Workshop on Texture in Electronic Applications
NIST, 10-11 October 2000

POLYDOMAIN ARCHITECTURE OF EPITAXIAL FERROELECTRIC FILMS

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OUTLINE

- **Introduction**
- **Strain Relaxation in Epitaxial Films by Polydomain Formation:** Two-domain structures (partial relaxation), three-domain structures (complete relaxation), misfit dislocation formation.
- **Experimental Analysis of Polydomain Structures via XRD:** Determination of internal stresses, determination of domain fractions, tilting of domains, determination of the tilt angle
- **Comparison with TEM and AFM results**
- **Conclusions**

INTRODUCTION

- Structural phase transformations such as:
  - ✓ Order-disorder
  - ✓ Ferroelastic (or Martensitic)
  - ✓ Ferromagnetic
  - ✓ Ferroelectric

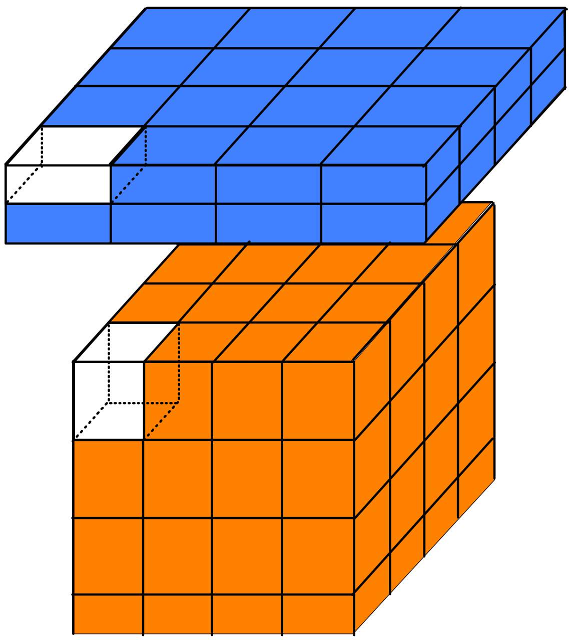
are accompanied by a **self-strain**.

- The phase transformation involves a reduction in the symmetry of the crystal upon cooling, usually resulting in multiple crystallographic variants (**domains**) of the lower-symmetry phase.

- If this transformation occurs in a constrained media, the resultant increase in the total strain energy of the system can be reduced by formation of a **POLYDOMAIN (TWIN)** structure *.

* A. L. Roitburd, Phys. Stat. Sol. (a) **37,** 329 (1976); S. Little and A. Zangwill, Phys. Rev. B, **46**, 7981 (1992)

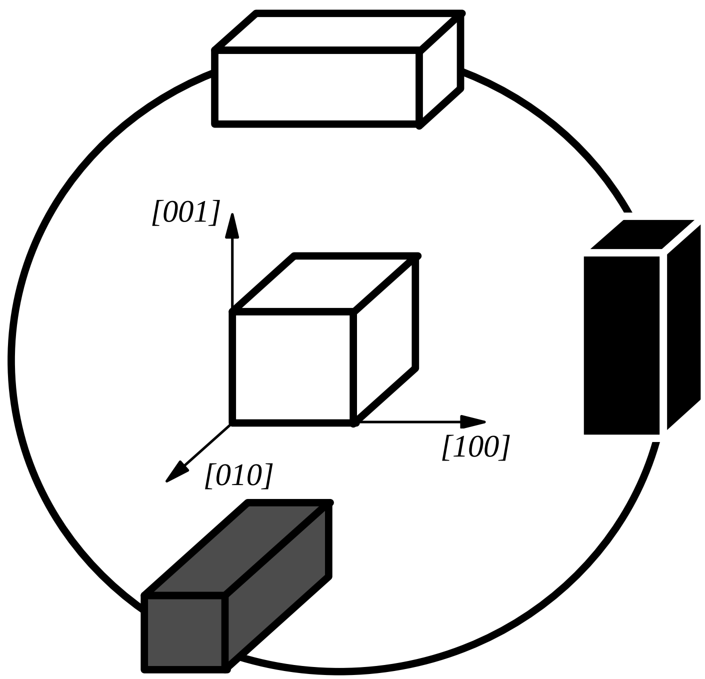
CONSTRAINT CONDITION



Epitaxial matching of a tetragonal lattice with a cubic substrate.

- Ferroelectric perovskites such as $BaTiO_3$, $PbTiO_3$ and PZT solutions (%Zr<50) undergo a ferroelectric transformation where the cubic paraelectric phase (*m3m*) transforms to a tetragonal ferroelectric phase (*4mm*) at T_C.
- Films are grown at temperatures above T_C.
- Epitaxial growth on a cubic substrate such that $(001)_{film}//(001)_{substrate}$.
- Mechanical boundary conditions $s_1=s_2$, $s_3=0$ (no normal stress out-of-plane), and $s_4=s_5=s_6=0$ (no shear stresses).

DOMAINS OF THE TETRAGONAL PHASE



- There are 3 different orientational variants (or **DOMAINS**) of the product tetragonal phase with self-strains given by:

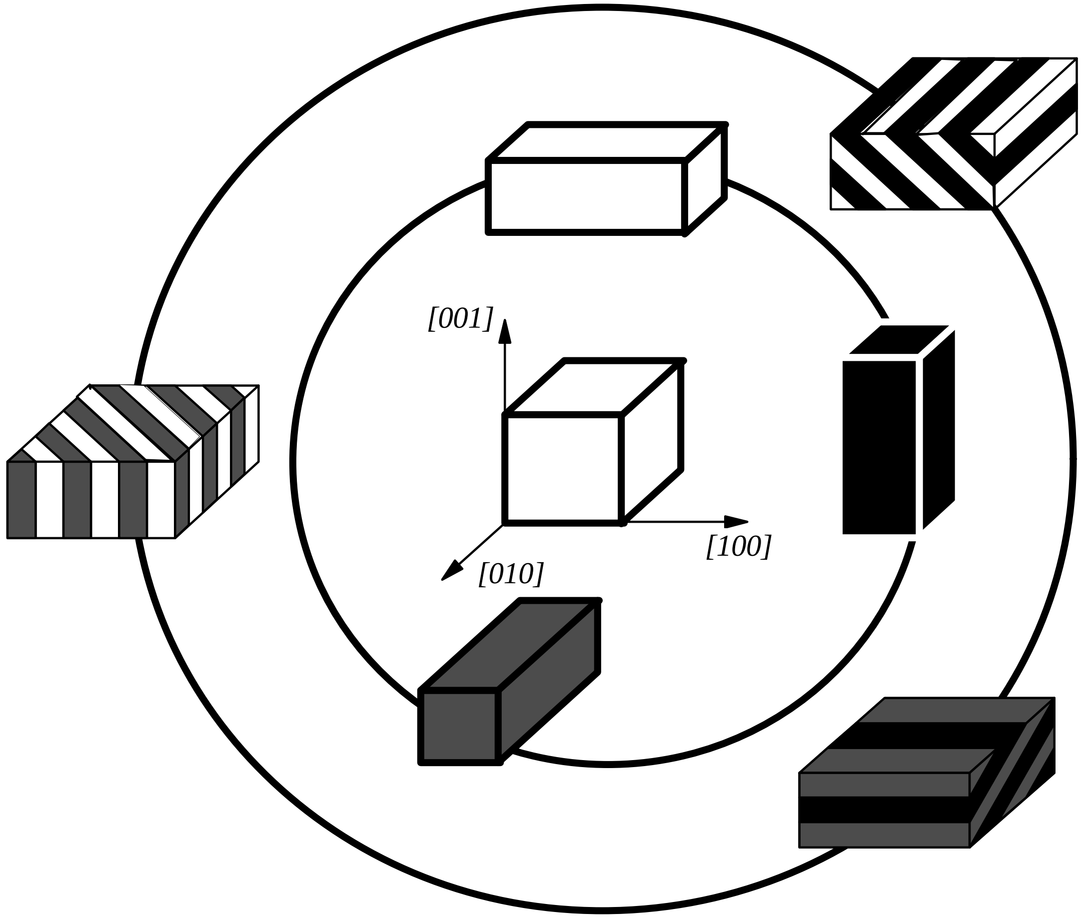
$$\hat{e}_1 = \begin{pmatrix} e_0' & 0 & 0 \\ 0 & e_0 & 0 \\ 0 & 0 & e_0 \end{pmatrix} \quad \hat{e}_2 = \begin{pmatrix} e_0 & 0 & 0 \\ 0 & e_0' & 0 \\ 0 & 0 & e_0 \end{pmatrix} \quad \hat{e}_3 = \begin{pmatrix} e_0 & 0 & 0 \\ 0 & e_0 & 0 \\ 0 & 0 & e_0' \end{pmatrix}$$

where $e_0'=(c-a_0)/a_0$, $\varepsilon_0=(a-a_0)/a_0$, a and c are the lattice parameters of the film in the ferroelectric state and a_0 is the lattice parameter in the paraelectric state.

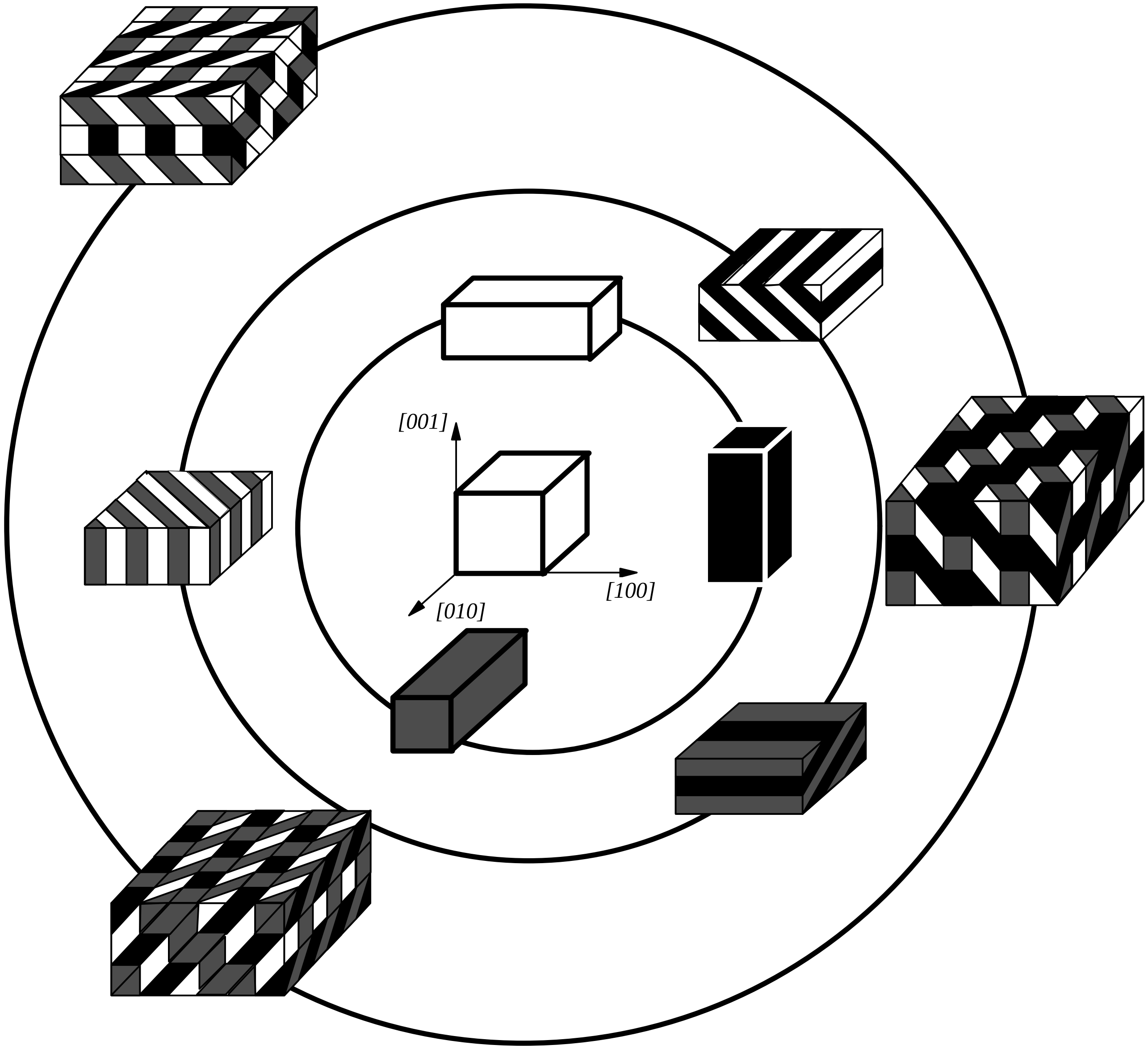
- There are
    - 3 distinct **ELASTIC**,
    - 6 distinct **ELECTRICAL** domains.

- Elastic energy of film is reduced by **formation of polydomain structures** consisting of a uniform mixture of domains.

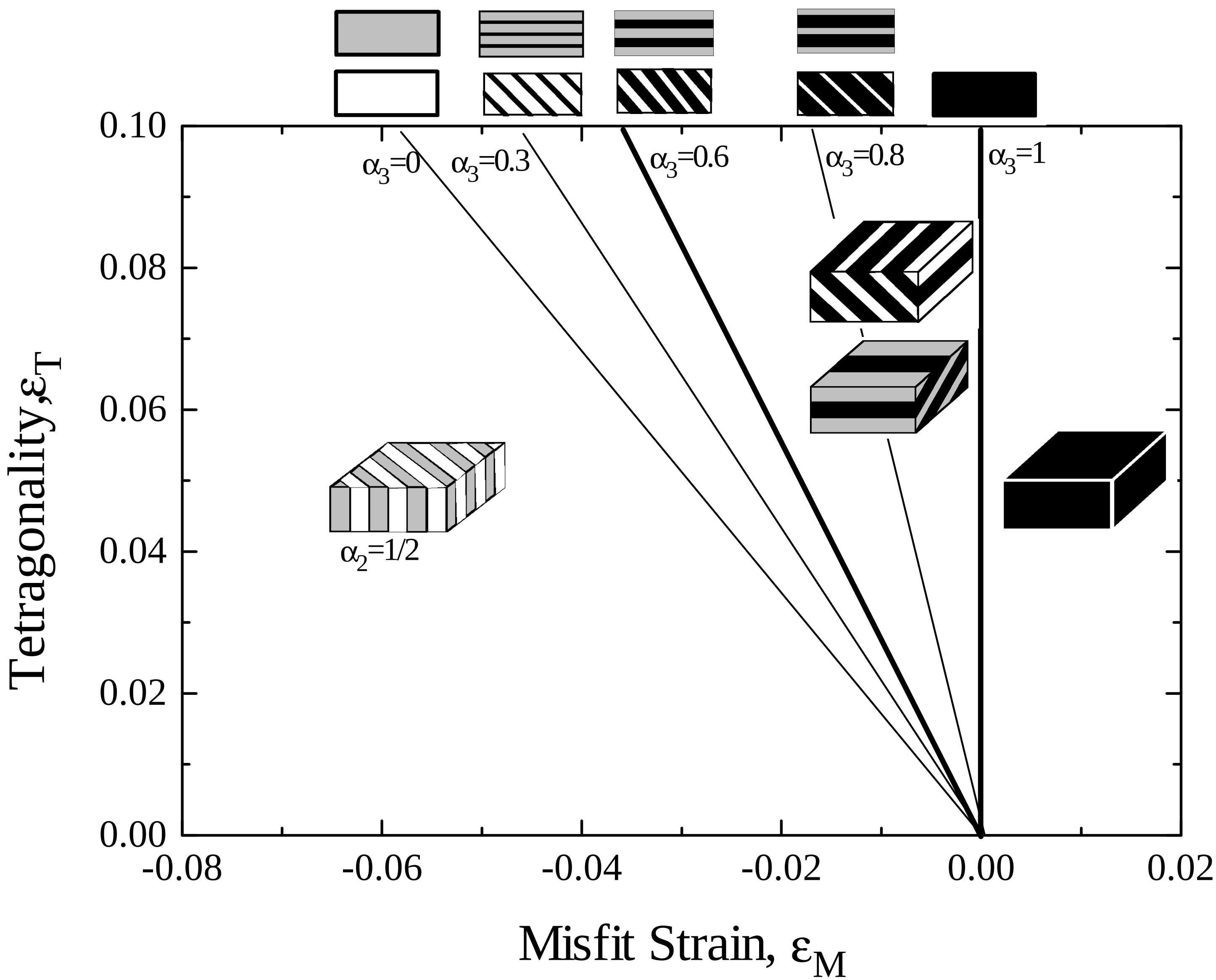
2-DOMAIN POLYTWINS



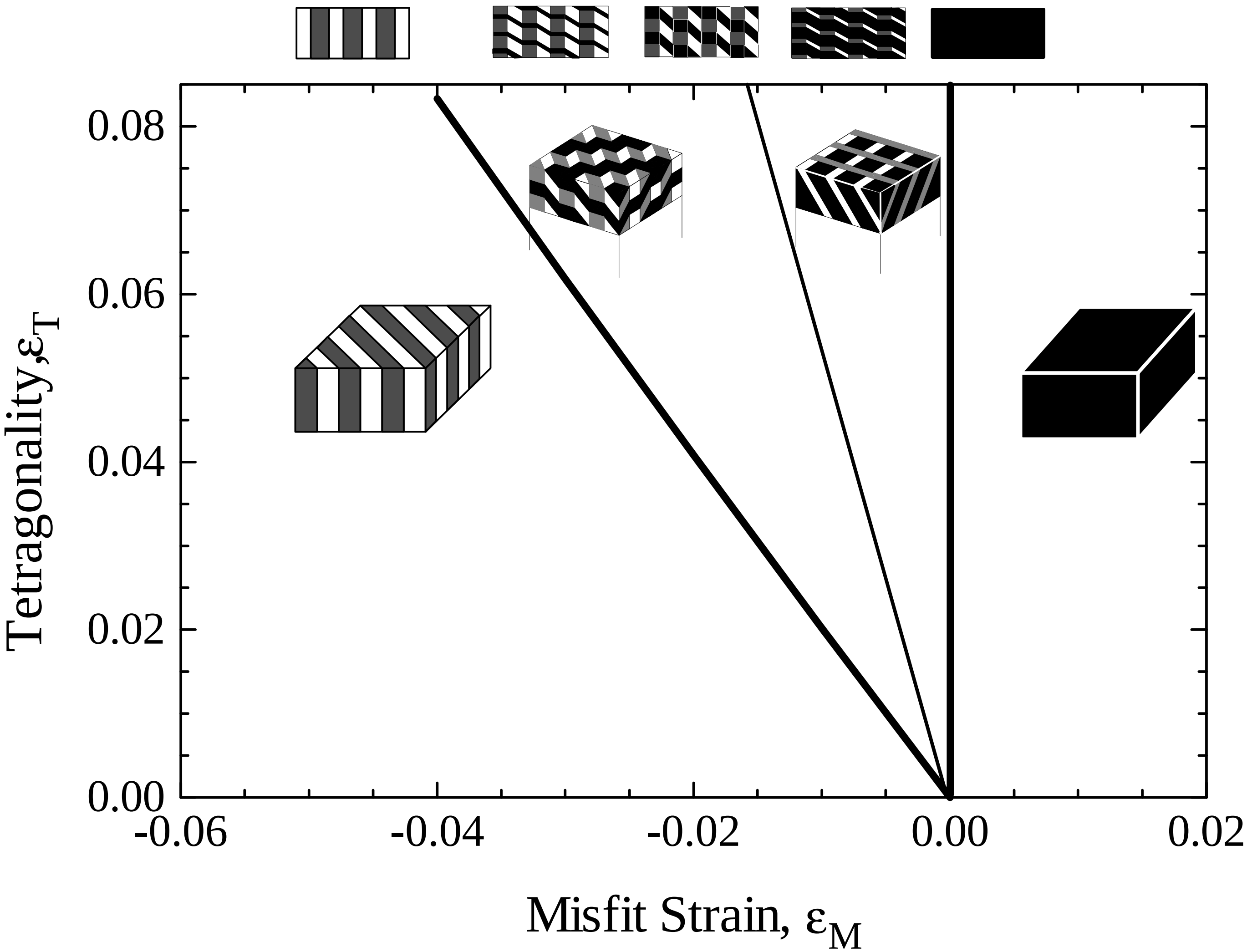
3-DOMAIN POLYTWINS



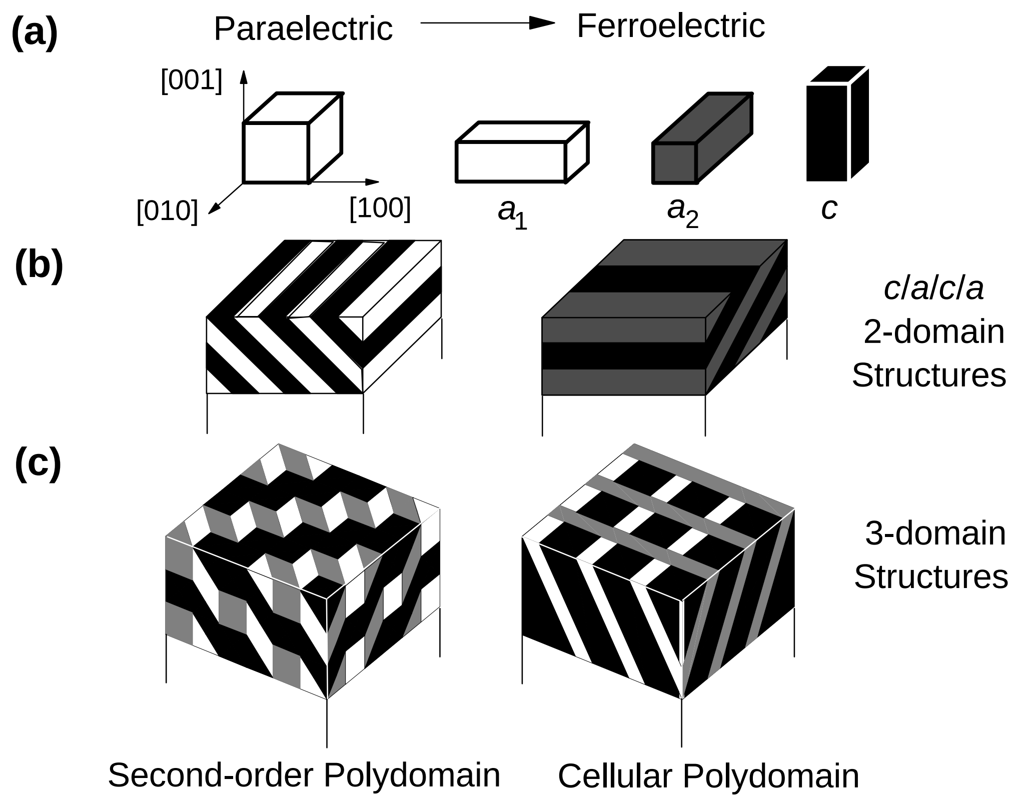
DOMAIN STABILITY MAP FOR 2-DOMAIN STRUCTURES



DOMAIN STABILITY MAP FOR 3-DOMAIN STRUCTURES



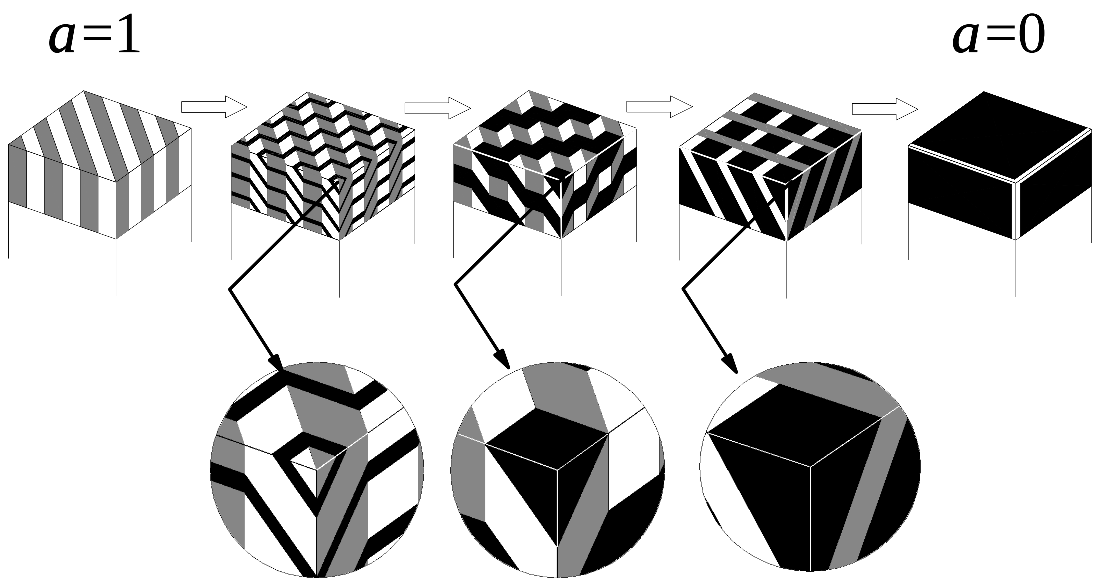
DOMAIN MORPHOLOGY



(a) Cubic paraelectric phase and the three ferroelectric tetragonal variants, (b) the simple *c/a/c/a* polydomain structures, and (c) the 3-domain architectures; second-order polytwin and the cellular arrangement of the domains.

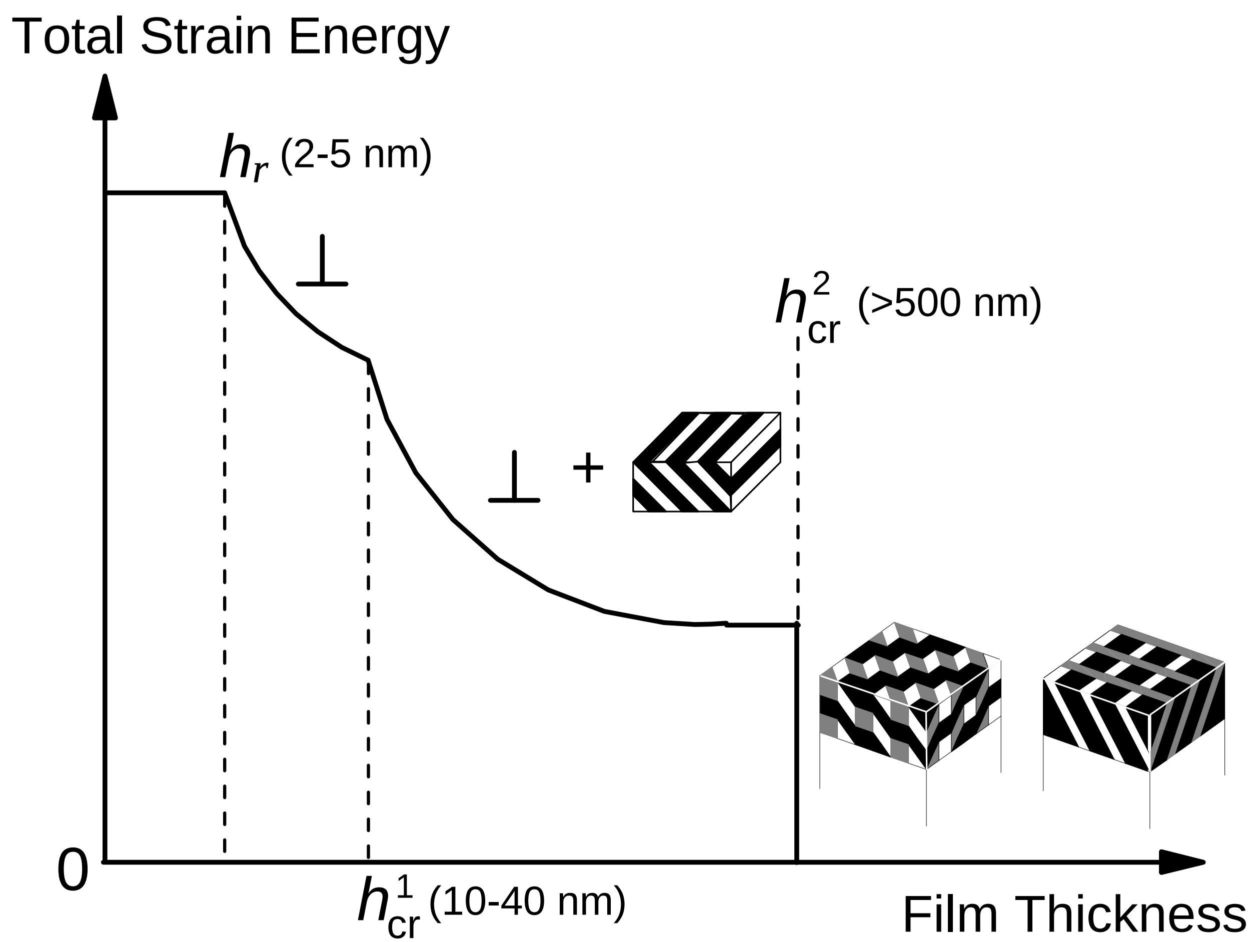
A.L. Roytburd, S.P. Alpay, L.A. Bendersky, V. Nagarajan, and R. Ramesh, “Three-domain Architecture of Stress-free Epitaxial Ferroelectric Films,” J. Appl. Phys., *in press*.

DOMAIN MORPHOLOGY



Schematic evolution of the domain architecture as a function of the a-domain fraction, a.

SUMMARY OF RELAXATION MECHANISMS



EXPERIMENTAL METHODS

- 500 nm thick $PbZr_{0.2}Ti_{0.8}O_3$ (PZT 20/80) film was grown on (001) $SrTiO_3$ by **pulsed laser deposition** (PLD) at 650^{o}C and 100 mTorr oxygen partial pressure.

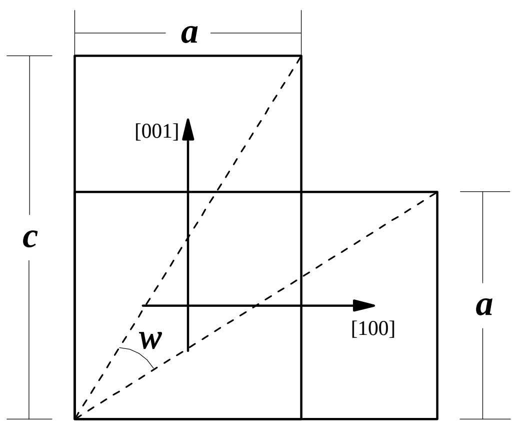
- The thickness of the film was established on the basis of calibration done on other films grown at similar deposition conditions and by TEM.

- **XRD** experiments were carried out on a Siemens D5000 four-circle diffractometer with monochromatized Cu K_a radiation. Crystallographic characterization was accomplished with standard q-$2q$ scans, q rocking curves, and f-scans.

- **TEM**: Phillips 430 operated at 300 keV. Plain-view specimens were prepared by dimpling and ion milling from a substrate side.

TILTING OF DOMAINS

- The domain fractions in an epitaxial polydomain ferroelectric film consisting of *a*- and *c*-domains can be simply determined from the relative integrated intensities of 00*l* and *h*00 type reflections of the film from a *q-2q* scan.



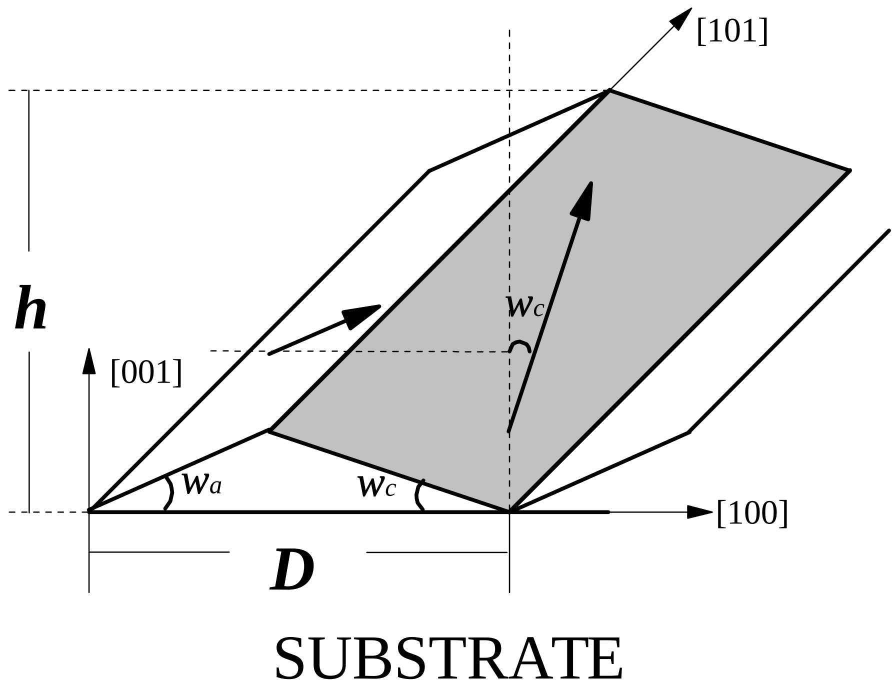
The tilt in polydomain films consisting of *a*- and *c*-domains when brought together at the (101) interface due to the tetragonality of the lattice. The tetragonality is highly exaggerated.

- This method only gives <u>qualitative</u> and sometimes even <u>inaccurate</u> values because of the tilt of the *a*- and *c*-domains away from the (*h*00) or (00*l*) planes of the substrate The tilt is given by:

$$w = 2\,tan^{-1}\left(\frac{c}{a}\right) - \frac{p}{2}$$

- The tilt is accommodated in both *a*- <u>and</u> *c*-domains, depending on their volume fractions *a*.

$$\frac{\tan w_a}{\tan w_c} = \frac{a}{1-a}$$



The accommodation of tilt in polydomain films consisting of *a*- and *c*-domains. Tilt angles are highly exaggerated.

- Depending on the *c*-angle resolution 4-circle XRD *h*00 type of reflections of the film may disappear.
- If x-ray diffractometer perfectly aligned with respect to the *c* angle, even if the film has a significant amount of *a*-domains, the *h*00 type of peaks will be absent from the *q*-2*q* XRD pattern.

- This domain structure results in a four-fold tilt of the (*h*00) and (00*l*) planes of the film away from the [00*l*] direction of the substrate along $[h00]$, $[\bar{h}00]$, $[0k0]$, and $[0\bar{k}0]$.

- Four-fold splitting of the *a*- and *c*-domains is readily observed in q-rocking curves and q-c scans (area maps) *.

* see e.g., C. M. Foster, Z. Li, M. Buckett, D. Miller, P. M. Baldo, L. E. Rehn, G. R. Bai, D. Guo, H. You, and K. L. Merkle, J. Appl. Phys. **78,** 2607 (1995).

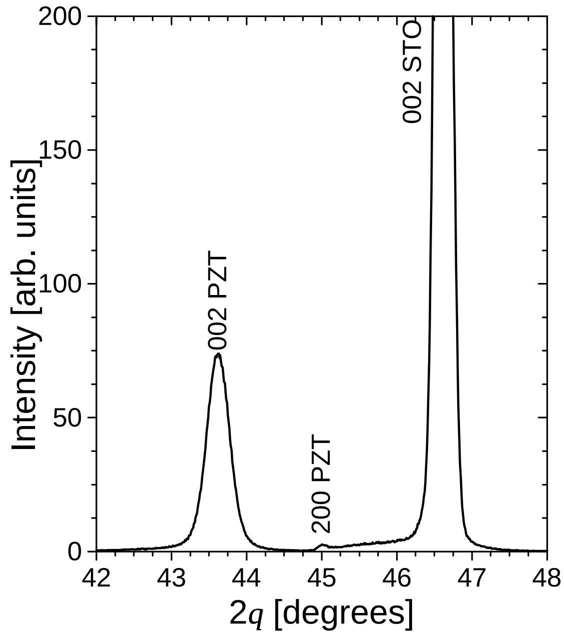
- Therefore, in order to obtain the domain populations in the twinned film more accurately, the integrated intensities of the q-c scans of the 00*l* and *h*00 peaks of the film should be employed.

- If the relative intensities of the q-rocking curves of 00*l* and *h*00 peaks of the film are used to calculate the *c*-domain fraction as **:

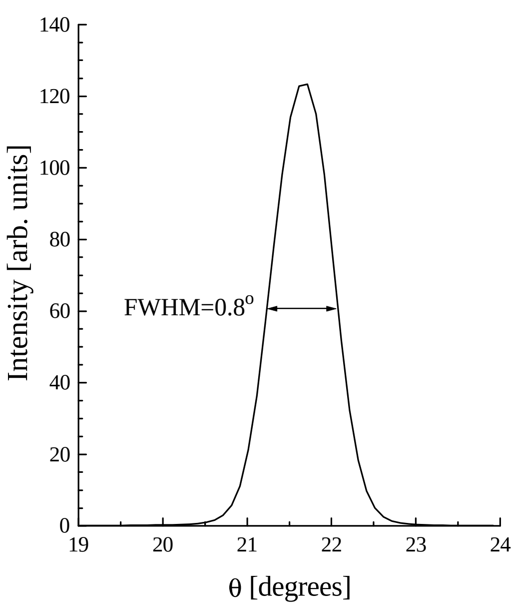
$$a \cong \frac{A_c}{A_c + 4A_a}$$

** Y. M. Kang and S. Baik, J. Appl. Phys. **82,** 2532 (1997).

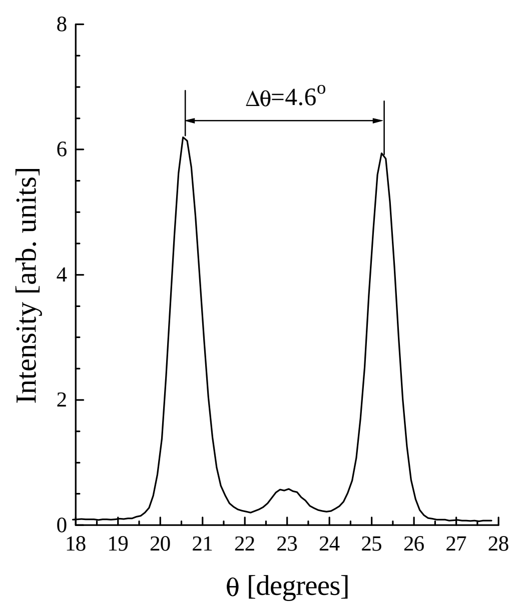
X-RAY DIFFRACTION



(a)



(b)

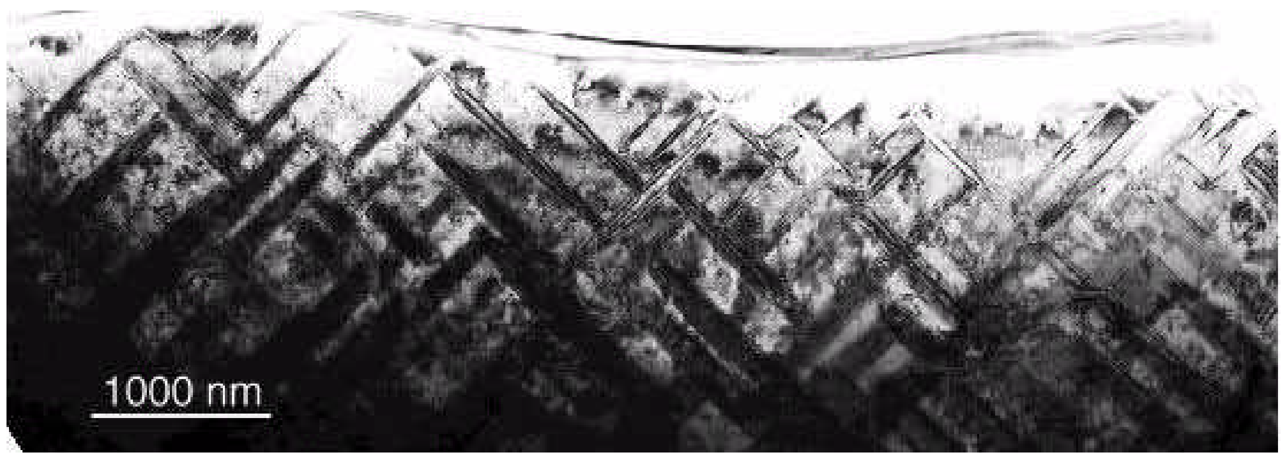


(c)

q-2*q* XRD patterns (a) in the range 40-50°, and *q* rocking curves around 002 PZT peak (b) and around 200 PZT peak (c).

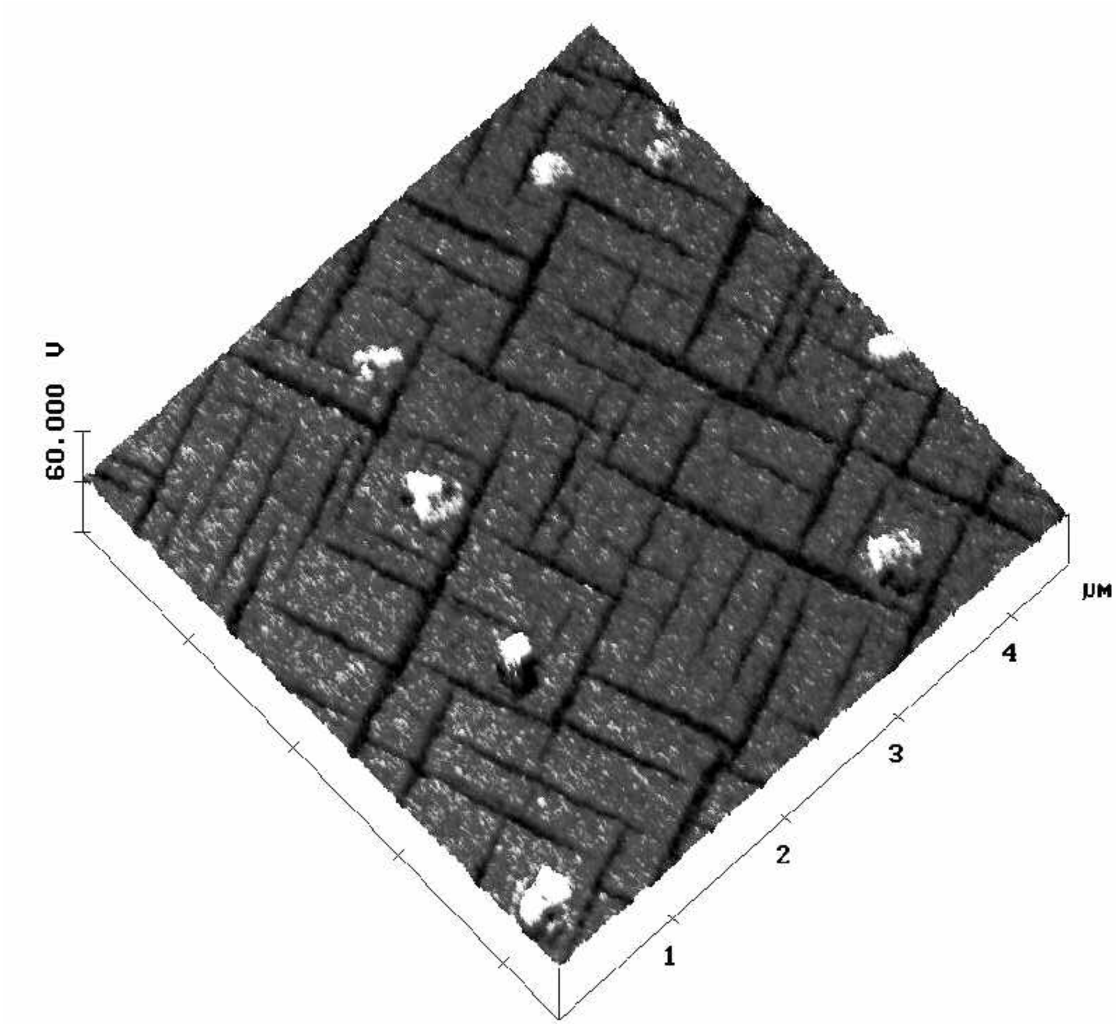
TRANSMISSION ELECTRON MICROSCOPY

c/a/c/a 2-domain Structure (200 nm PZT 20/80 on $SrTiO_3$)



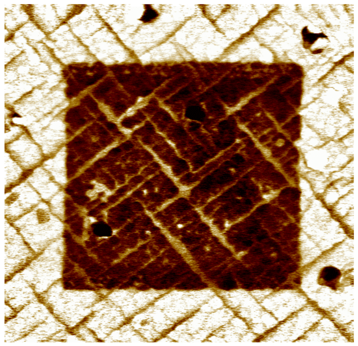
Cellular 3-domain Structure (500 nm PZT 20/80 on $SrTiO_3$)

ATOMIC FORCE MICROSCOPY

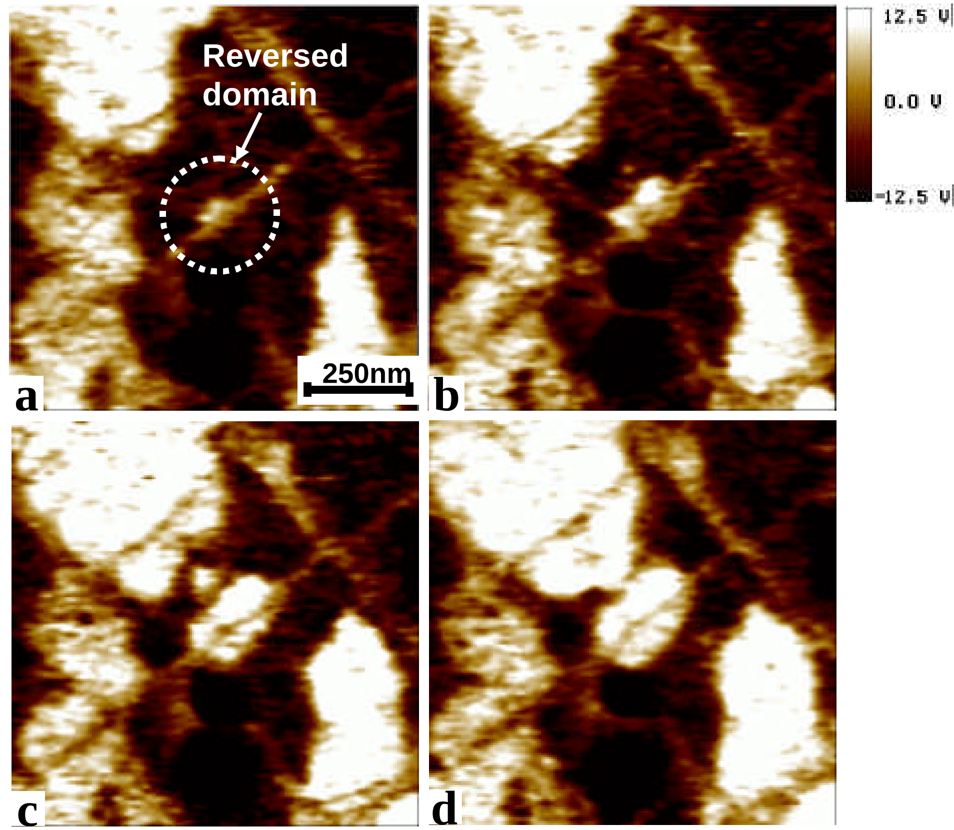


From C. S. Ganpule, V. Nagarajan, *et al.,*"Role of 90 degrees domains in lead zirconate titanate thin films," Appl. Phys. Lett. **77**, 292 (2000)

ATOMIC FORCE MICROSCOPY



AFM micrograph of 500 nm $PbZr_{0.2}Ti_{0.8}O_3$ film on STO substrate. 3-D structure is clearly visible. The reversed polarization state is “written” inside the black square with the tip of the AFM.



Nucleation of reversed domains occurs preferentially along 90° domain walls.

From C. S. Ganpule, V. Nagarajan, *et al.,*”Role of 90 degrees domains in lead zirconate titanate thin films,” Appl. Phys. Lett. **77**, 292 (2000)

CONCLUSIONS

- Epitaxial ferroelectric films undergoing a cubic-tetragonal phase transformation relax internal stresses polydomain structures.The most commonly observed polydomain structure is the *c/a/c/a* polytwin which relieves the internal stresses only partially.
- Relatively thicker films may **completely** reduce internal stresses if all three variants of the ferroelectric phase are brought together such that the film has the same in-plane size as the substrate.
- XRD studies of 500 nm thick (001) $PbZr_{0.2}Ti_{0.8}O_3$ films on (001) $SrTiO_3$ grown by pulsed laser deposition show that the internal stresses are completely relived and all three variants of the tetragonal phase are present.
- TEM and AFM studies reveal the presence of the cellular 3-domain morphology.
- The 3-domain structure may play an important role in the switching characteristics of ferroelectric films.