Size effects on stability and polarization dynamics in ferroelectrics

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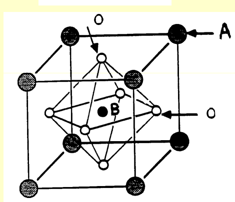
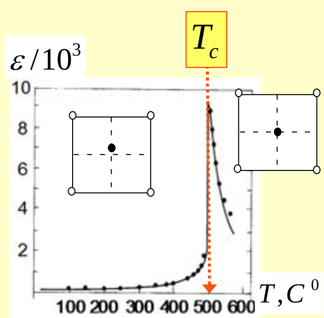
Ferroelectrics

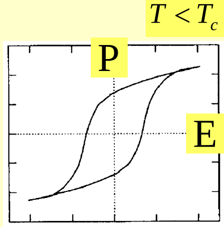
$PbTiO_3$



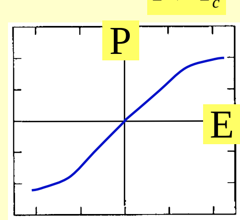
A= Pb **B = Ti**



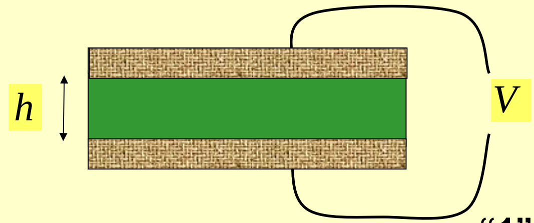
$T < T_c$

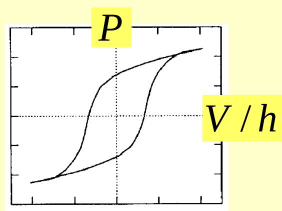


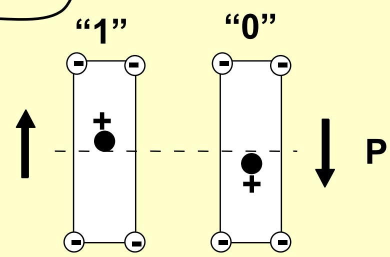
$T > T_c$



Storage of information in a ferroelectric







Small thickness → Small control voltage

Thin films !!!!!

Size effect in ferroelectric thin films

Materials:

$Pb(Zr,Ti)O_3$ (PZT)
$SrBi_2Ta_2O_9$

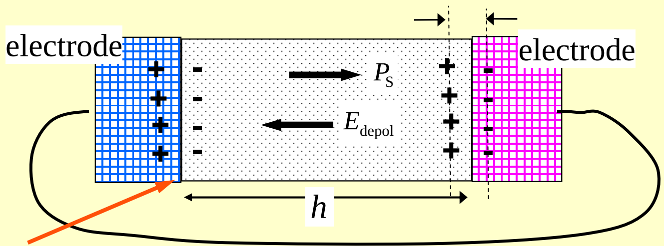
Thickness < 100 nm

<u>The</u> problem for down-scaling
→ ferroelectric/electrode coupling

Surface interaction | Incomplete screening | Surface induced asymmetry

Ferroelectric/electrode coupling

Surface interaction	Incomplete screening	Surface-induced asymmetry
Interface locally suppresses ferroelectricity	Bound and free charges are separated at interface	Interface “likes” one direction of polarization

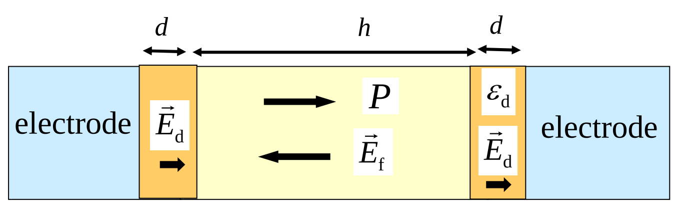


Can be modeled as a passive layer

$$E_{depol} \propto \frac{P_S}{h}$$

Energy of ferroelectric capacitor

$$\Phi_{bulk} = h\left(\frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4\right) + \Phi_{surf} + \Phi_{el}$$



$$\Phi_{surf\text{-}I} = \frac{\eta}{2}P^2 + \vec{\varsigma}\vec{P} \qquad \Phi_{surf\text{-}II} = \frac{\eta}{2}P^2 - \vec{\varsigma}\vec{P}$$

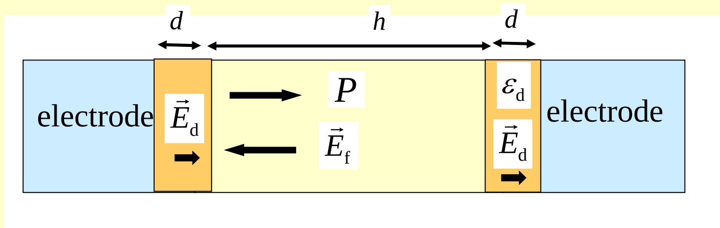
$$D_f = P + \varepsilon_b E_f \qquad D_d = \varepsilon_d E_d$$

ε_b-background permittivity

$$\Phi_{el} = h\frac{\varepsilon_b E_f^{\ 2}}{2} + 2d\,\frac{\varepsilon_d E_d^{\ 2}}{2}$$

$$\varepsilon_b \cong 10 \qquad \varepsilon_b << \varepsilon_f$$

Electrostatic energy of short-circuited capacitor



$$\Phi_{\mathrm{el}} = h\frac{\varepsilon_{\mathrm{b}} E_{\mathrm{f}}^{\ 2}}{2} + 2d\frac{\varepsilon_d E_{\mathrm{d}}^{\ 2}}{2}$$

$$D_{\mathrm{f}} = P + \varepsilon_{\mathrm{b}} E_{\mathrm{f}}$$

$$D_{\mathrm{d}} = \varepsilon_{\mathrm{d}} E_{\mathrm{d}}$$

Electrostatics

$$P + \varepsilon_{\mathrm{b}} E_{\mathrm{f}} = \varepsilon_{\mathrm{d}} E_{\mathrm{d}}$$

$$hE_{\mathrm{f}} + 2dE_{\mathrm{d}} = 0$$

$$E_{\mathrm{d}} = \frac{hP}{h\varepsilon_{\mathrm{d}} + 2d\varepsilon_{\mathrm{b}}}$$

$$E_{\mathrm{f}} = -\frac{2dP}{h\varepsilon_{\mathrm{d}} + 2d\varepsilon_{\mathrm{b}}}$$

$$\Phi_{\mathrm{el}} = \frac{dhP^2}{h\varepsilon_{\mathrm{d}} + 2d\varepsilon_{\mathrm{b}}}$$

Total energy of short-circuited real capacitor

$$h\varepsilon_{\mathrm{d}} >> 2d\varepsilon_{\mathrm{b}}$$

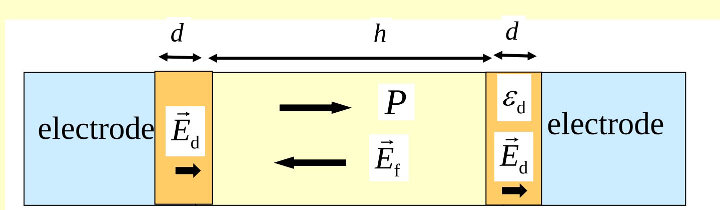
$$\lambda \equiv d/(\varepsilon_{\mathrm{d}}/\varepsilon_0)$$

$$E_{\mathrm{f}} \approx -\frac{2\lambda}{h\varepsilon_0}P$$

$$\Phi_{\mathrm{el}} \approx \frac{\lambda P^2}{\varepsilon_0}$$

manly electrostatic energy in the dead layers

$$\Phi = \Phi_{\mathrm{bulk}} + \Phi_{\mathrm{surf}} + \Phi_{\mathrm{el}}$$



$$\Phi_{\mathrm{surf\text{-}I}} = \frac{\eta}{2}P^2 \qquad \Phi_{\mathrm{el}} = \frac{\lambda P^2}{\varepsilon_0} \qquad \Phi_{\mathrm{surf\text{-}II}} = \frac{\eta}{2}P^2$$

Suppression of homogeneous polarization state

$$\Phi = h\left(\frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4\right) + \frac{\lambda P^2}{\varepsilon_0} + \eta P^2 = h\left(\frac{\alpha *}{2}P^2 + \frac{\beta}{4}P^4\right)$$

$$\alpha = \frac{T - T_0}{C\varepsilon_0}$$

$$\alpha * = \alpha + 2\frac{\lambda / \varepsilon_0 + \eta}{h}$$

Curie-Weiss constant

electrostatic

surface, short-range

$$\Delta T_c(h) = -2C\frac{\lambda + \eta\varepsilon_0}{h}$$

$$h_{\text{crit}}(T) = 2(\lambda + \eta\varepsilon_0)\frac{C}{T_c - T}$$

Suppression of homogeneous polarization state; test feature

$$\Phi = h\left(\frac{\alpha *}{2}P^2 + \frac{\beta}{4}P^4\right)$$

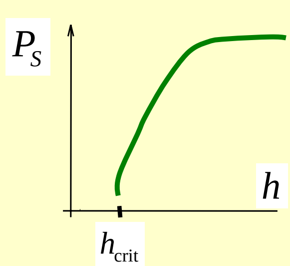
$$\alpha * = -2(\lambda + \eta\varepsilon_0)\left(\frac{1}{h_{\text{crit}}} - \frac{1}{h}\right)$$

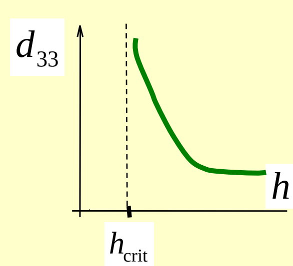
$$h_{\text{crit}}(T) = 2(\lambda + \eta\varepsilon_0)\frac{C}{T_c - T}$$

$$P_S^2 = -\alpha * / \beta$$

$$\varepsilon = -1/2\alpha *$$

$$d_{33} = 2QP_S\,\varepsilon \propto 1/\sqrt{\alpha^*}$$





Multi-scale approach to the size effect

Phenomenology applicable to any h

$$\Phi = h\left(\frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4\right) + \frac{\lambda P^2}{\varepsilon_0} + \eta P^2$$

$$\beta P^2 = -\alpha + 2\frac{\lambda/\varepsilon_0 + \eta}{h}$$

$$E_{\mathrm{f}} = -\frac{2\lambda}{h\varepsilon_0}P$$

***Ab initio* calculations (can be done for small *h*)**

To calculate

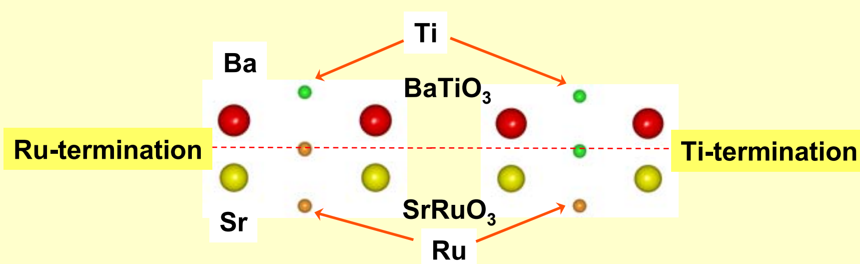
$$\beta \quad P(h) \quad E_{\mathrm{f}}(h)$$

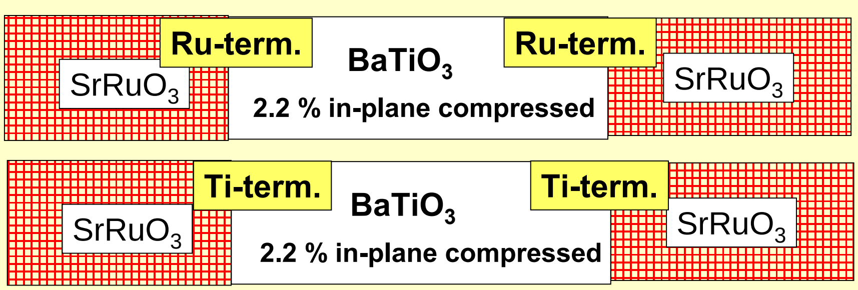
$$\frac{\partial P^2}{\partial(1/h)} \Rightarrow \lambda/\varepsilon_0 + \eta$$

$$\frac{\partial}{\partial h}\left(\frac{P}{E_{\mathrm{f}}}\right) \Rightarrow 1/\lambda$$

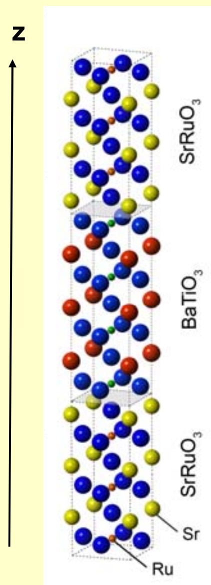
(Tagantsev *et al.*, 2008)

System under consideration





Calculations



$SrRuO_3/BaTiO_3/SrRuO_3$ stack

Frozen phonons
"hard" electrode

$\Delta E(\xi)$

Energy as a function of the amplitude of the soft-mode displacements

Full relaxation
"normal" electrode

$\Delta E(x_z^{(1)}, x_z^{(2)}, x_z^{(3)}......)$

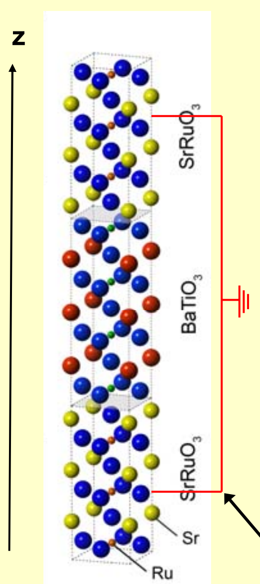
$\min[\Delta E]$

all atoms

$(x_z^{(1)}, x_z^{(2)}, x_z^{(3)}......)$

u_m = 2.2% -in-plane compression
to stabilize tetragonal phase

Technical



$SrRuO_3/BaTiO_3/SrRuO_3$ stack

Frozen phonons

$\Delta E(\xi)$

Full relaxation

$(x_z^{(1)}, x_z^{(2)}, x_z^{(3)}......)$

VASP

DFT with **GGA**

Monkhorst-Pack grid = 6x6x1

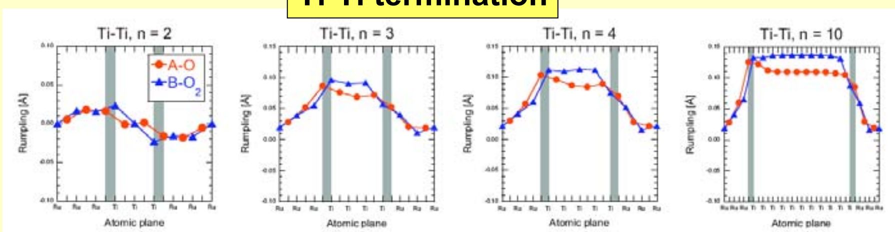
$E_{cut\text{-}off}$ = 400 eV

$F_{H\text{-}F}$ < 1 meV/A;

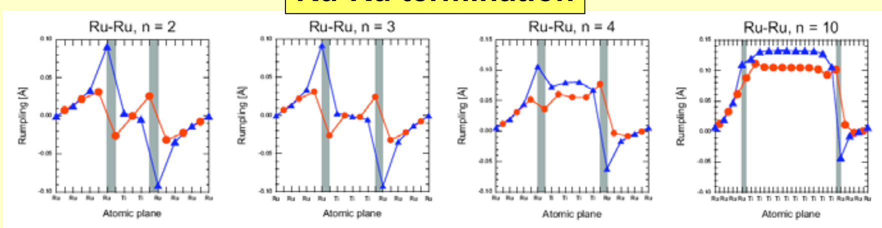
Short-circuited stack = periodic boundary conditions

Full relaxation - rumplings

Ti-Ti termination



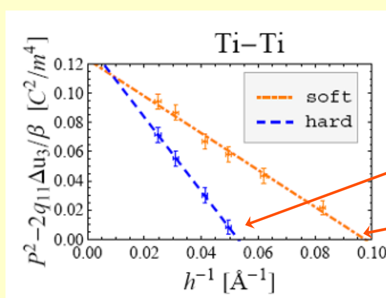
Ru-Ru termination



(Tagantsev *et al.*, 2008)

Determination of λ and η

$$\frac{\partial P^2}{\partial(1/h)} \Rightarrow \lambda/\varepsilon_0 + \eta$$

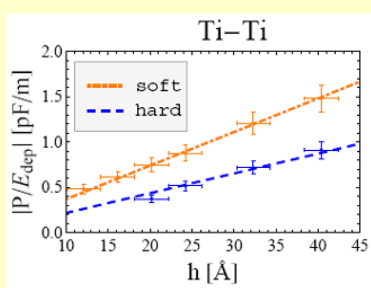


Critical thickness

~ 20 Å

~ 10 Å

$$\frac{\partial}{\partial h}\left(\frac{P}{E_d}\right) \Rightarrow \frac{1}{\lambda}$$



Parameters of SRO/BTO interface

Shift of T_C $\Delta T_c(h) = -2C\dfrac{\lambda + \eta\varepsilon_0}{h}$

Parameter	Soft electrode (real)		Hard electrode	
electrostatic	Ti–Ti	Ru–Ru	Ti–Ti	Ru–Ru
λ	0.12 ± 0.01 Å	0.13 ± 0.01 Å	0.20 ± 0.01 Å	0.10 ± 0.01 Å
$\varepsilon_0\eta$ short-range	± 0.01 Å	0.01 ± 0.01 Å	0.02 ± 0.01 Å	0.08 ± 0.01 Å

- $\varepsilon_0\eta$ is much smaller than the expected "atomic estimate"~ 2 Å
- For realistic interfaces, the short-range contribution is relatively small

$C \cong 1.5\times10^5$ K

$\lambda + \eta\varepsilon_0 \approx 1.2\times10^{-2}$ nm

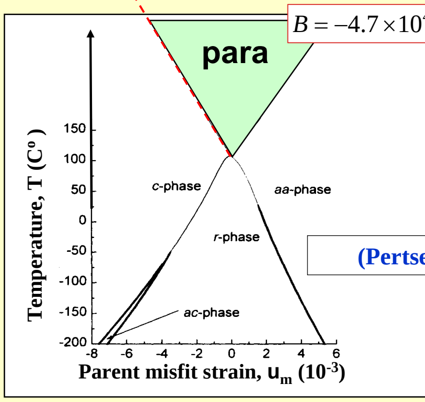
$$\Delta T_c(h) = -\frac{A}{h}$$

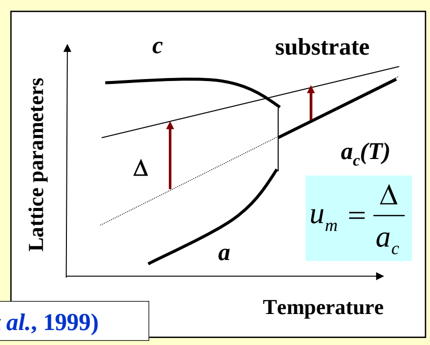
$$A \approx 2C\lambda = 3.6\times10^3 \text{ K nm}$$

Size effect in STO/SRO/BTO/SRO system

$\Delta T_c(u_m) = B \times u_m$

$B = -4.7\times10^4$ K





(Pertsev *et al.*, 1999)

$$\Delta T_c = Bu_m - \frac{A}{h} \qquad A = 3.6\times10^3 \text{ K nm}$$

$BaTiO_3$ on $SrTiO_3$ substrate

$$h_{\text{crit}} = \frac{A}{T_c - T + Bu_m}$$

$u_m|_{RT} \cong -0.022$ ➡ $\Delta T_c(u_m) \cong 1000$ K

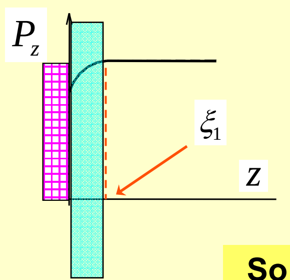
$h_{\text{crit}}(300\text{ K}) \cong 3.2$ nm

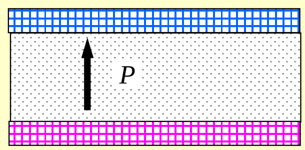
Where is the gradient term?

$$\Phi_{\mathrm{bulk}}/h = \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \cancel{\frac{\kappa}{2}\left(\frac{\partial P}{\partial z}\right)^2}$$

(Kretchmer & Binder, 1979)

Out-of-plane geometry





BaTiO$_3$

$\xi_1 \cong 0.03 - 0.2$ nm

ξ_1 is too small

Solution to the problem

Taken into account by

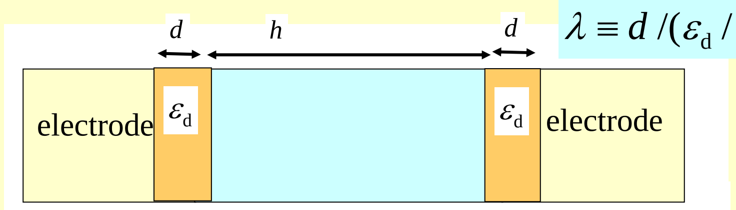
$$\Phi_{\mathrm{surf}} = \frac{\eta}{2}P^2$$

$$P = const$$

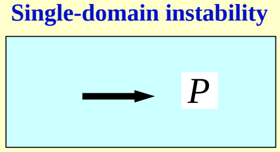
(Tagantsev *et al.*, 2008)

Domain instability and size effect

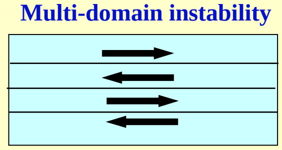
$$\lambda \equiv d/(\varepsilon_{\mathrm{d}}/\varepsilon_0)$$



Single-domain instability



Multi-domain instability

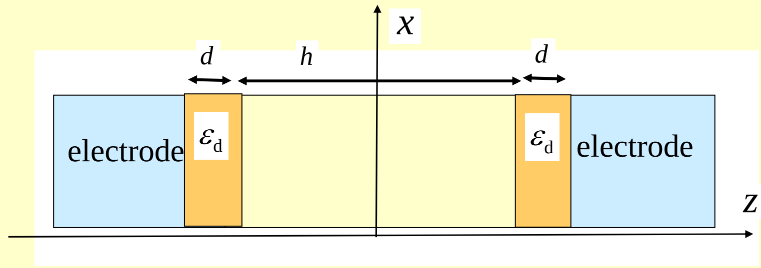


$$T_{\mathrm{SD}} = T_{\mathrm{c}} - \frac{2\lambda C}{h}$$

?

T_{c} T

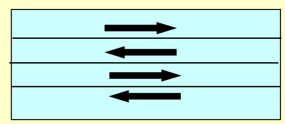
Chensky-Tarasenko instability



First-harmonics approximation to domain pattern (“soft” domain pattern)

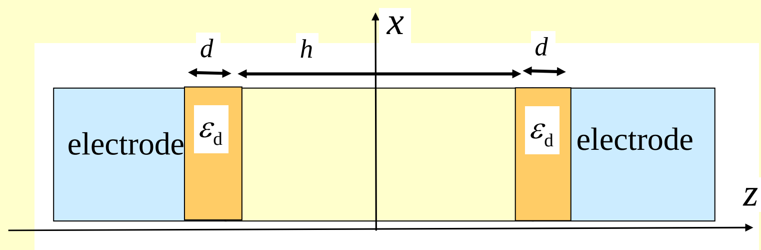
Multi-domain instability

$$P_z = a\cos kx \cos qz$$



(Chensky&Tarasenko, 1982)

Chensky-Tarasenko instability- mathematical problem



$$\Phi = \int_{-h/2}^{h/2}\left[\frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{D}{2}\left(\frac{\partial P}{\partial x}\right)^2 + \frac{\varepsilon_b}{2}E_z^2 + \frac{\varepsilon_{xx}}{2}E_x^2\right]dzdx + \varepsilon_d\int_{h/2}^{h/2+d}E^2 dzdx$$

Ferroelectric

$$D_z = P_z + \varepsilon_b E_z$$

$$D_x = \varepsilon_{xx}E_x$$

Dead layer

$$\vec{D} = \varepsilon_d\vec{E}$$

$$P_z = a\cos kx \cos qz$$

$$\mathrm{div}\vec{D} = 0 \qquad \mathrm{curl}\vec{E} = 0$$

Chensky-Tarasenko instability-result

Critical normalized thickness of the passive layer

$$\lambda_m^2 = \frac{3D\varepsilon_0^2}{\varepsilon_{xx}}$$

$$\lambda \equiv d/(\varepsilon_d/\varepsilon_0)$$

Single-domain instability

$$T_S = T_c - \frac{2\lambda C}{h}$$

Nothing new !

$$\lambda < \lambda_m$$

T_c T

Domain period

$$\frac{W}{2} = \sqrt{h_{CT} h}$$

$$h_{CT} = \pi\sqrt{\varepsilon_{xx} D}$$

Multi-domain instability

$$T_M = T_c - \frac{2\lambda_m C}{h}$$

$$\lambda > \lambda_m$$

T_c T

Chensky-Tarasenko instability-result for STO/SRO/BST/SRO

$$\lambda_m^2 = \frac{3D\varepsilon_0^2}{\varepsilon_{xx}}$$

$BaTiO_3$ on $SrTiO_3$ @ RT

$$\frac{\varepsilon_{xx}}{\varepsilon_0} \approx 200 \qquad \sqrt{D\varepsilon_0} \cong 0.17\,\overset{0}{\mathrm{A}} \qquad \lambda_m \cong 0.02\,\overset{0}{\mathrm{A}}$$

$BaTiO_3/SrRuO_3$ interface

$$\lambda \cong 0.12\,\overset{0}{\mathrm{A}}$$

$\lambda > \lambda_m$ $\Rightarrow$ **domain instability happens first**

Chensky-Tarasenko instability- result for STO/SRO/BST/SRO@RT

$SrRuO_3/BaTiO_3/SrRuO_3/SrTiO_3$ @ RT

$\lambda \cong 0.12\,\mathring{A}$ $\lambda_m \cong 0.02\,\mathring{A}$ $\lambda > \lambda_m$ **domain instability**

Critical thickness

$\Delta T_c = Bu_m - \dfrac{A_{\mathrm{dom}}}{h}$ $A_{\mathrm{dom}} = 2C\lambda_m = 0.6\times 10^3\ \mathrm{K\ nm}$ $h_{\mathrm{crit}}(300\ \mathrm{K}) \cong 0.5\ \mathrm{nm}$

Domain period

$\dfrac{W}{2} = \sqrt{h_{\mathrm{CT}} h}$ $h_{\mathrm{CT}} = \pi\sqrt{\varepsilon_{xx} D} \approx 0.75\,\mathrm{nm}$ $h = 30\,\mathrm{nm}$ $\dfrac{W}{2} \approx 5\,\mathrm{nm}$

Chensky-Tarasenko theory- domain states in field (soft-domain approximation)

Competing states

$\lambda > \lambda_m$

$P_z = p$

Single-domain instability

$T_{\mathrm{S}} = T_{\mathrm{c}} - \dfrac{2\lambda C}{h}$

$P_z = a\cos kx \cos qz$

Multi-domain instability

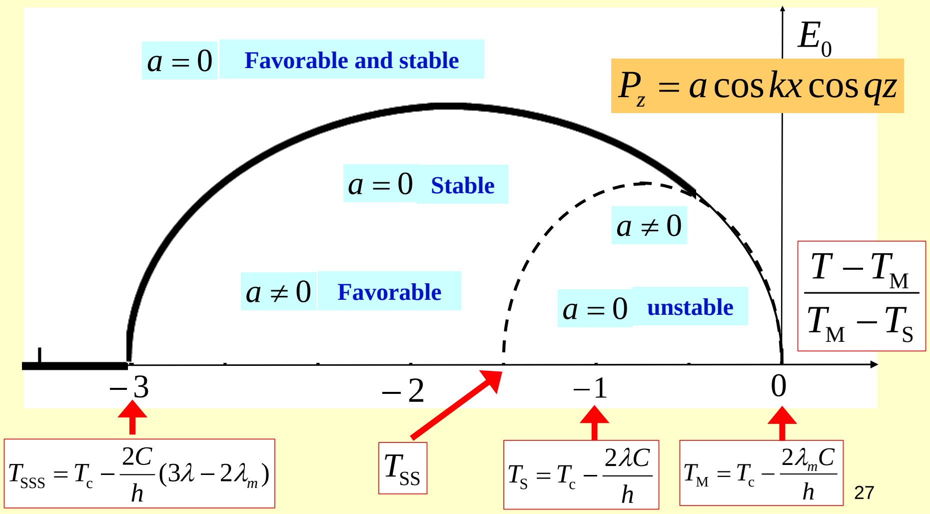
$T_{\mathrm{M}} = T_{\mathrm{c}} - \dfrac{2\lambda_m C}{h}$

T_{c} T

$$\Phi/\mathrm{volume} = \frac{\alpha'(T - T_{\mathrm{S}})}{2}p^2 + \frac{\beta}{4}p^4 + \frac{\alpha'(T - T_{\mathrm{M}})}{8}a^2 + \frac{9\beta}{256}a^4 + \frac{3\beta}{8}a^2p^2 - pE_0$$

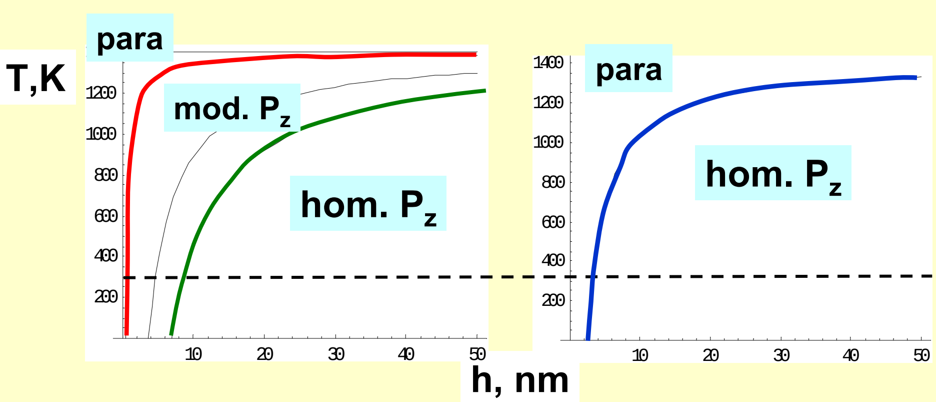
Chensky-Tarasenko theory- map of domain state in field (soft-domain approximation)

$\lambda > \lambda_m$



Domain state map in field in soft-domain approximation for STO/SRO/BST/SRO

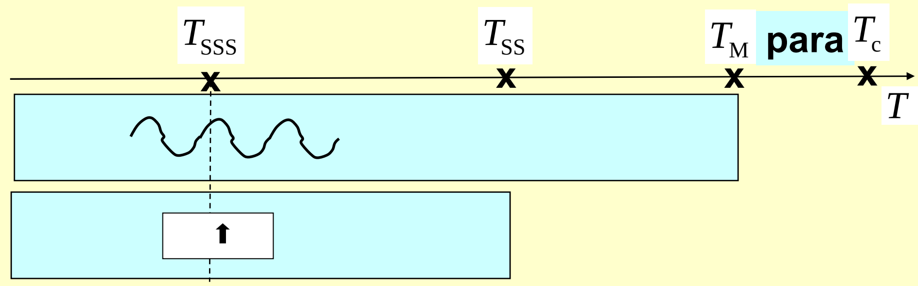
$E_0=0$



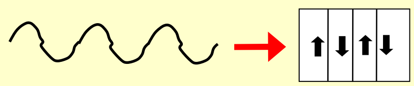
Single/multi domain scenario

Single domain scenario

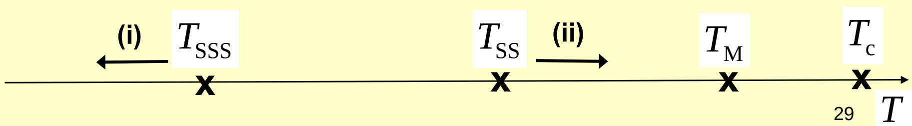
Soft-domain approximation and real life



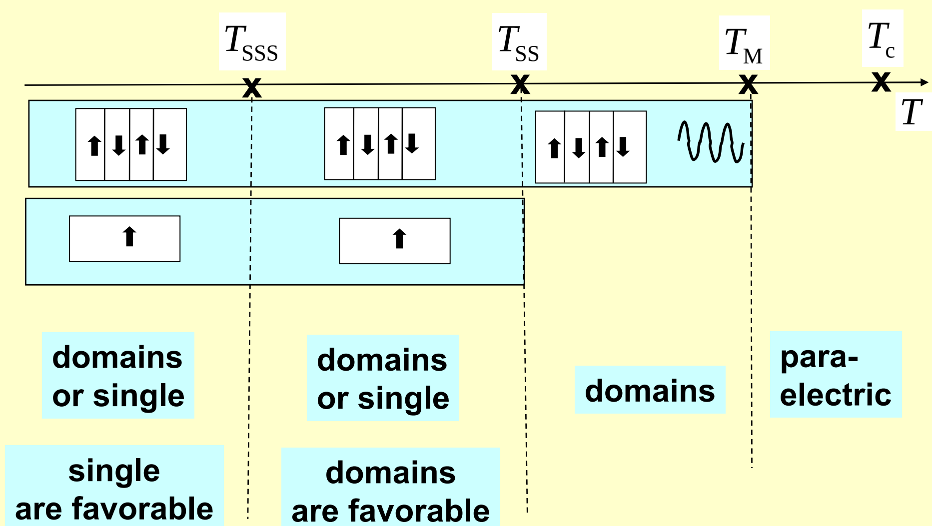
(i) High harmonics on cooling



(ii) Elastic effects (Pertsev&Kohlstedt , 2007)

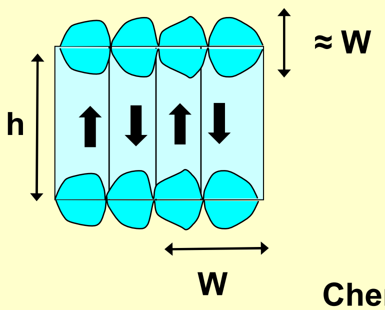


Domain state of ferroelectric capacitor



Chensky-Tarasenko theory vs. classical Mitsui-Furuichi theory (1953)

Mitsui theory (λ>>h)



$$\Phi_{\mathrm{el}} \propto W \qquad \Phi_{\mathrm{wall}} \propto \frac{h}{W}$$

$$\min[\Phi_{\mathrm{wall}} + \Phi_{\mathrm{el}}] \rightarrow W \propto \sqrt{h}$$

$$\frac{W}{2} = \sqrt{h_{\mathrm{M}} h} \qquad h_{\mathrm{M}} = 1.7\sqrt{\varepsilon_{xx} D}$$

Chensky-Tarasenko theory (λ << h)

$$\frac{W}{2} = \sqrt{h_{\mathrm{CT}} h} \qquad h_{\mathrm{CT}} = \pi\sqrt{\varepsilon_{xx} D}$$

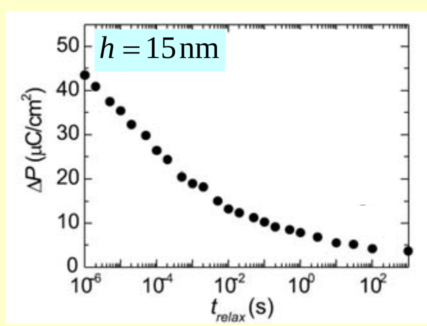
!!!!The available theories do not cover all situations!!!!

Experiment: STO/SRO/BST/SRO

(Kim *et al.*, 2005)

$h = 5-30$ nm; RT

Single domain state is metastable



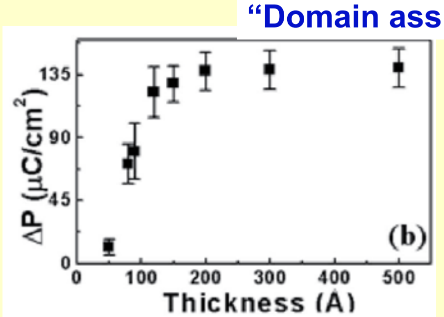
First-harmonics-approximation theory for h = 15 nm

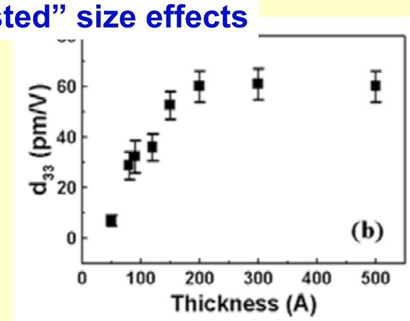
$T_{\mathrm{SSS}} = 750$ x — $T_{\mathrm{SS}} = 1100$ x — $T_{\mathrm{M}} = 1350$ x — $T_{\mathrm{c}} = 1400$ x → T, K

Meta-stability of S-D state

Experiment: STO/SRO/PZT/SRO

"Domain assisted" size effects



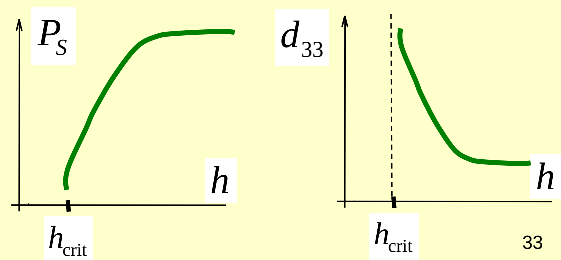


(Nagarajan *et al.*, 2006)

$PbZr_{0.2}Ti_{0.7}O3$

$h = 5 - 50$ nm; RT

"homogeneous" size effects



Conclusions

The size effect in ferroelectric films is controlled by misfit strain (u_m), screening conditions (λ), parameters of ferroelectric (λ_m), and temperature (T)

$$T_{SSS} = T_c - \frac{2C}{h}(3\lambda - 2\lambda_m)$$

$$T_S = T_c - \frac{2C}{h}(1.5\lambda - 0.5\lambda_m)$$

$$T_M = T_c - \frac{2\lambda_m C}{h}$$

$$T_c(u_m)$$

T

With the thickness reduction, the single domain state starts competing, first of all, with a multi-domain state

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