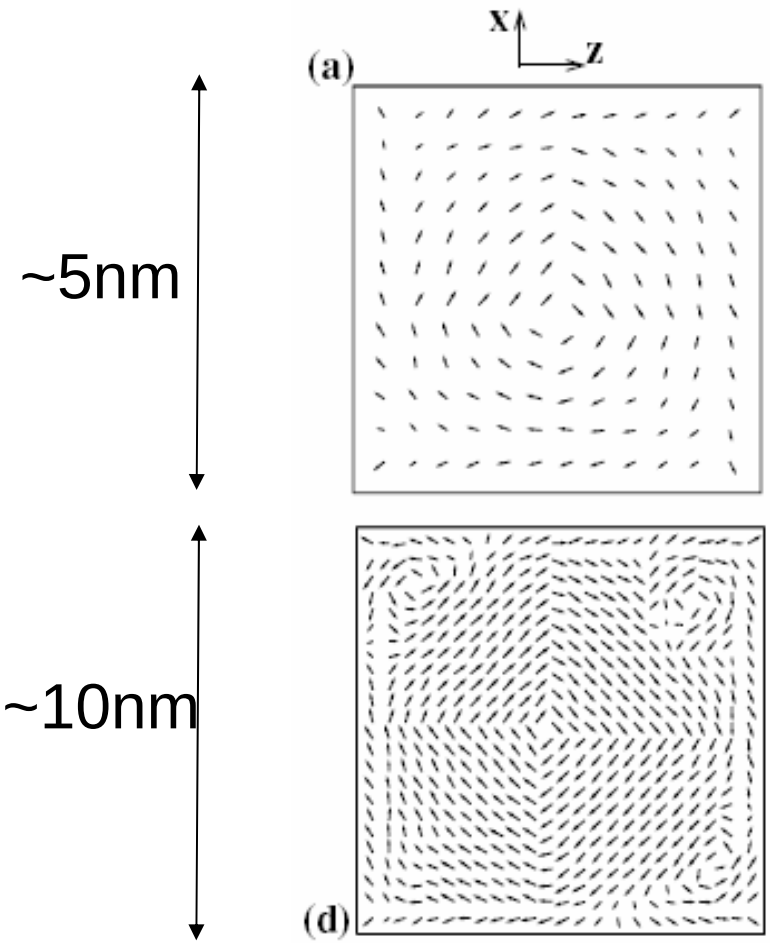
Flux / Field Closure Domains in Ferroelectric Nanodots



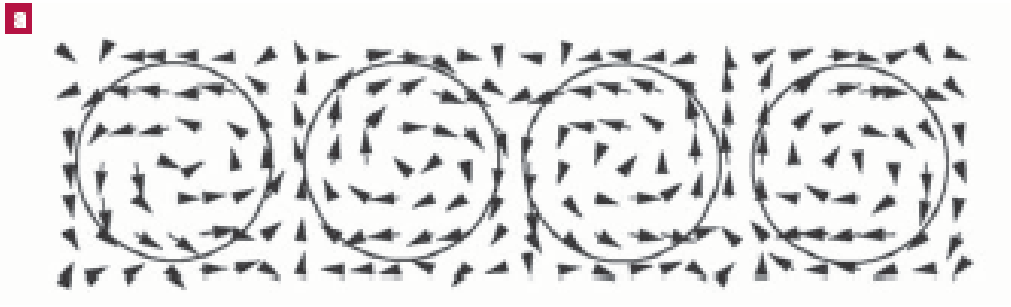
C. Kittel, Rev. Mod. Phys., **21**, 541 (1949)



Modelling of ferroelectric dots and nanowires



Fu and Bellaiche PRL, **91**, 257601 (2003)



Naumov *et al.* Nature, **432**, 737 (2004) and J. F. Scott, Nature Materials, **4**, 13 (2005)

Ferroic Vortices in Minerals

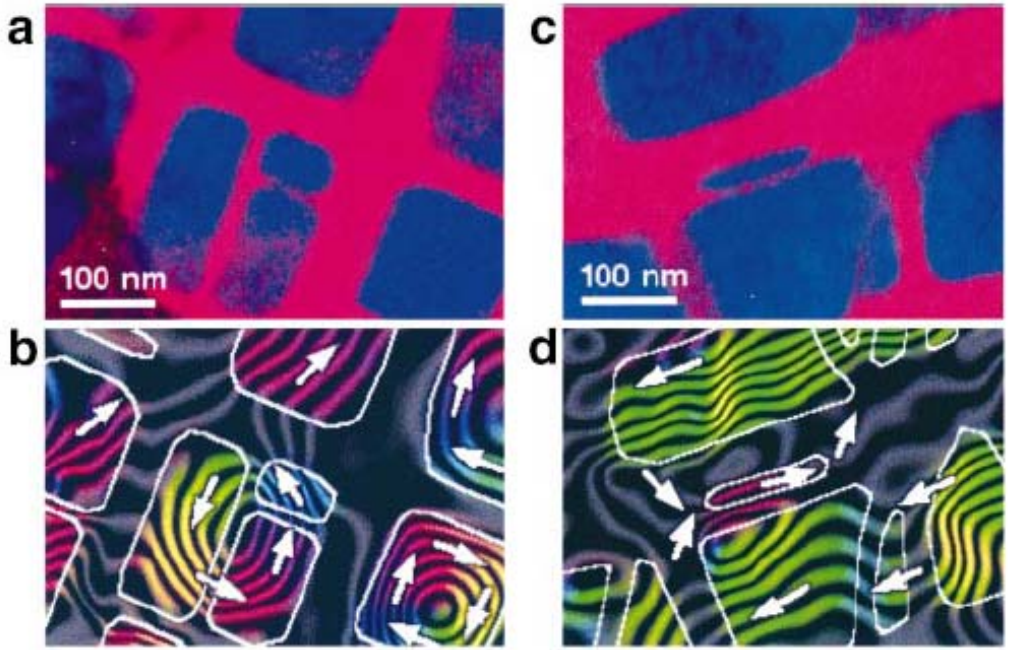
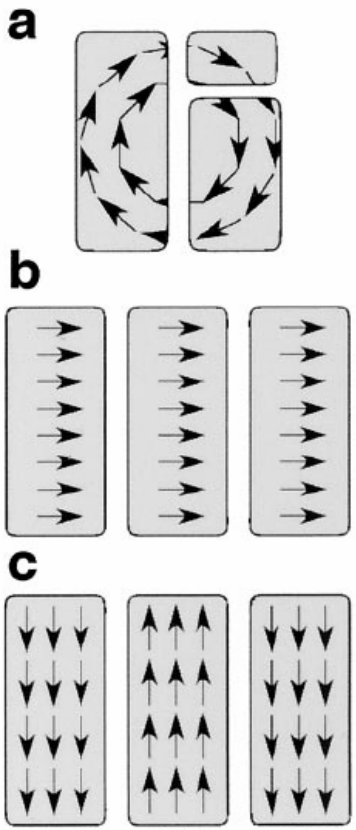


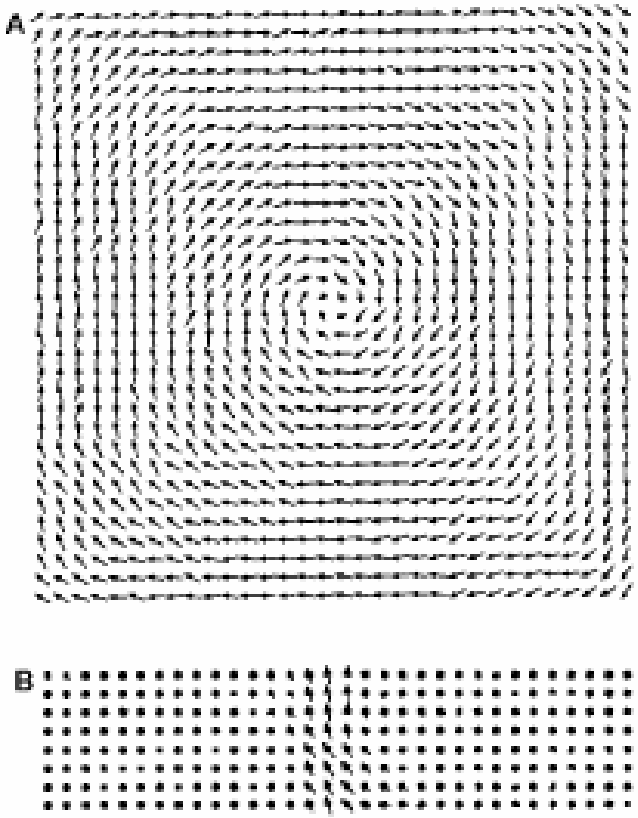
Fig. 4. (*a* and *c*) Chemical maps (blue = Fe, red = Ti) from two regions not shown in Figs. 1 and 3. (*b* and *d*) The corresponding magnetic microstructures, in the same format as Fig. 3. (*b*) Three adjacent magnetite-rich regions combining to form a single vortex; (*d*) a small region that is magnetically antiparallel to its larger neighbors.

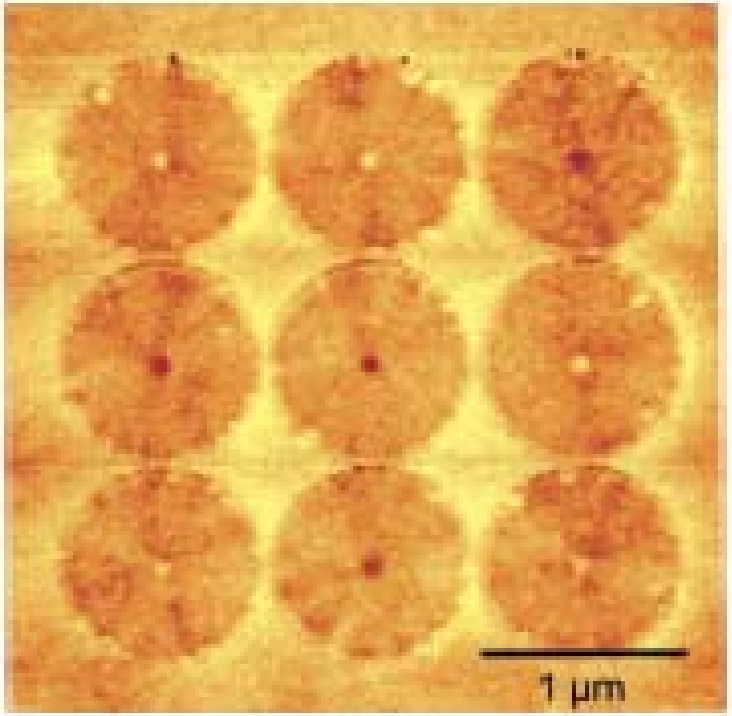


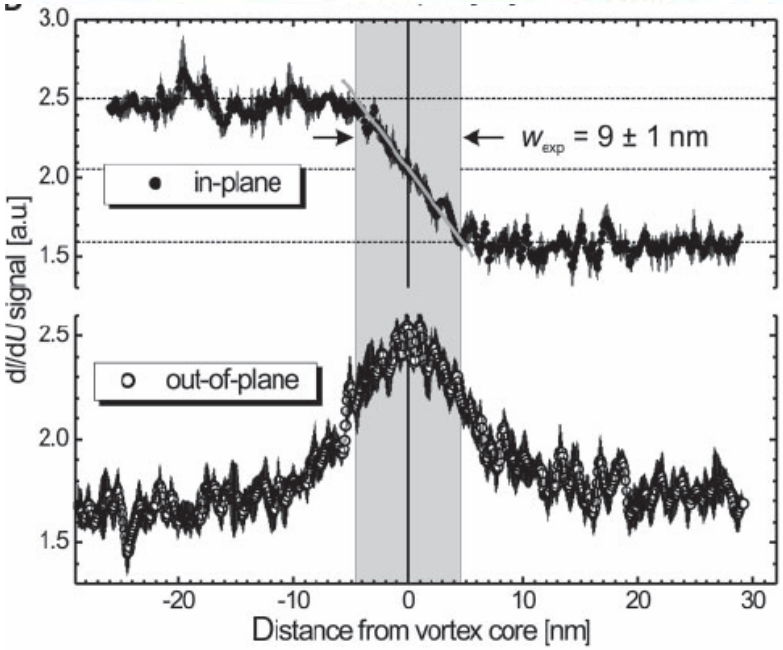
Harrison *et al.,* PNAS, **99**, 16556 (2002)

Vortex core observations in Ferromagnets

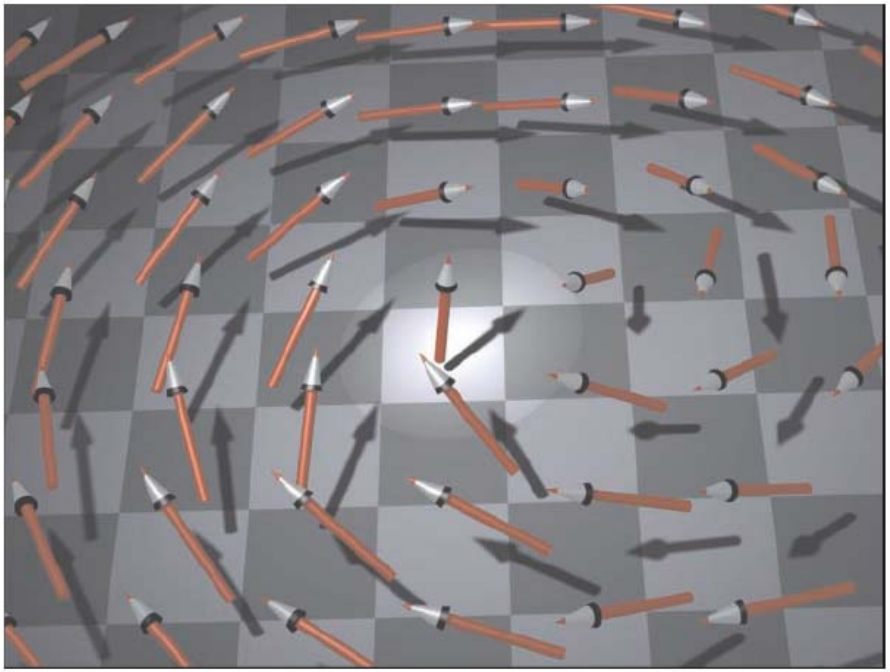
Shinjo et al. Science, 289, 930 (2000)







Wachowiak *et al.,* Science, **298**, 577 (2002)



Wachowiak *et al.*, Science, **298**, 577 (2002)

N. D. Mermin, Rev. Mod. Phys., **51**, 591 (1979)

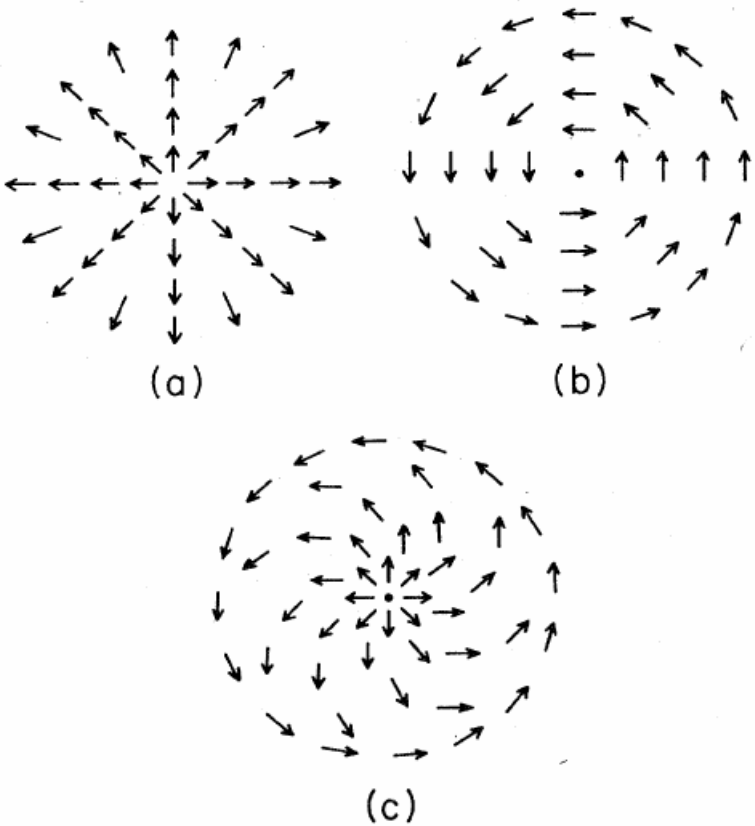
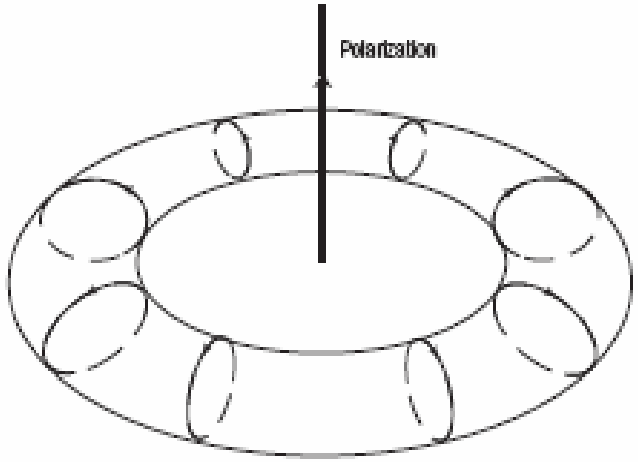
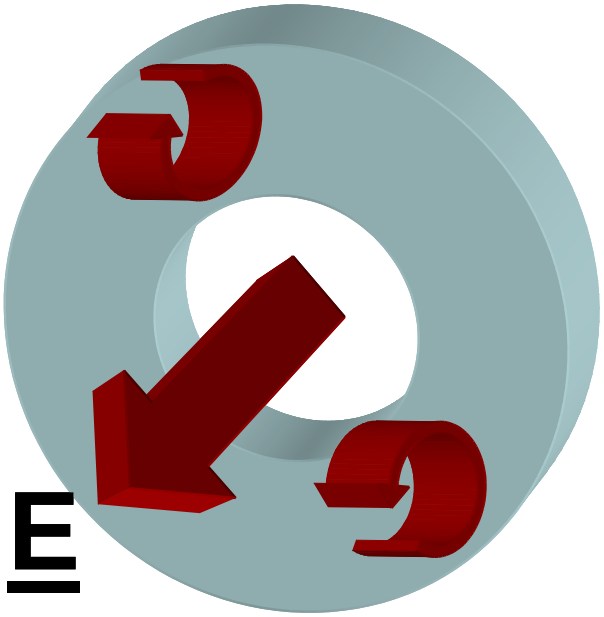


FIG. 5. (a) and (b). Two planar spin configurations with winding numbers +1. (c) Configuration (b) has been altered to coincide with configuration (a) in the core region near the singular point, but remains unaltered away from the core region.

More complex morphologies - ferroelectric solenoids ?

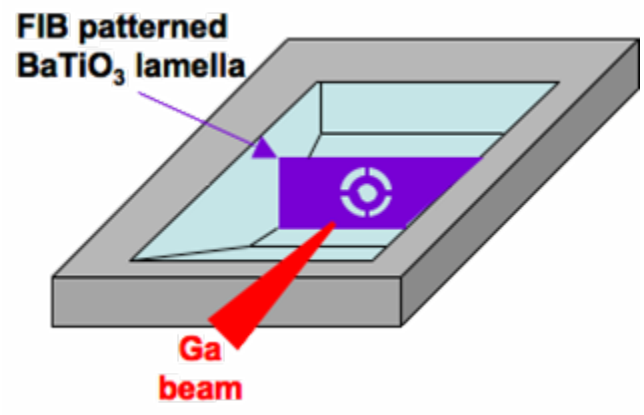
Suggests nanoscale ferroelectric solenoid



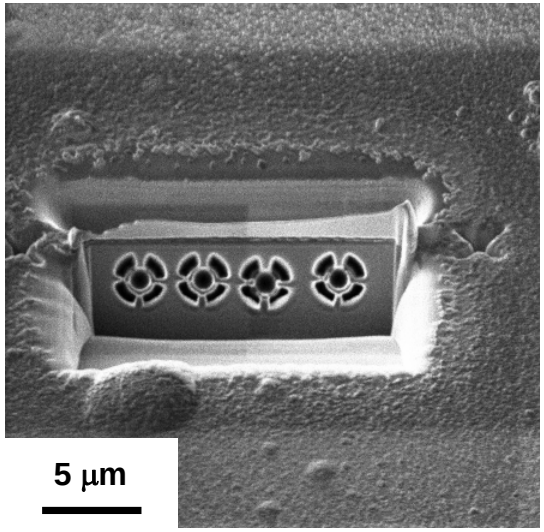


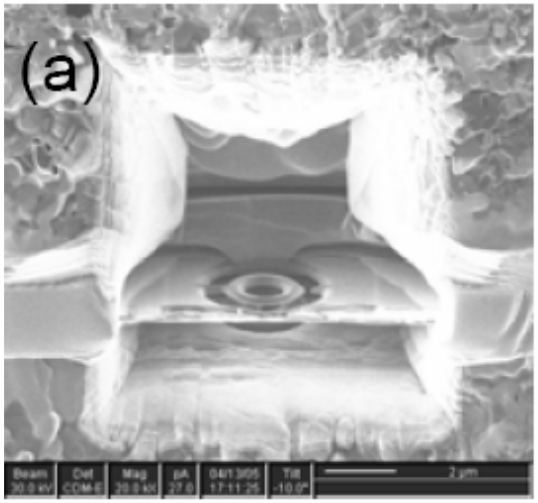
Gorbatsevich & Kopaev, Ferroelectrics, **161,** 321 (1994)
and J. F. Scott, Nature Materials, **4**, 13 (2005)

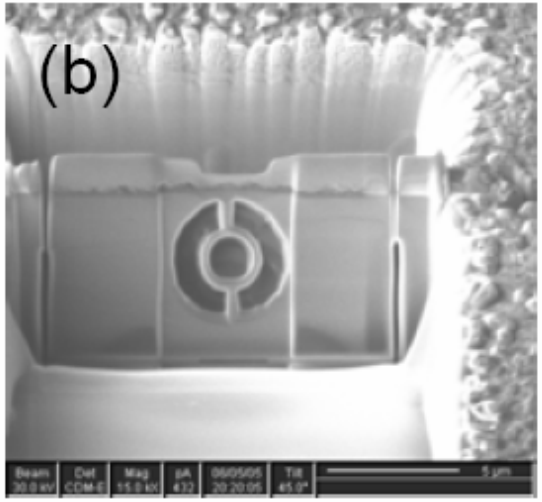
Toroidal Nanoscale Ferroelectrics



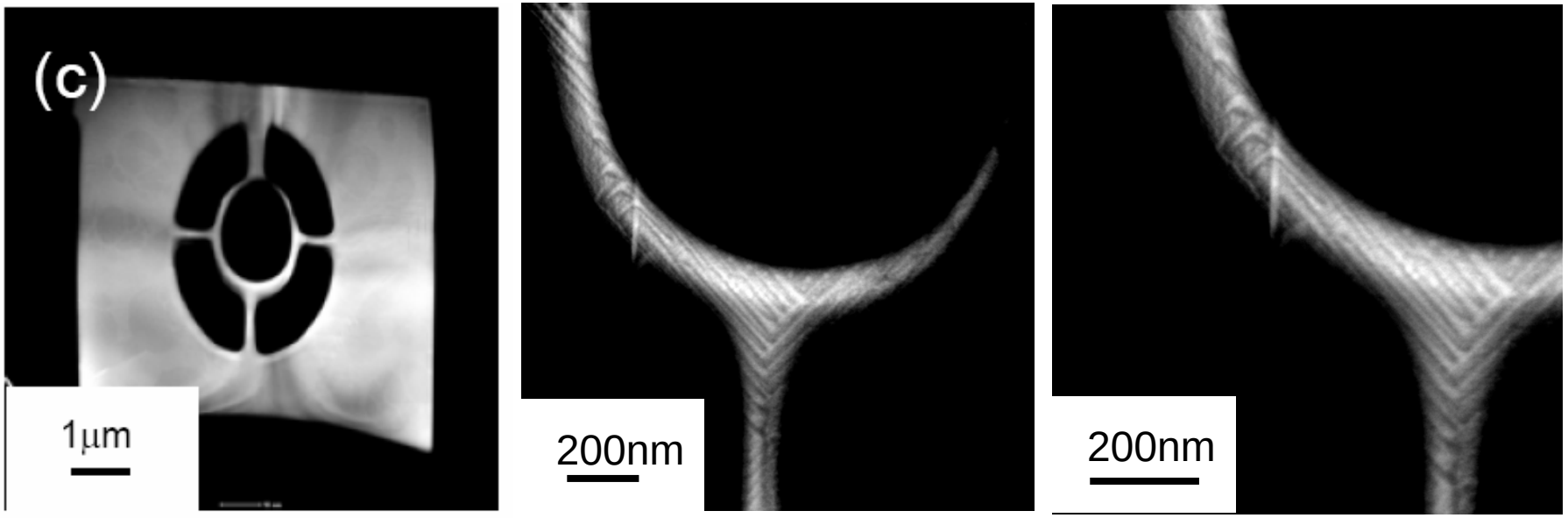
Secondary electron images generated by Ga-ion primary beam on FIB





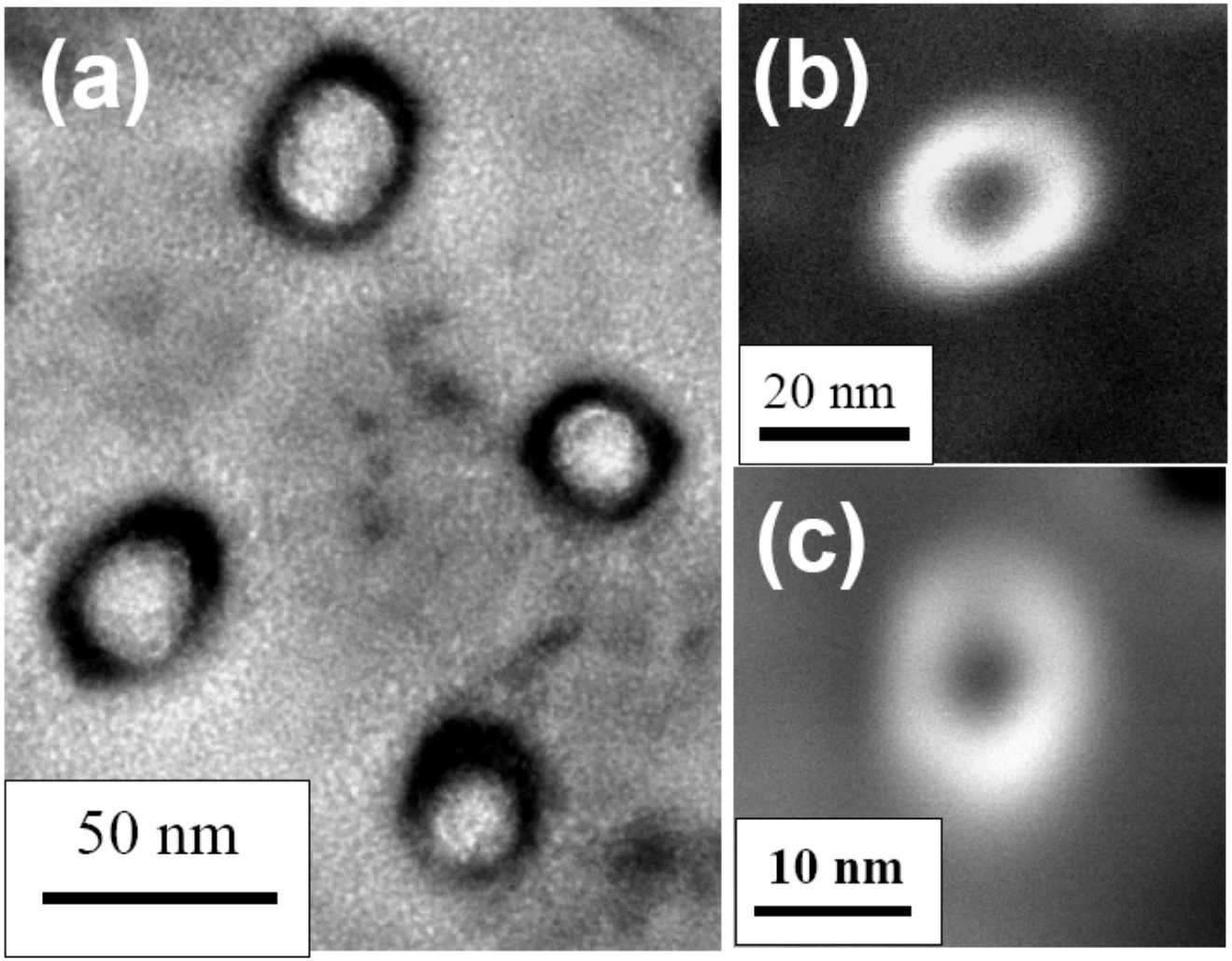


Domain imaging clearly shows no evidence of vortices down to ~100nm



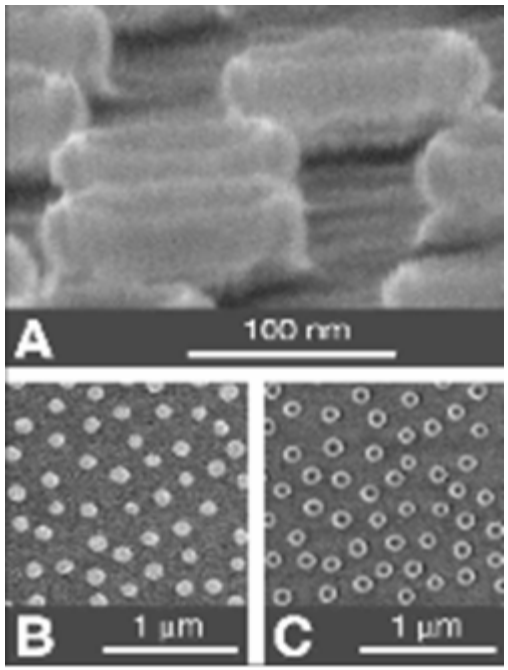
Conventional {110} oriented domain walls, with predictable periodicities. Need to push dimensions down below that achievable with FIB alone or look at systems in which polar rotation is easier (MPB systems or relaxors below T_f).

Ferroelectric nanorings made by TEM sectioning PZT-internally coated nanoporous alumina

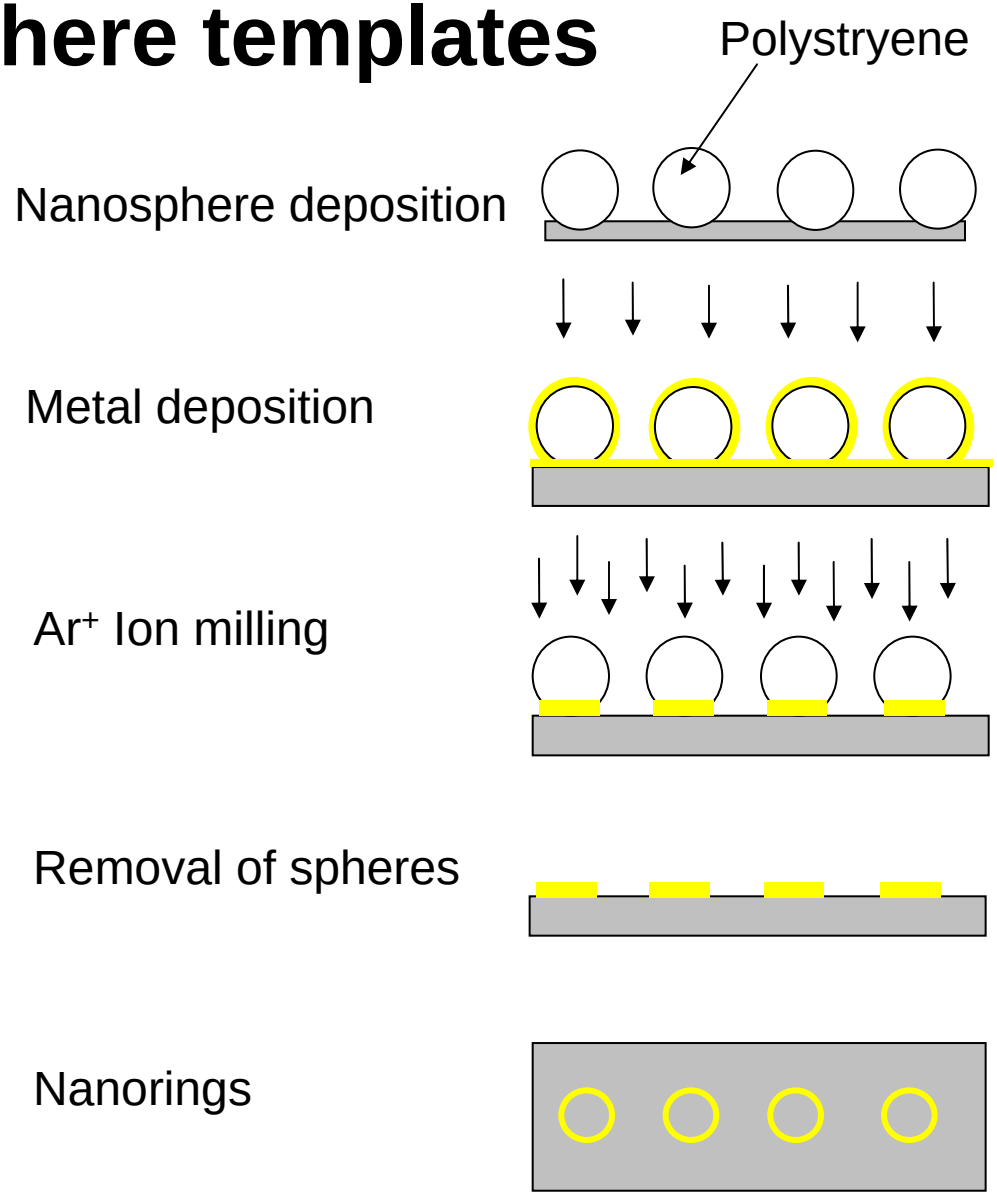


Zhu *et al*., APL **89**, 122913 (2006) – rings made, but not yet evidence of vortex domains

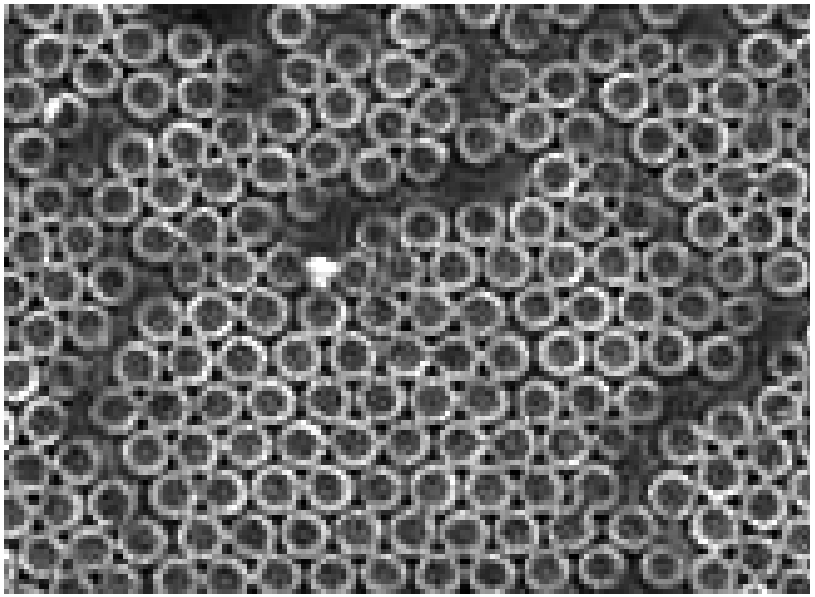
Rings using latex sphere templates



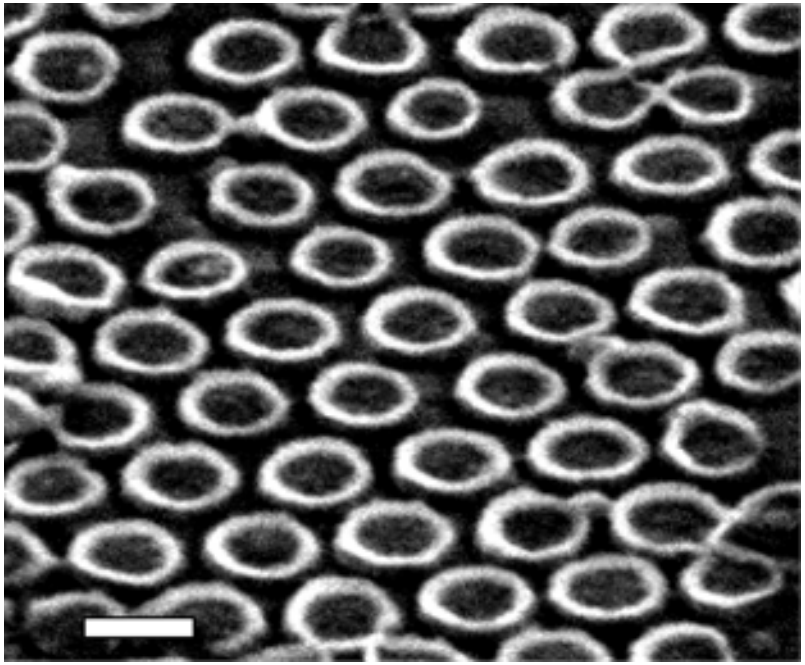
Aizpurua *et al*., PRL **90**, 574011 (2003)



PZT nanoring arrays



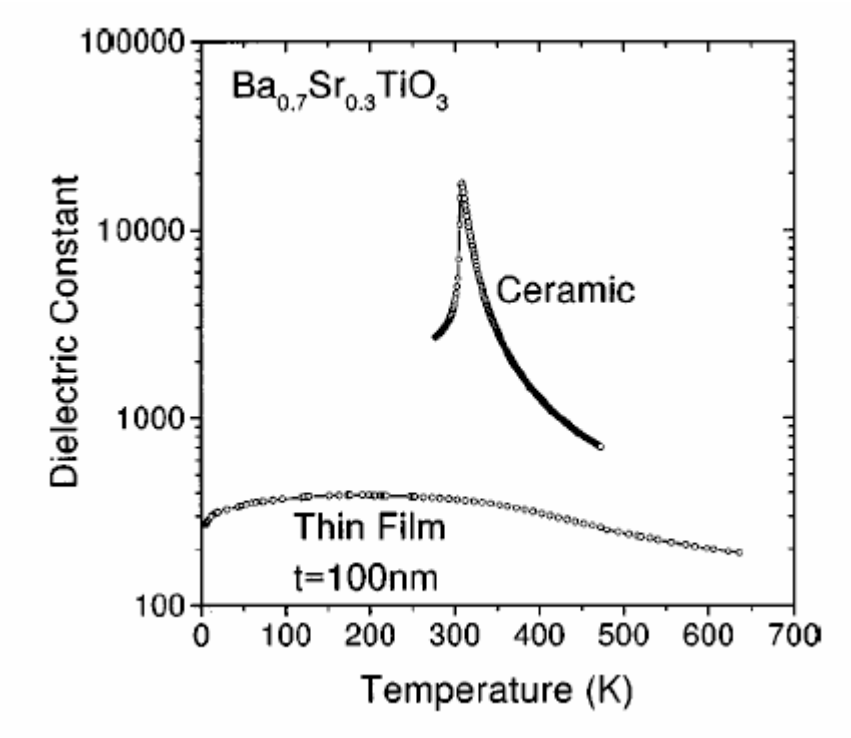
300nm



100nm

As yet no evidence of vortex domain formation

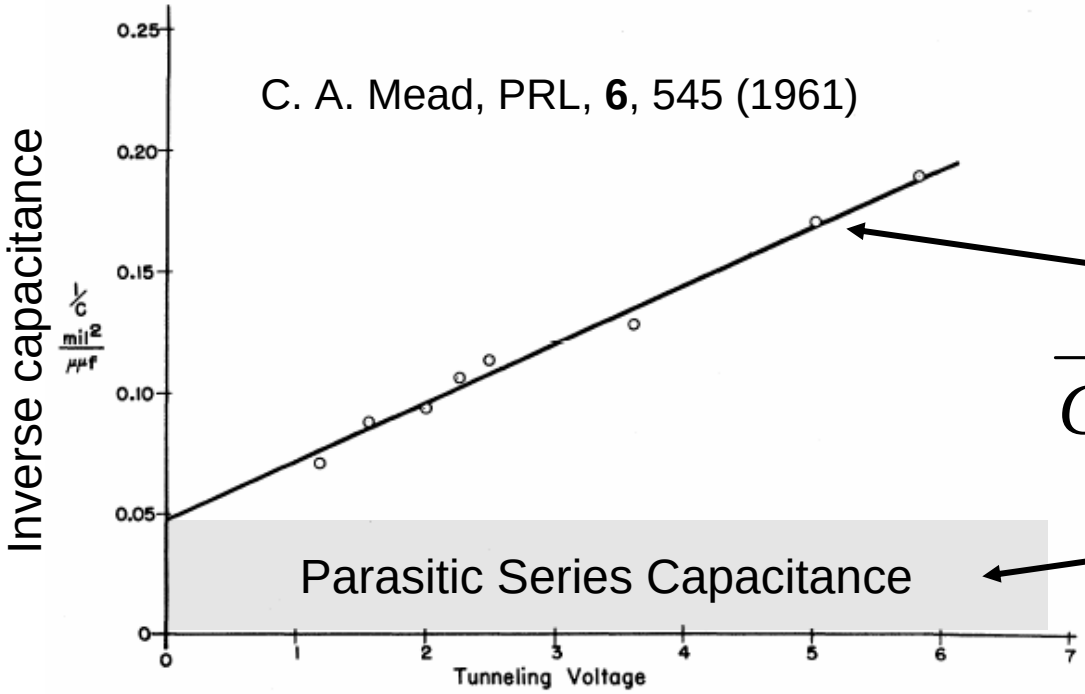
Size effects on *dynamics* of ferroelectrics – focus on permittivity



Move from bulk / single crystal to thin film results in dramatic collapse in low-field permittivity, smearing of Curie anomaly, and apparent migration of Curie ‘peak’ mainly to lower temperatures:

Shaw *et al.* APL (1999), also Parker *et al.* APL (2002)

Reduction in permittivity rationalised by series capacitance ‘dead layer’



$$\frac{1}{C_{eff}} = \frac{1}{C_{bulk}} + \frac{1}{K}$$

Film Thickness

Vol 443|12 October 2006|doi:10.1038/nature05148 nature

LETTERS

Origin of the dielectric dead layer in nanoscale capacitors

Massimiliano Stengel[1] & Nicola A. Spaldin[1]

Atomistic simulations with applied field – novel step.
Conclude **intrinsic** 'dead-layer' due to imperfect nature of screening from real electrodes.
Smaller screening length – less apparent 'dead-layer' effect.

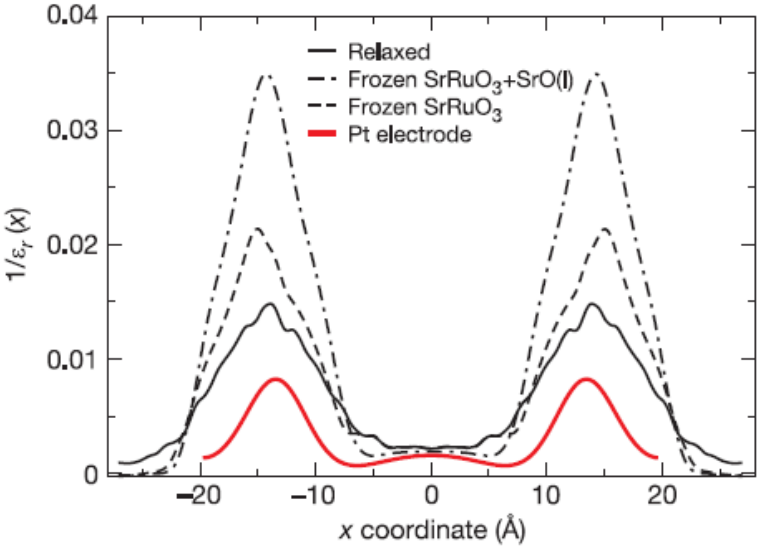


Figure 3 | Influence of the ionic contribution to the screening on the magnitude of the dead layer. Black lines show the inverse permittivity profiles obtained by freezing the ions in the $SrRuO_3$ electrodes. The fully relaxed result of Fig. 1 (solid curve) is compared to the frozen-electrode profiles, respectively allowing (dashed) or not allowing (dot-dashed) the interfacial SrO(I) layer to relax. The calculated profile for a Pt/$SrTiO_3$ capacitor (shown as a thick red curve) demonstrates the superior properties that can be achieved by using elemental metals as electrodes.

Origin of the series capacitance ?

Falls into 3 distinct groups:

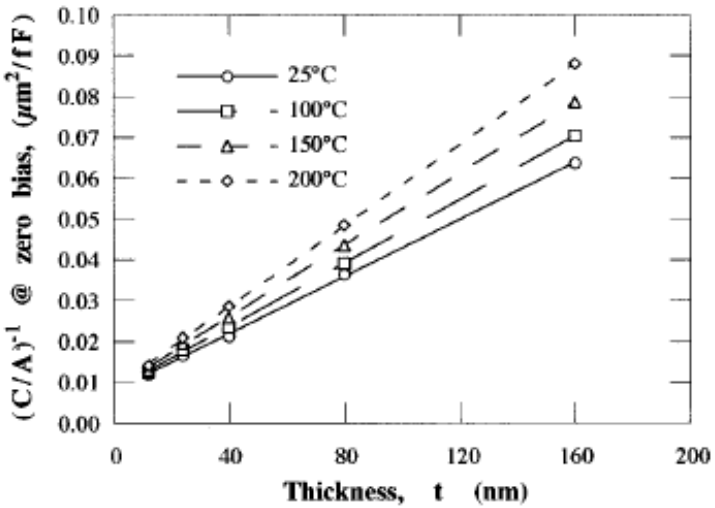
(I) Relating to unavoidable physics associated with the ferroelectric-electrode boundaries (ideas such as Schottky barrier-induced interfacial capacitance, fundamental polarisation suppression to allow P=0 at electrode-ferroelectric boundary, imperfect charge screening in the electrode, fundamental asymmetry issues);

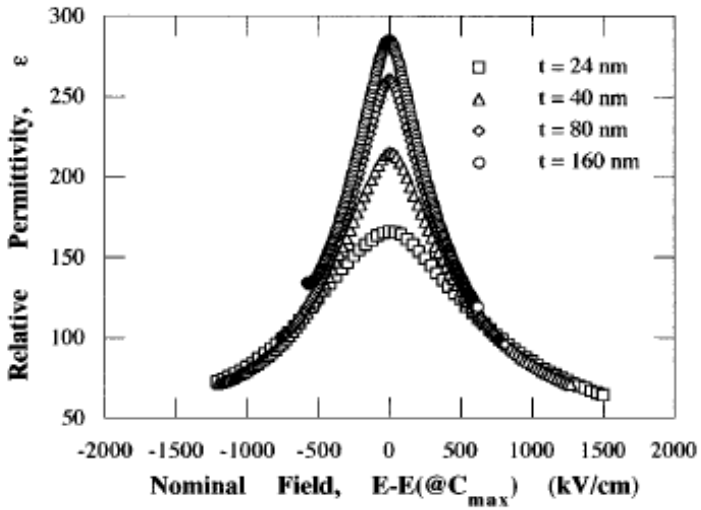
(II) Processing problems associated with the electrode-ferroelectric boundary which could be engineered out (such as distinct interfacial microstructure or chemistry or defects, strain coupling)

(III) Through-film microstructure – the issues of grain boundaries.

What does experiment tell us about origin of series capacitance ?

Classical work by Basceri *et al.* JAP one of the earliest attempts to identify the electrical characteristics of the series cap component.





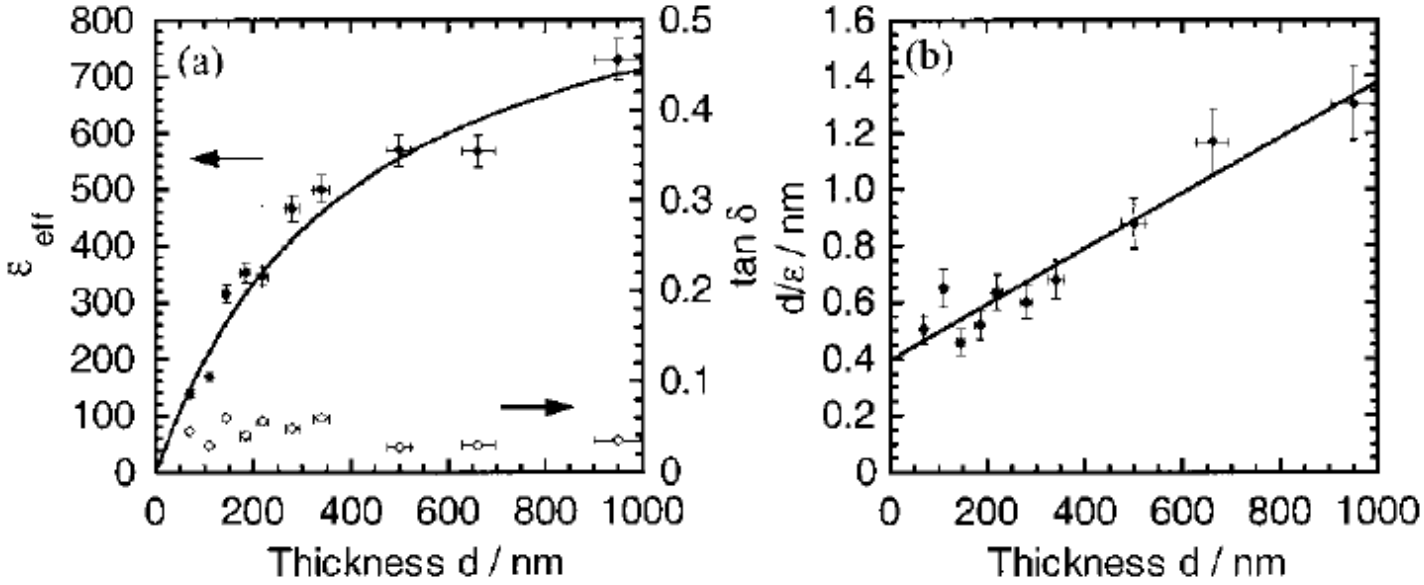
Broadly temperature independent; bias field tends to reduce the influence of the series capacitance

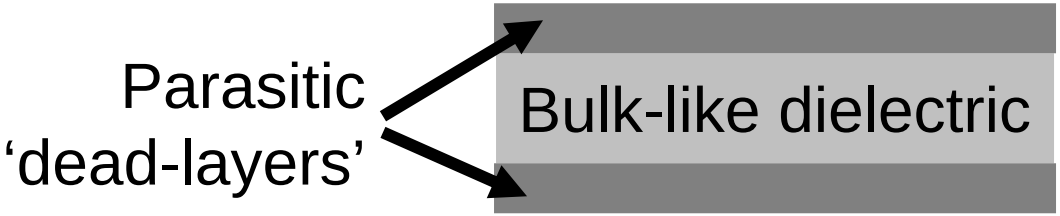
Work at Queen's Belfast and Cambridge

APPLIED PHYSICS LETTERS VOLUME 78, NUMBER 12 19 MARCH 2001

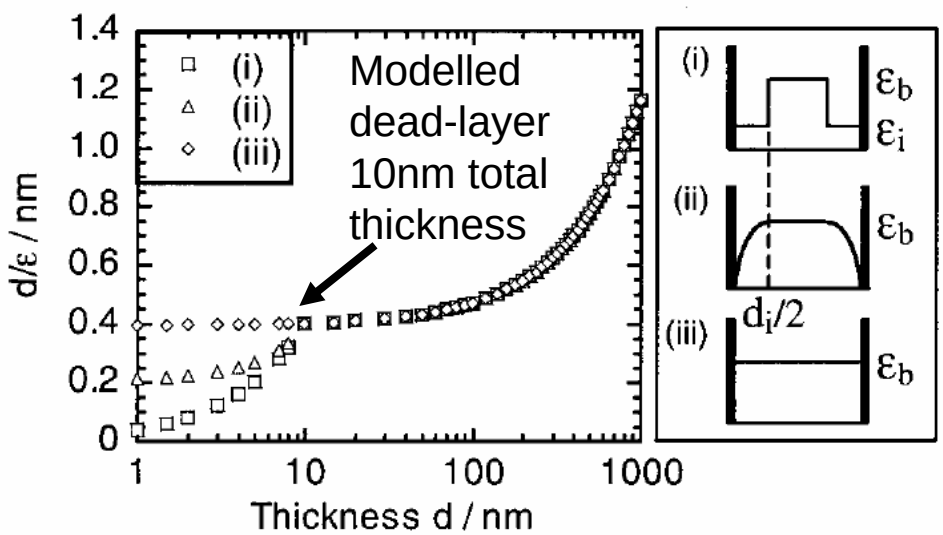
Investigation of dead-layer thickness in $SrRuO_3/Ba_{0.5}Sr_{0.5}TiO_3/Au$ thin-film capacitors

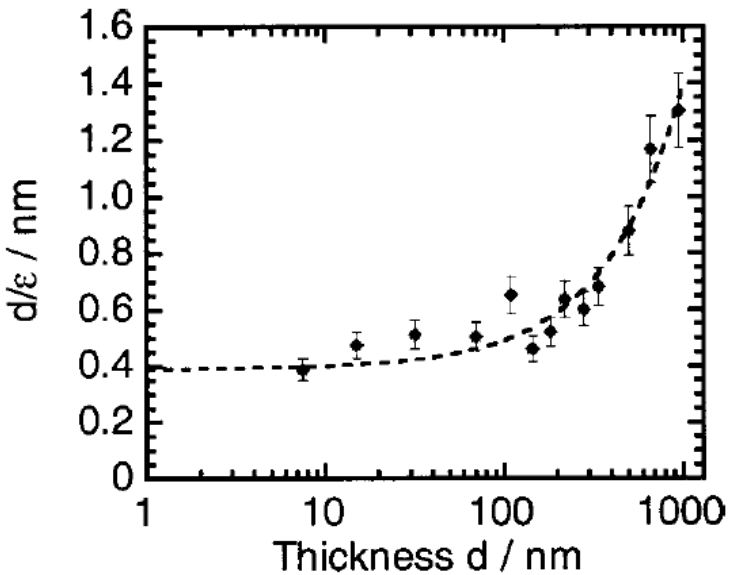
L. J. Sinnamon, R. M. Bowman, and J. M. Gregg[a)]
Department of Pure and Applied Physics, Queen's University Belfast, Belfast BT7 1NN, Ireland





Idea that as make total ferroelectric layer thinner, eventually bulk-like component disappears, at which point series capacitance behaviour should break down (nothing in series with dead-layer).



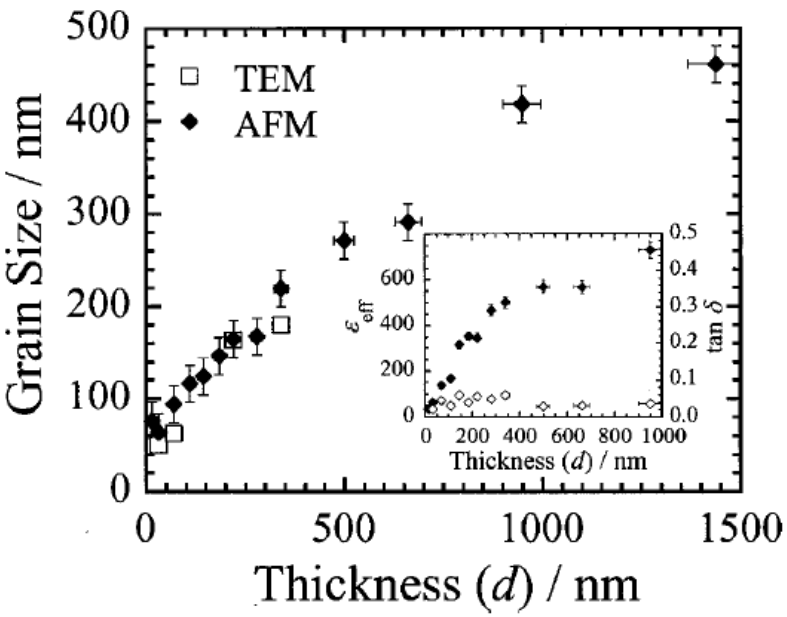


Case (iii) – no dead-layer

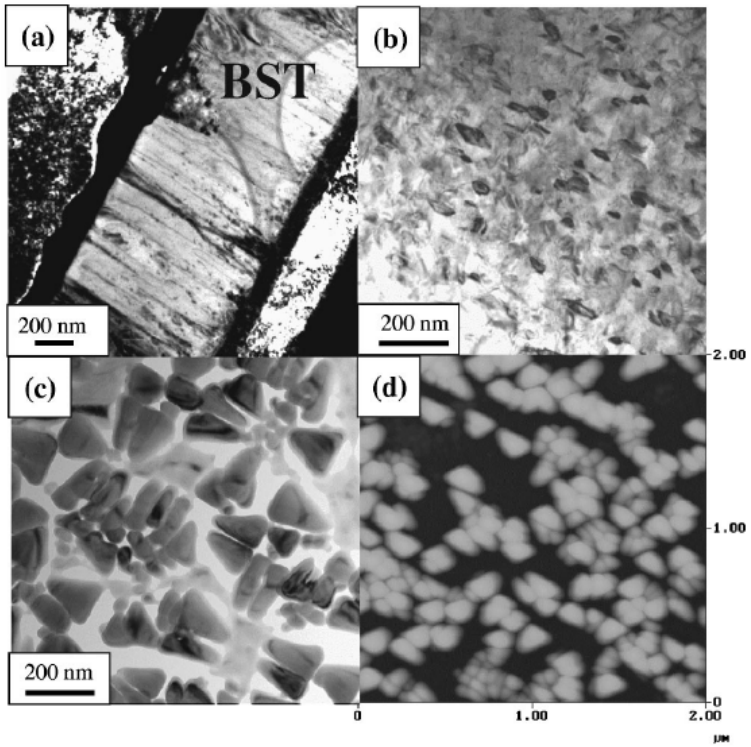
APPLIED PHYSICS LETTERS VOLUME 81, NUMBER 4 22 JULY 2002

Exploring grain size as a cause for "dead-layer" effects in thin film capacitors

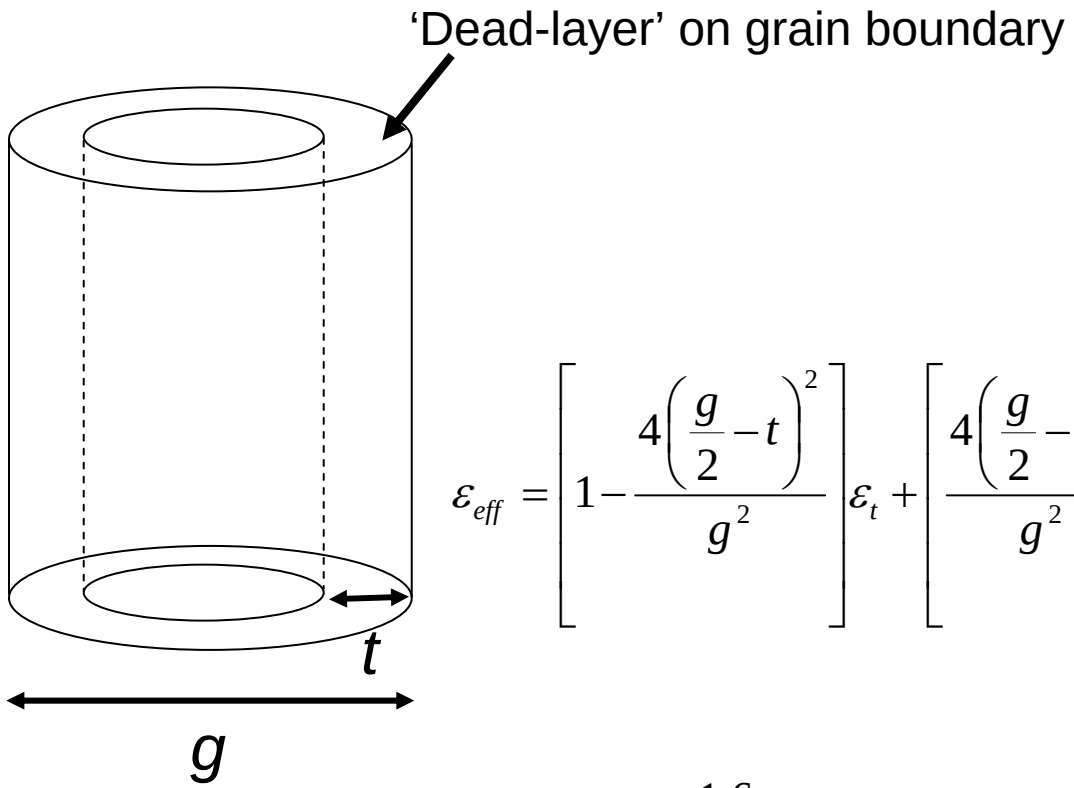
L. J. Sinnamon, M. M. Saad, R. M. Bowman, and J. M. Gregg[a)]
Department of Pure and Applied Physics, Queen's University Belfast, Belfast BT7 1NN, United Kingdom



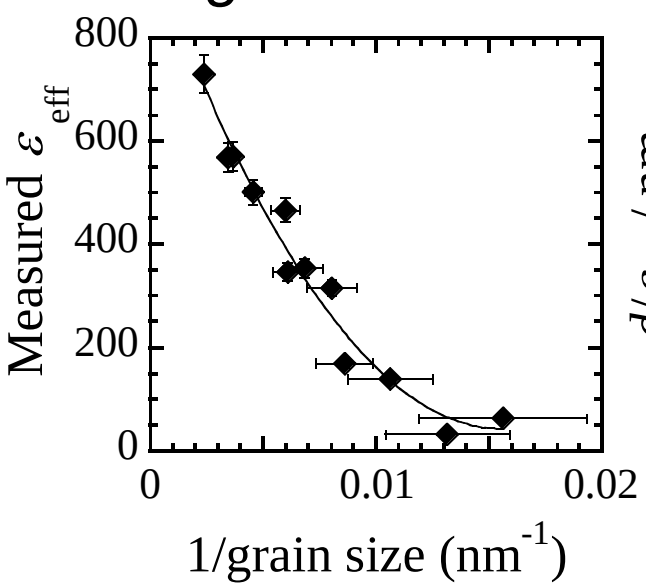
Noticed that permittivity fall-off with film thickness maps very well to grain size variation with thickness – coincidence ?

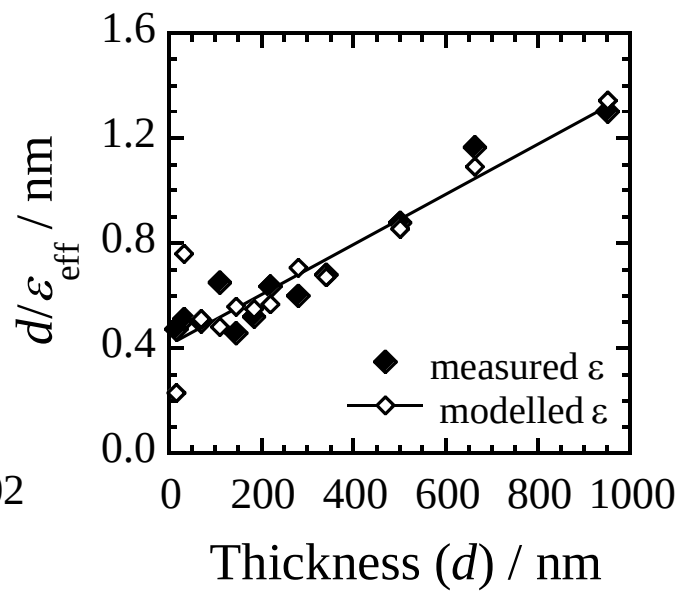


Columnar microstructure suggests grain boundary layers should act electrically in parallel, and hence usually ignored as source of series capacitance….BUT..



$$\varepsilon_{eff} = \left[1 - \frac{4\left(\frac{g}{2} - t\right)^2}{g^2}\right]\varepsilon_t + \left[\frac{4\left(\frac{g}{2} - t\right)^2}{g^2}\right]\varepsilon_b = \frac{4t^2}{g^2}\left(\varepsilon_b - \varepsilon_t\right) - \frac{4t}{g}\left(\varepsilon_b - \varepsilon_t\right) + \varepsilon_b$$





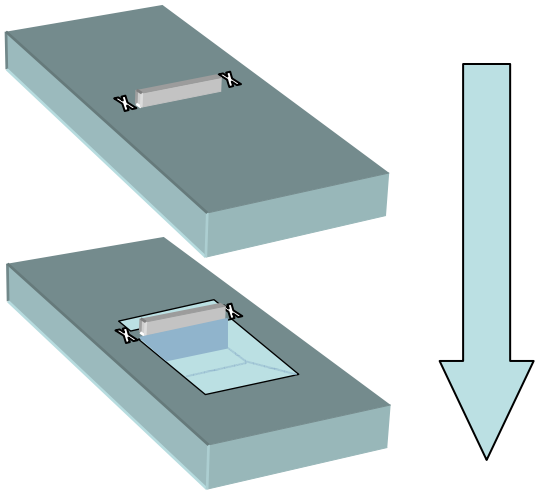
t ~ 15 - 20nm

Worries about grain boundaries helped motivate a study using thin single crystals

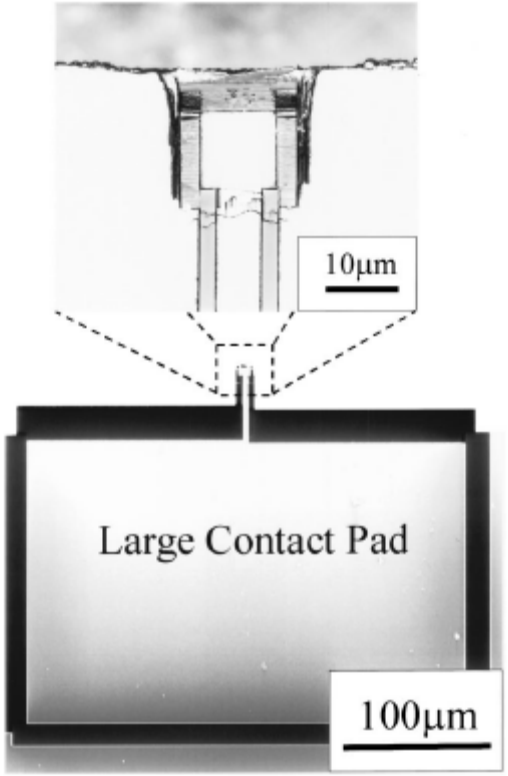
APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 7 16 FEBRUARY 2004

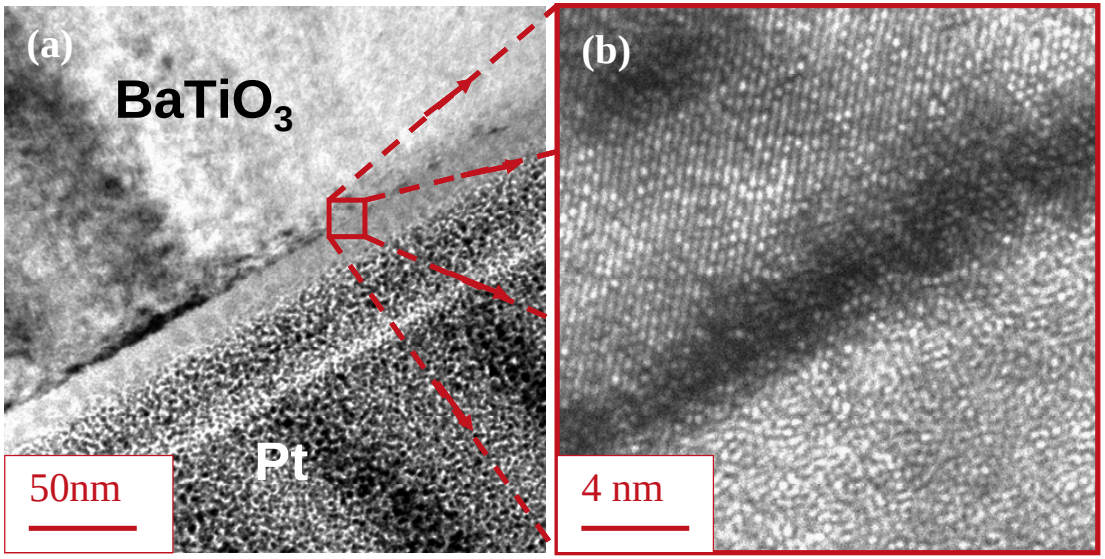
Characteristics of single crystal "thin film" capacitor structures made using a focused ion beam microscope

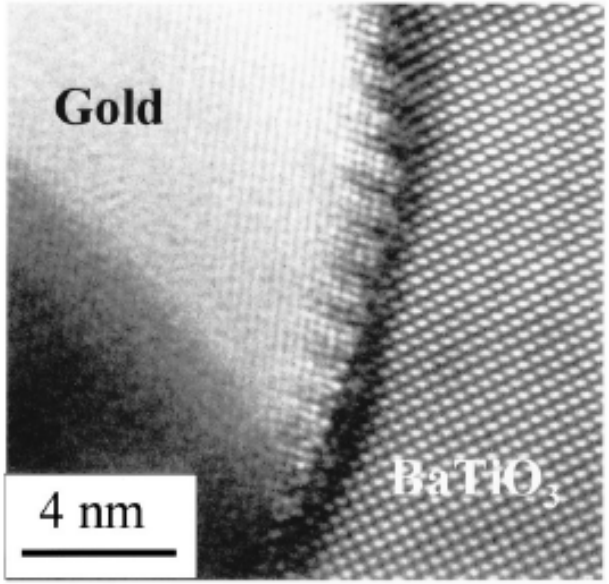
M. M. Saad, R. M. Bowman, and J. M. Gregg[a)]
Department of Pure and Applied Physics, Queen's University Belfast, Belfast BT7 1NN, United Kingdom



Normal FIB process for cutting lamellae was altered such that lamella was an overhanging 'lip' at the crystal edge



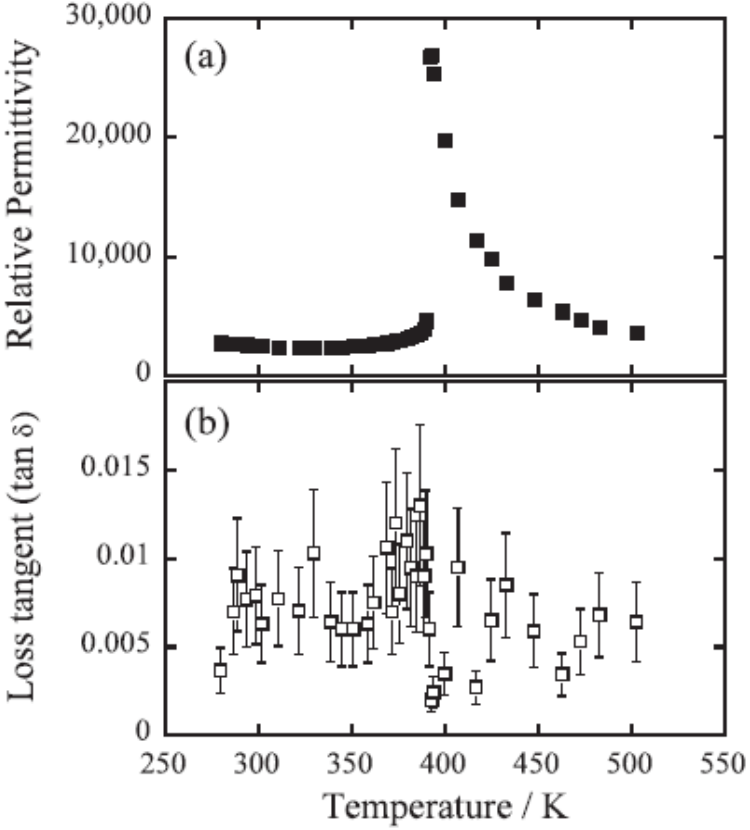




FIB process issues – Ga implant and damage could cause and obvious ‘dead-layer’, such that the single crystal experiments would be worthless.

Post-FIB thermal anneal seemed to recover interface quality.

Functional Measurements



INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) L451–L456 PII: S0953-8984(04)86238-6

LETTER TO THE EDITOR

Intrinsic dielectric response in ferroelectric nano-capacitors

M M Saad[1], P Baxter[1], R M Bowman[1], J M Gregg[1], F D Morrison[2] and J F Scott[2]

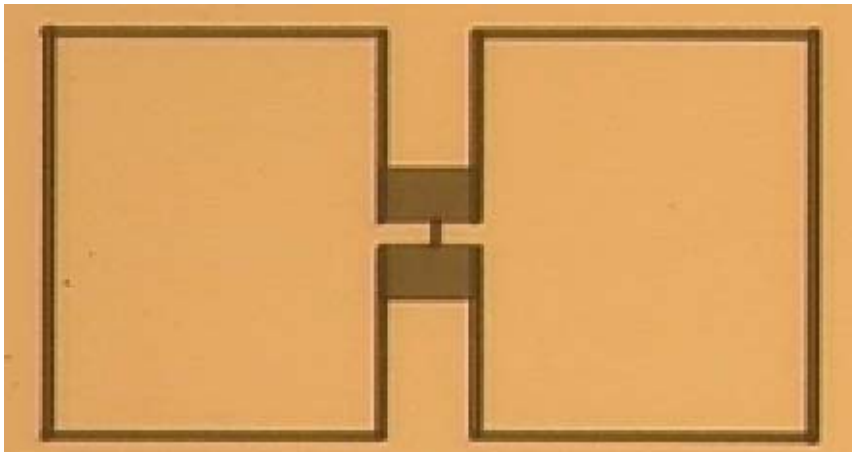
75nm single crystal lamella of $BaTiO_3$ showed no characteristics of ‘dead-layer’ series capacitance behaviour.

Implication that all causes of interfacial capacitance are extrinsic and can be engineered out.

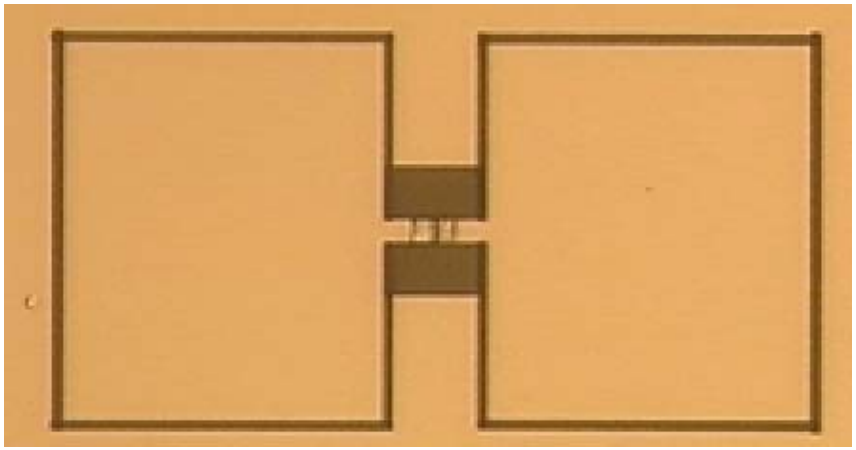
But…..no experiment is perfect.

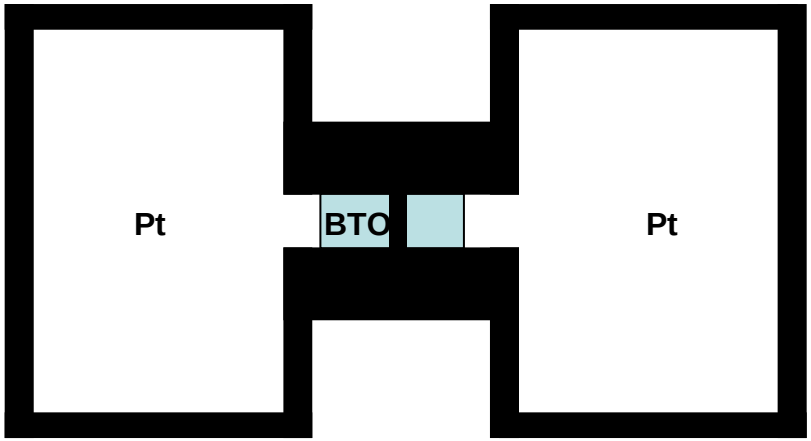
Optical Picture and Structure

Dummy Pad

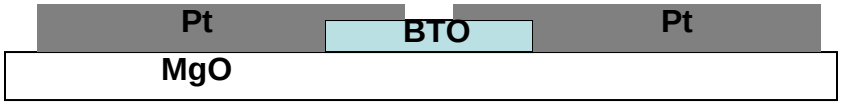


Sample Pad



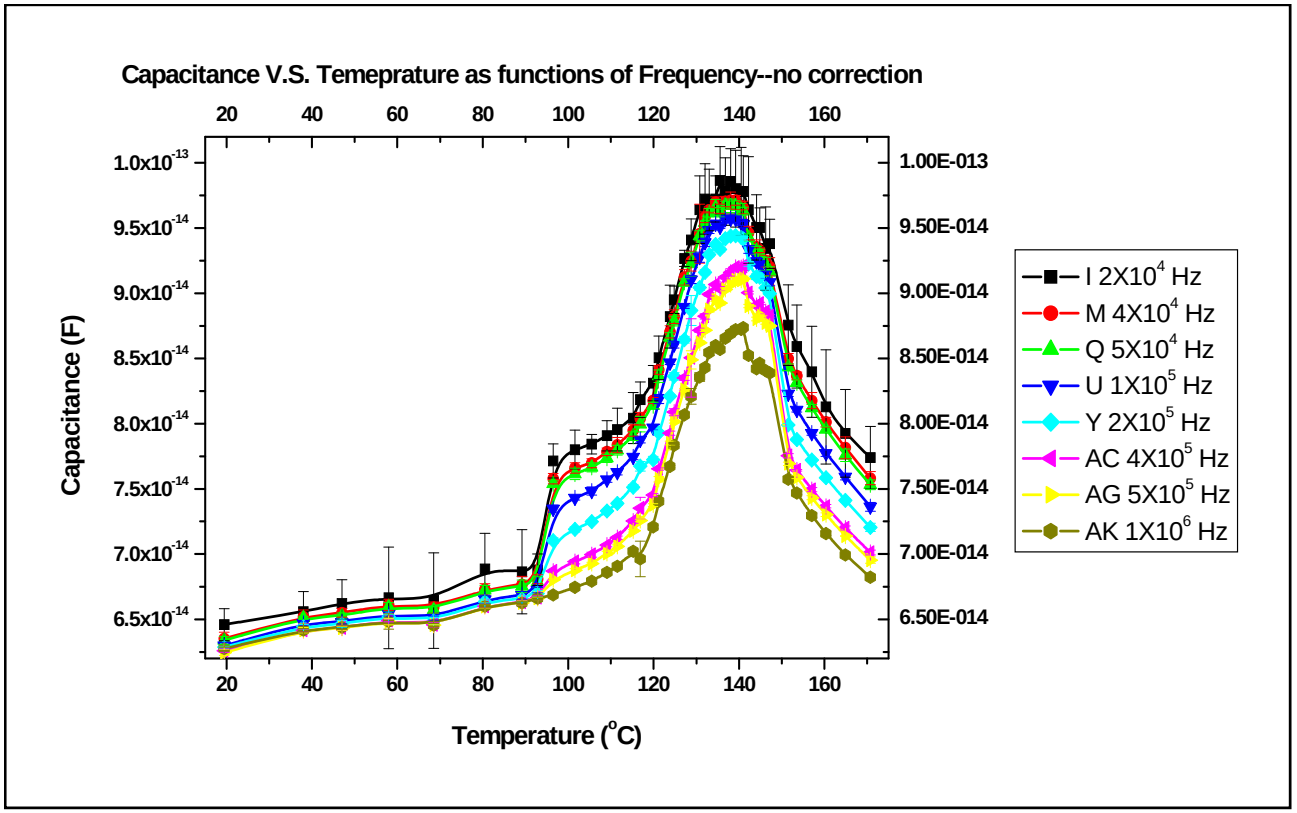


Top View



Cross Section

Very early data – all of the Ga-implant has not yet been annealed out of the structure



T_c appears to be same as bulk; but peak is rounded – need to anneal to remove Ga-implant, but these experiments should prove to be critical