清華大學
Tsinghua University

多铁性磁电复合薄膜

南 策文

清华大学材料科学与工程系

致 谢

林元华， 刘刚， 周剑平， 邓朝勇， 施展
何泓材， 王瑶， 马静， 张毅， 王婧， 李铮， 刘静

- 国家自然科学基金会
- 国家科技部973计划

提　纲

I. 背 景

II. 1－3型柱状复合薄膜

III. 0－3型颗粒复合薄膜

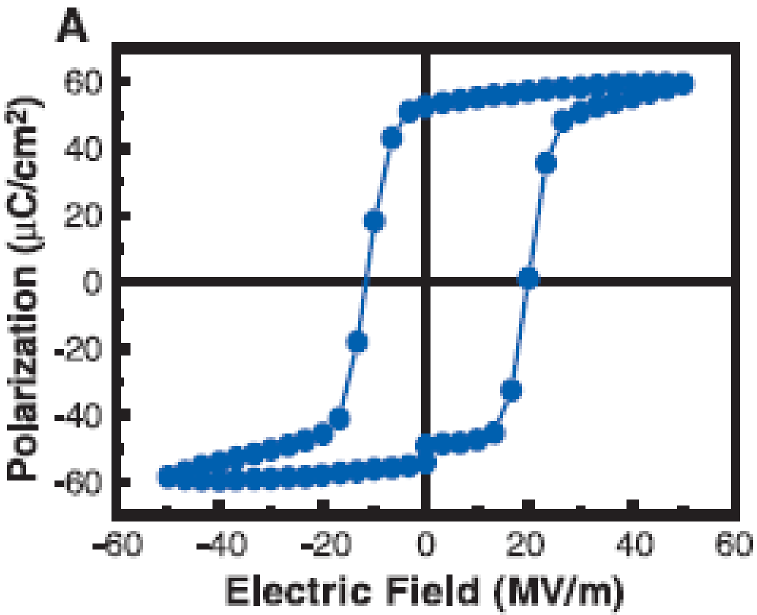
IV. 2－2型叠层复合薄膜

V. 单层薄膜复合

VI. 结 语

I. 背 景

铁性 (ferroics)



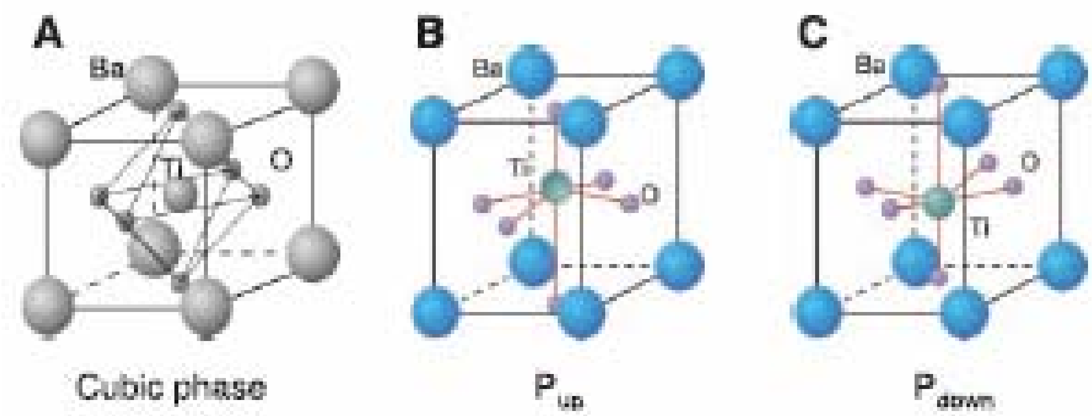
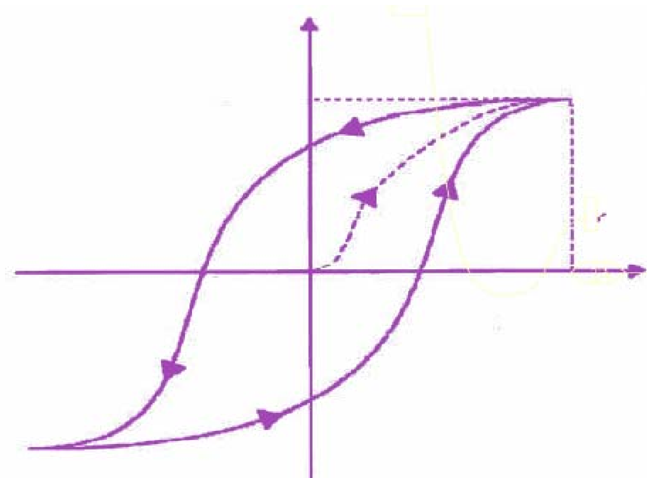


Fig. 1. Crystal structure of the perovskite ferroelectric $BaTiO_3$.

	驱动场	序参量	实例
铁电	电场	自发极化	$BaTiO_3$
铁磁	磁场	自发磁化	Fe_3O_4
铁弹	应力	自发胁变	$CaAl_2Si_2O_8$



多铁性与磁电

多铁性 (multi-ferroics):

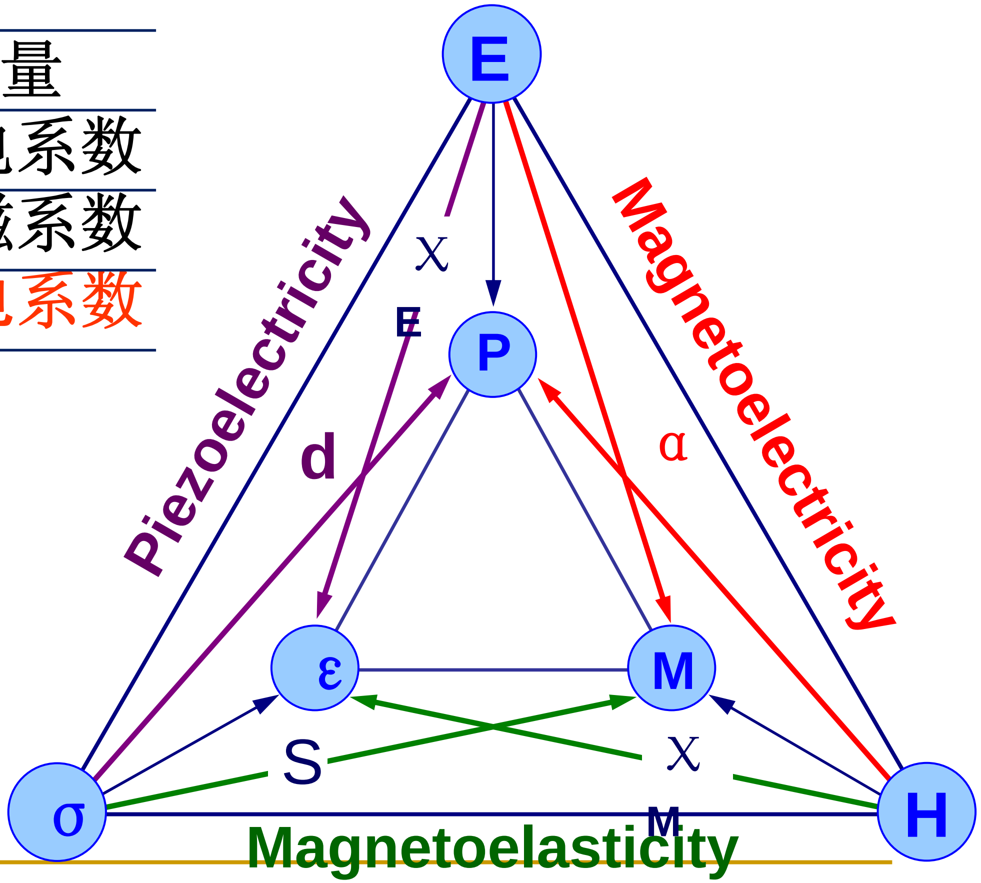
即具有两种或两种以上初级铁性体的特征

	驱动场	参量
铁弹铁电	电场和应力	压电系数
铁磁铁弹	磁场和应力	压磁系数
铁磁铁电	磁场和电场	磁电系数

$$\varepsilon = s\,\sigma + d^T E + q^T H$$

$$P = \kappa E + d\,\sigma + \alpha H$$

$$M = \chi H + q\,\sigma + \alpha E$$



多铁性 Magnetoelectrics

* 正磁电效应：

磁场 调控 电性

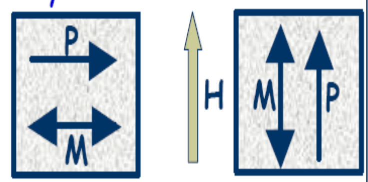
$P = a\,H$ or $E = a_E\,H$

* 逆磁电效应：

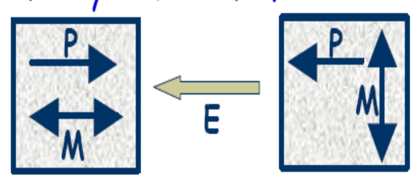
电场 调控 磁性

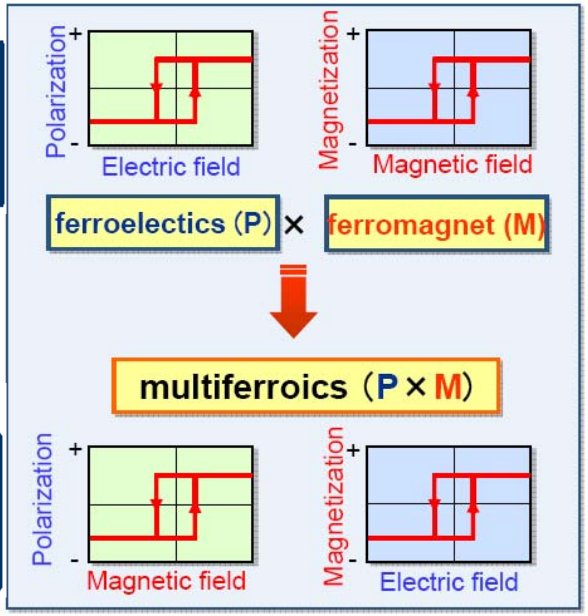
$M = a\ E$

Rotation of P axis by rotation of M:



Rotation of M axis by reversal of P :





(Tokura, *JMMM*, 2007)

多铁性磁电材料

清華大學 Tsinghua University

多铁性磁电化合物

- ✓ 本征效应
- □ 耦合微弱
- □ 低温、强场操纵
- □ 远离实际应用

☆$BiFeO_3$　A位孤对电子　B位磁性离子

☆$YMnO_3$　几何驱动

☆$TbMnO_3$　低对称性磁基态

多铁性磁电复合材料

铁电－铁磁复合

- □ 非本征效应
- ✓ 强耦合：巨磁电效应
- ✓ 室温、低场操纵
- ✓ 实际应用

- 块材
- 低维纳米结构

块体复合材料

- 陶瓷复合材料
  Philips Lab (*J Mater Sci*, 1974)

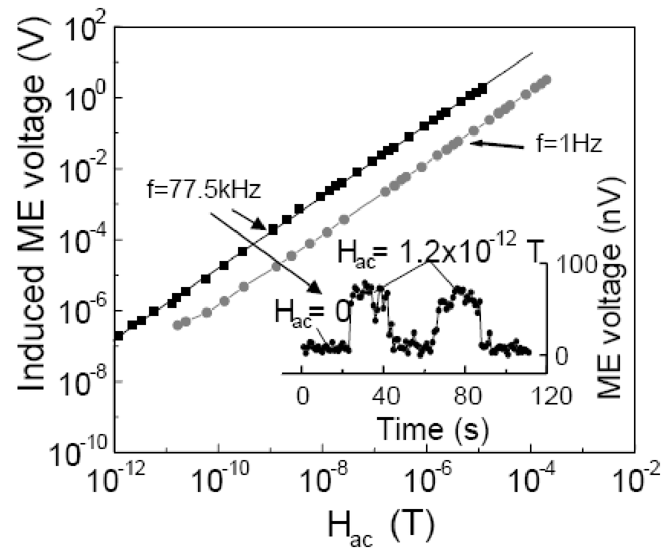
- 铁电－合金复合材料
  Nan et al. 理论预测 (*Phys Rev B*, 2001)
  Ryu et al. 实验 (*J Am Ceram Soc*, 2001)
  Dong et al. 实验(*Appl Phys Lett*, 2003)

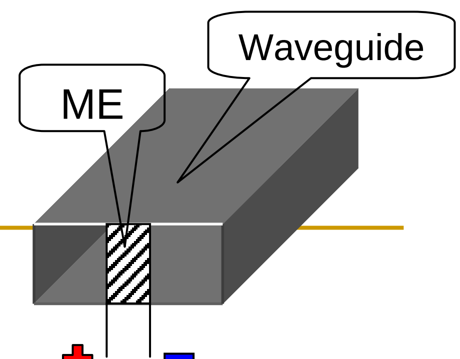
- 陶瓷－合金－高分子复合材料
  Nan et al. (*Appl Phys Lett*, 2002)
  Wan & Liu et al. (*J Appl Phys*, 2003)

应用

✓ (磁调控 电)传感器

✓ (电调控 磁)微波器件





Nan et al., *J. Appl. Phys.* 103, 031101 (2008).

为什么多铁性磁电复合薄膜？

- 应用驱动
- 纳米尺度耦合作用？

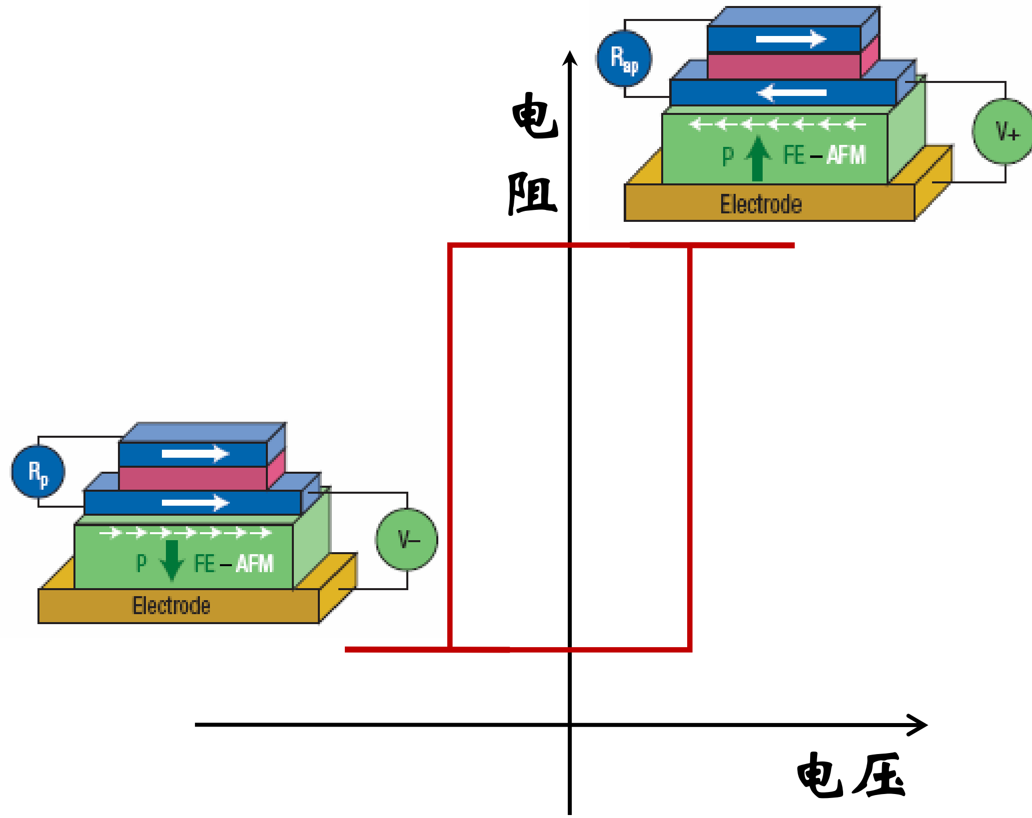
磁 调控 电：

✓ 微磁场传感器

电 调控 磁：

✓ 自旋电子器件

✓ 多态存储器件



磁电 RAMs

磁电储存器概念

Bibes et al., ***Nature Mater.*** 7, 425 (2008)

多铁性磁电复合薄膜

Main Historical Perspective:

2004 Zheng et al (*Science* 303, 2004): $CoFe_2O_4/BaTiO_3$ nanostructured films
2005 Nan et al. (*Phys. Rev. Lett.* 94, 2005): theoretical modeling
2005— Many groups: PZT/ferrites, $BiFeO_3$/ferrites, $BaTiO_3/LaSrMnO_3$, etc

Nanostructured films of ferroelectric and magnetic oxides:

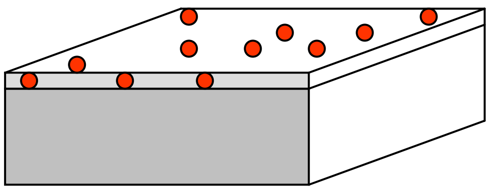
Processing: PLD or Sol-gel spin-coating

Strain-Mediated 耦合机制

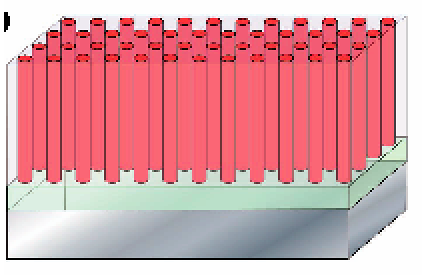
相组成与微结构

铁电相	磁性相
$BaTiO_3$，$PbTiO_3$，PZT	MFe_2O_4 (M=Co,Ni)
$BiFeO_3$	$(La,M)MnO_4$ (M=Ca,Sr)

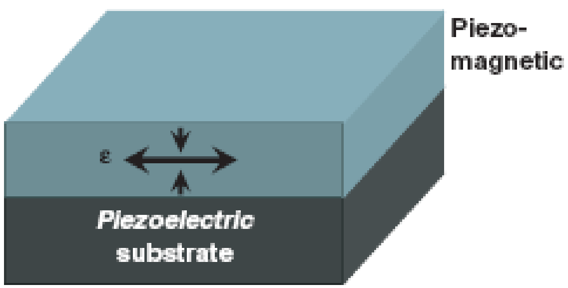
2-2 multilayers



0-3 particulate film



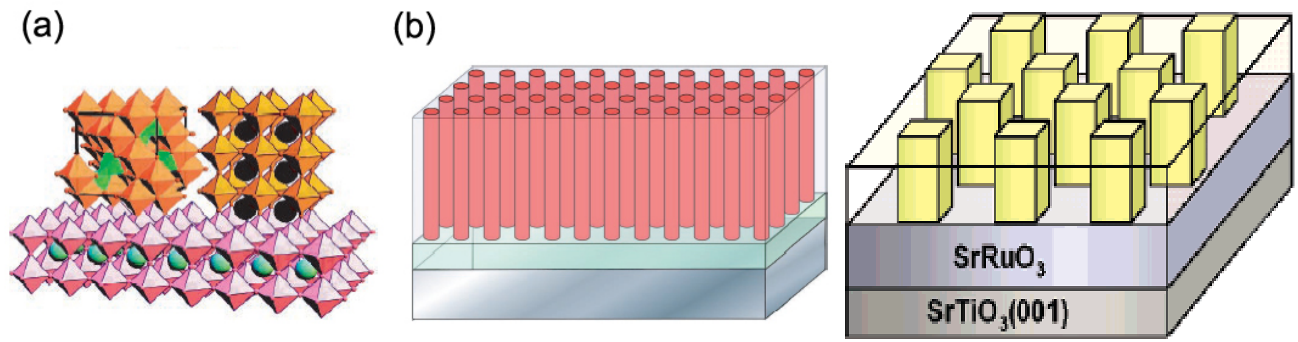
1-3 nanopillar array

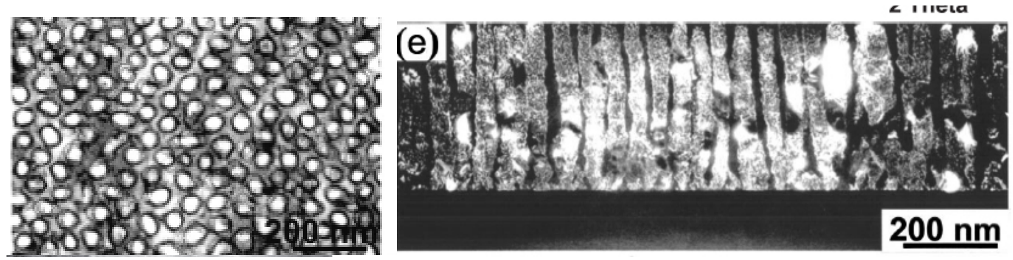


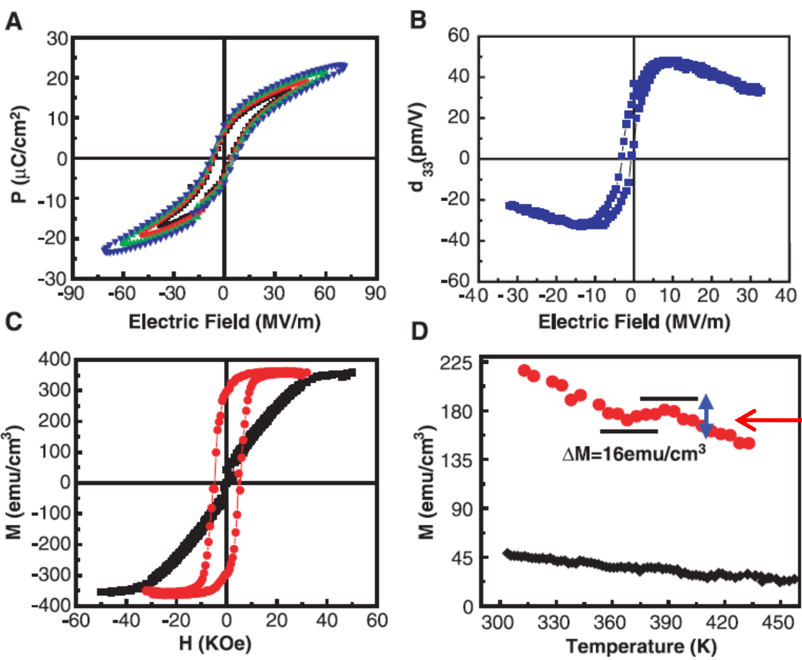
Single layer film

II、1–3型柱状复合薄膜

$0.35CoFe_2O_4$-$0.65aTiO_3$ ($BiFeO_3$) by PLD





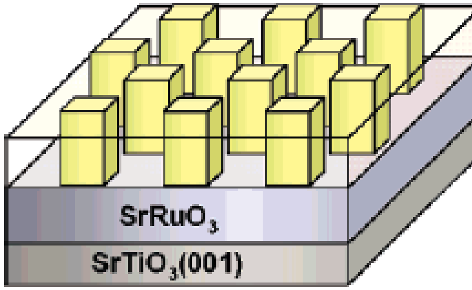


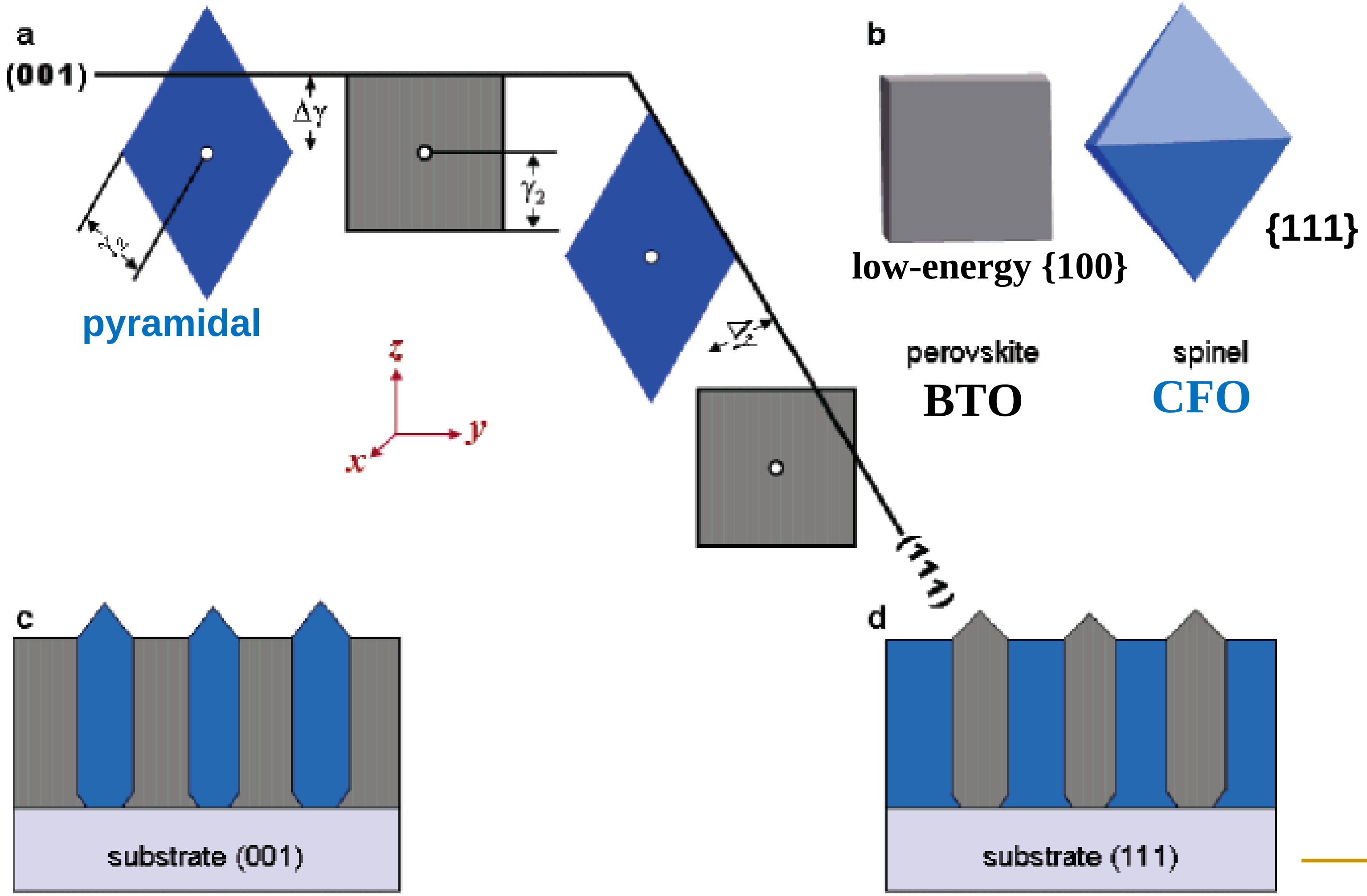
Elastic coupling between two nanophases

Strain-Mediated 耦合机制

(H. Zheng et al, *Science* 303, 2004)

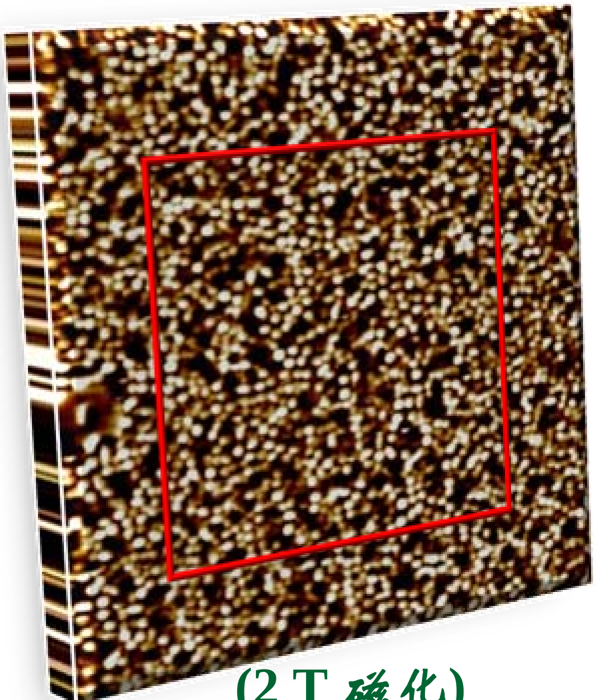
1-3 型柱状复合结构生长





(H. Zheng et al, *Adv. Mater*. 2006)

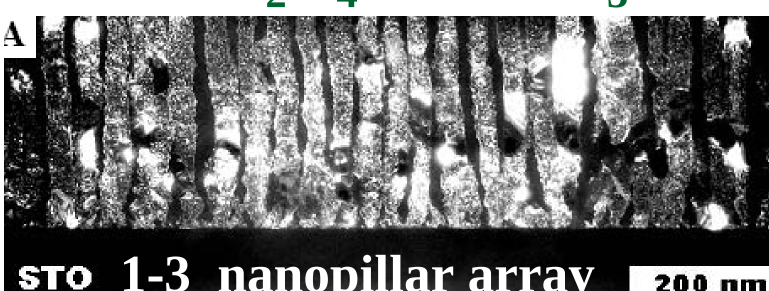
磁电耦合观察　MFM (磁力显微镜)



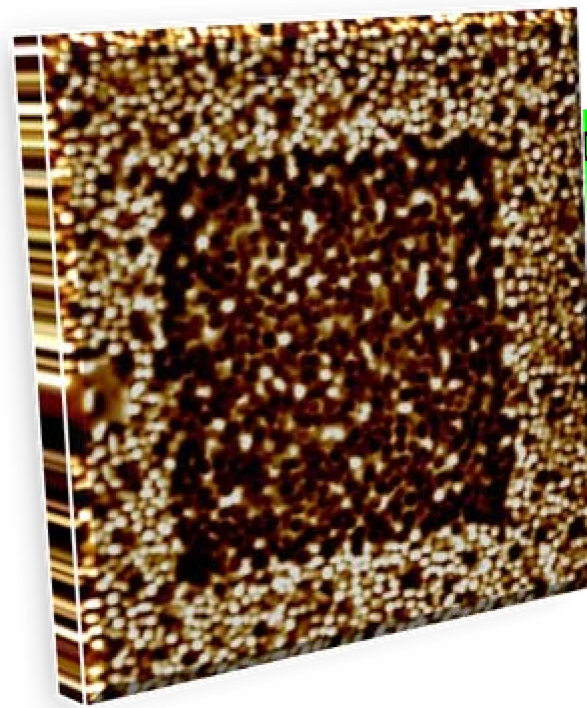
(2 T 磁化)

Tapping-lift MFM
after DOWN magnetization at 2T

$CoFe_2O_4$－$BaTiO_3$



Tapping-lift MFM
after electrical poling at -16V

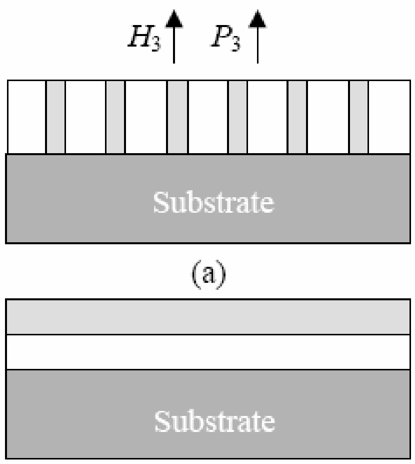


DOWN to UP:
80±5%

(电压＝16 V，700 Oe)

Zavaliche *et al.*, *Nano Lett.* 5, 1793 (2005).
Nano Lett. 7, (2007).

有效介质方法



(b)

$$\sigma = \mathbf{c}\varepsilon - \mathbf{e}^T\mathbf{E} - \mathbf{c}\varepsilon^{ms} - \sigma_s,$$

$$\mathbf{D} = \mathbf{e}\varepsilon + \kappa\mathbf{E} + \alpha\mathbf{H} + \mathbf{P}_s,$$

$$\mathbf{B} = \mu(\varepsilon, \mathbf{E}, \mathbf{H})\mathbf{H} + \mathbf{M}_s,$$

基片约束作用

$$\bar{\mathbf{P}} = \alpha^* \langle \mathbf{H} \rangle + \bar{\mathbf{P}}_s$$

$$\bar{\mathbf{P}} = (1-f)\left\{\mathbf{P}_s + (\kappa^p - \kappa^*)\mathbf{G}^\phi(\mathbf{P}_s - \mathbf{e}^p\mathbf{G}^u\sigma_s^p) + (\mathbf{e}^* - \mathbf{e}^p)\mathbf{G}^u(\sigma_s^p + \mathbf{e}^T\mathbf{G}^\phi\mathbf{P}_s)\right\}$$
$$+ f\mathbf{e}^*[\mathbf{I} - \mathbf{G}^u(\mathbf{c}^m - \mathbf{c}^p)]^{-1}(\mathbf{c}^m\varepsilon^{ms} + \sigma_s^m),$$

Nan, et al., *Phys. Rev. Lett.* 94, 197203 (2005)

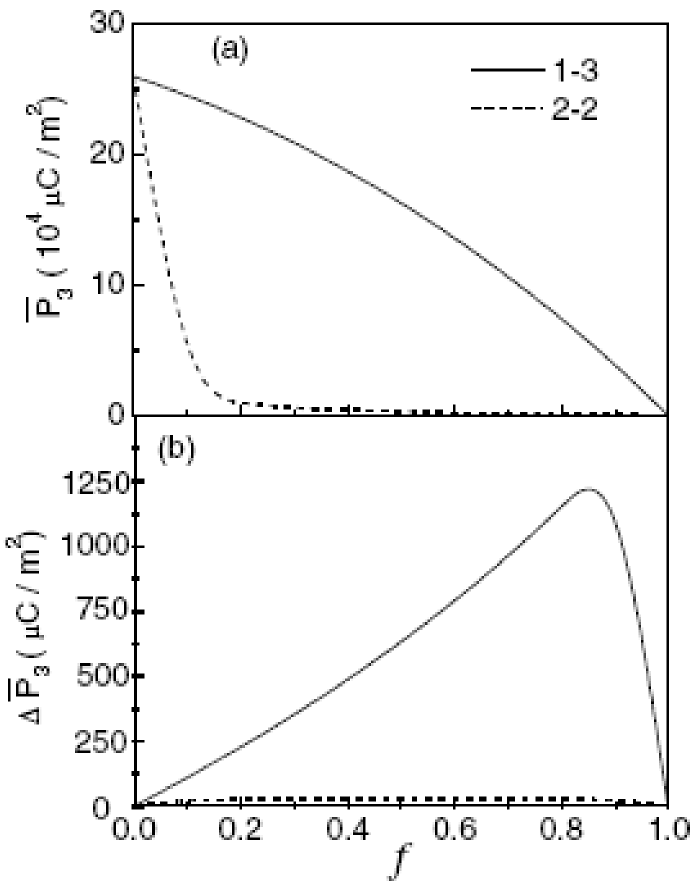
计 算 结 果

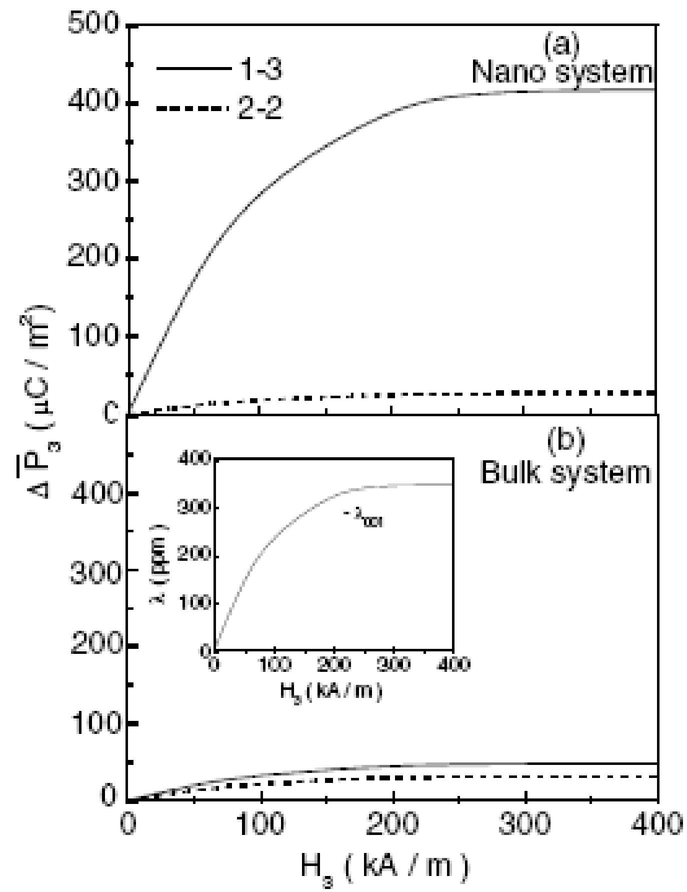
1-3 型：

$$\bar{P}_3 = (1-f)P_{s3} + \frac{2f(1-f)e^{p}_{31}}{\bar{k} + c^{p}_{11} - c^{p}_{12}}(\sigma^{p}_{11} - \sigma^{m}_{11}),$$

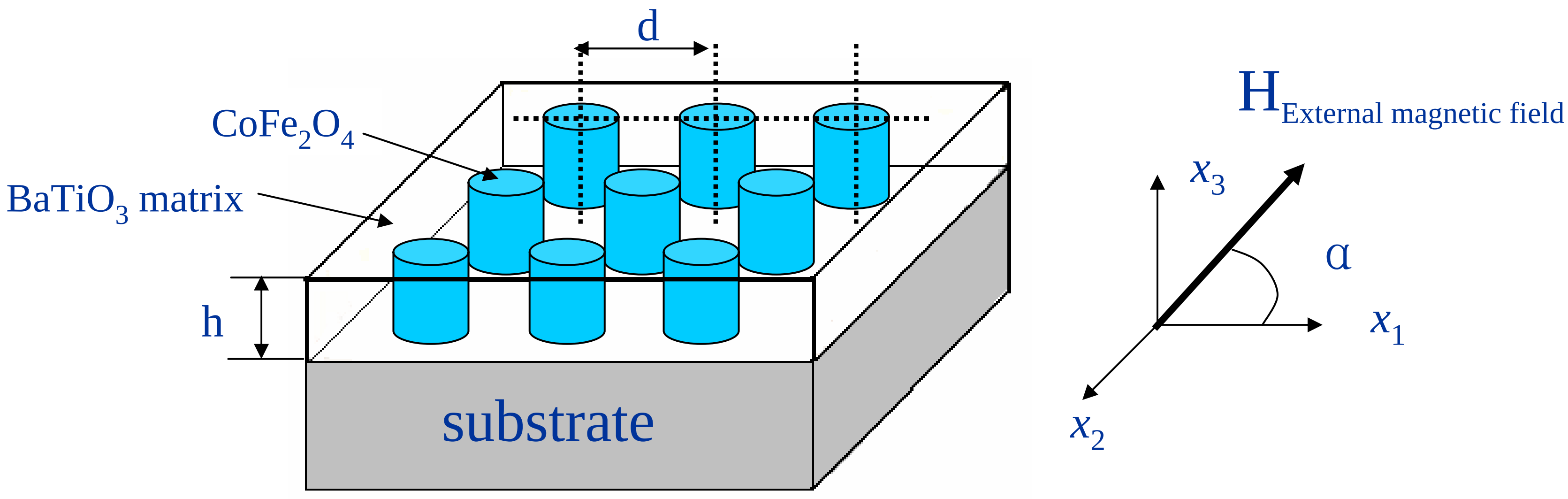
2-2 型：

$$\bar{P}_3 = (1-f)\frac{\kappa^{m}_{33}}{\bar{\kappa}_{33}}P_{s3} + \frac{f(1-f)e^{p}_{33}\kappa^{m}_{33}}{\bar{c}_{33}\bar{\kappa}_{33}}(\sigma^{p}_{33} - \sigma^{m}_{33})$$





相场方法 Phase-field method

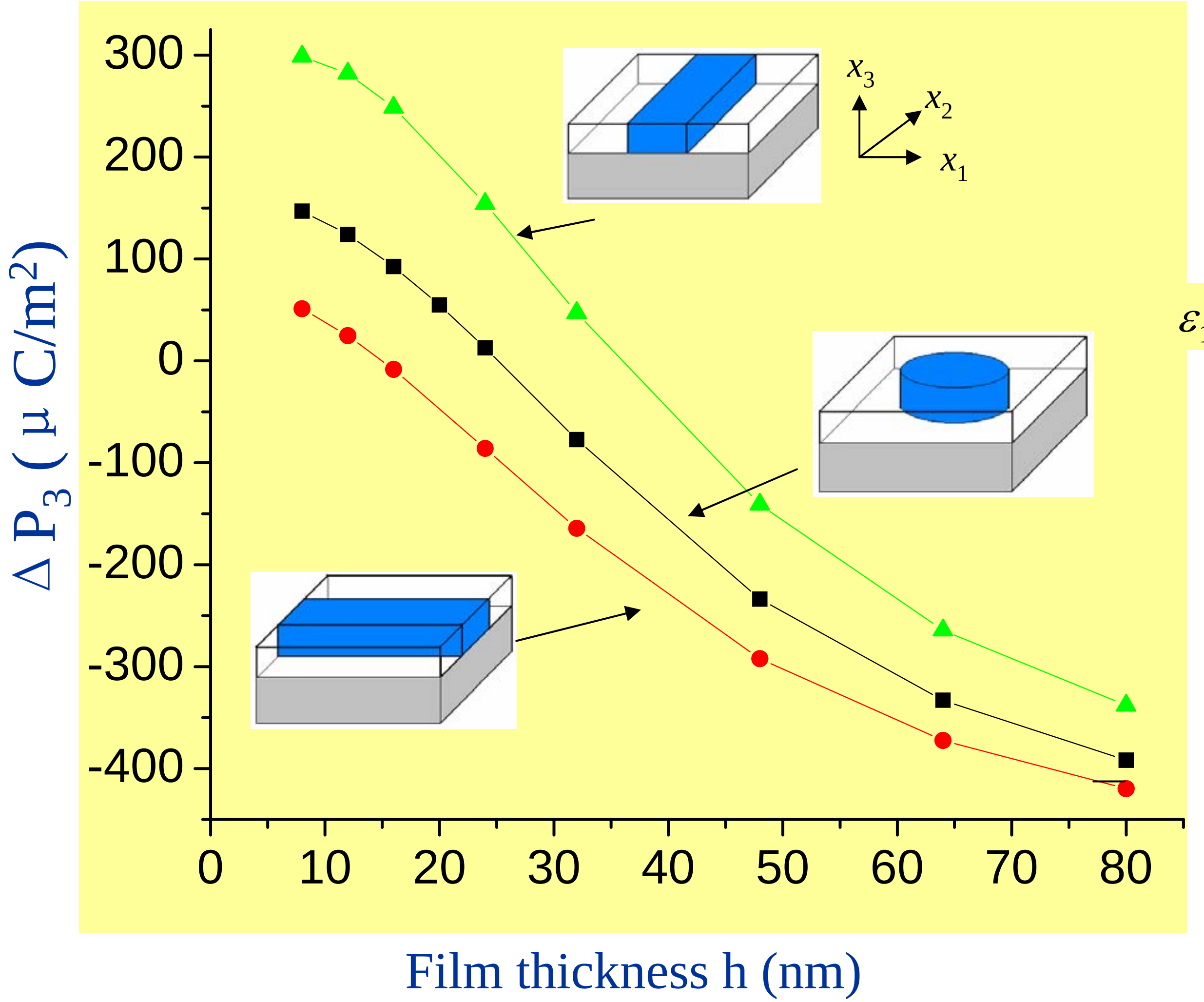


Magnetic-Field-Induced Electric Polarization (MIEP)

$$\Delta\overline{P}_3 = \overline{P}_3 - \overline{P}_3(H // x_1)$$

Zhang et al., *Appl. Phys. Lett.* 90, 052909 (2007)

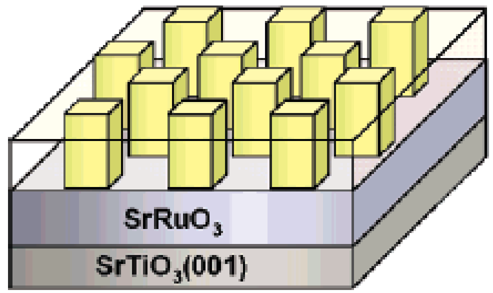
Phase-field method 结果



$\varepsilon_{11}^{s} = \varepsilon_{22}^{s} = -0.005$

Zhang et al., *Appl. Phys. Lett.* 90, 052909 (2007)

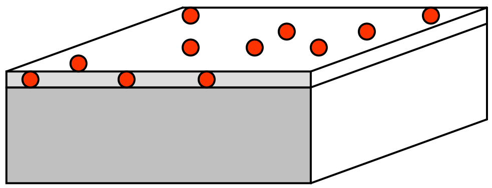
1-3型柱状复合薄膜

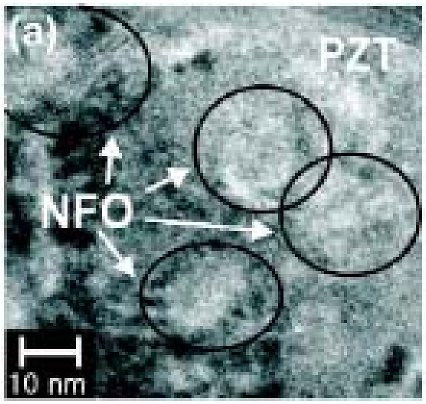


- 制备难度大、不易控制
- 柱状磁性氧化物导致漏电流大

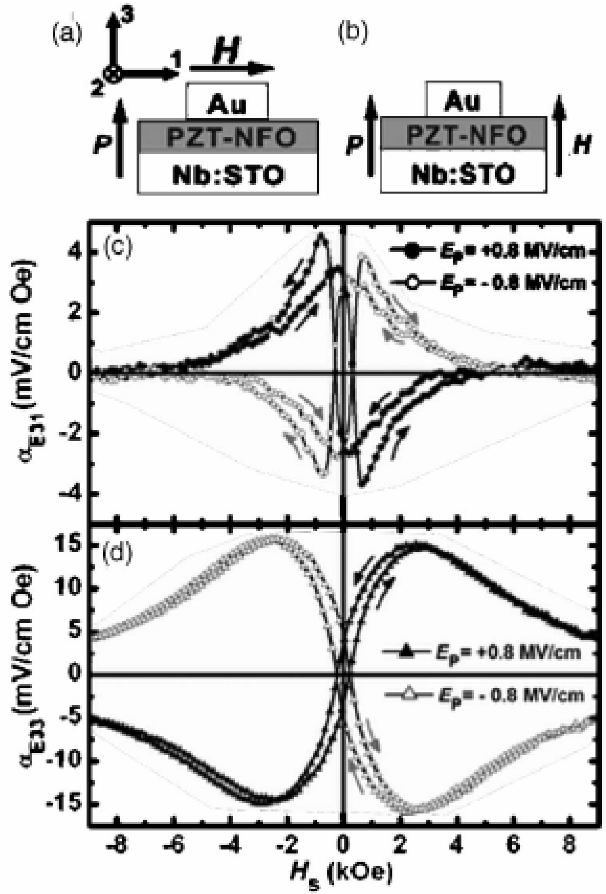
III、0－3型颗粒复合薄膜

磁场 调控 电性





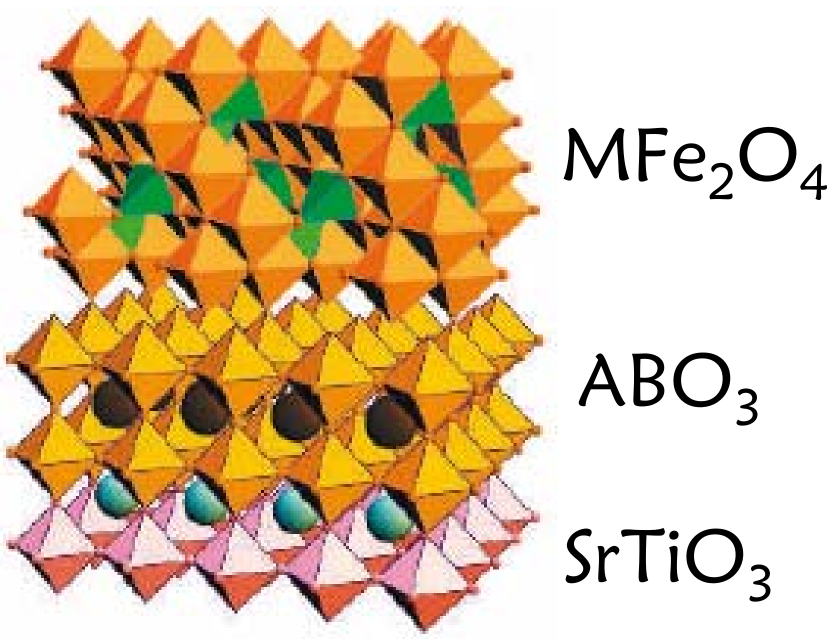
0.35NFO-0.65PZT on (001)STO by PLD

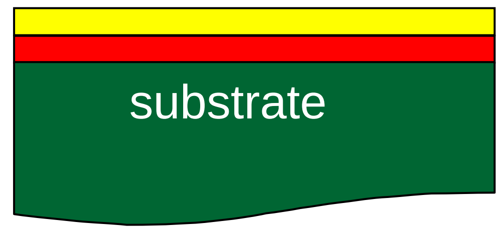


Strain-Mediated 耦合机制

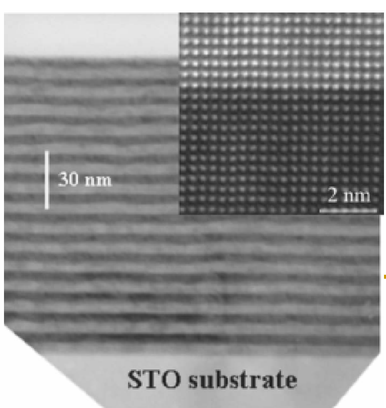
Ryu *et al.*, *Appl. Phys. Lett.*, **80, 102907 (2006)**

Ⅳ、2-2型叠层复合薄膜

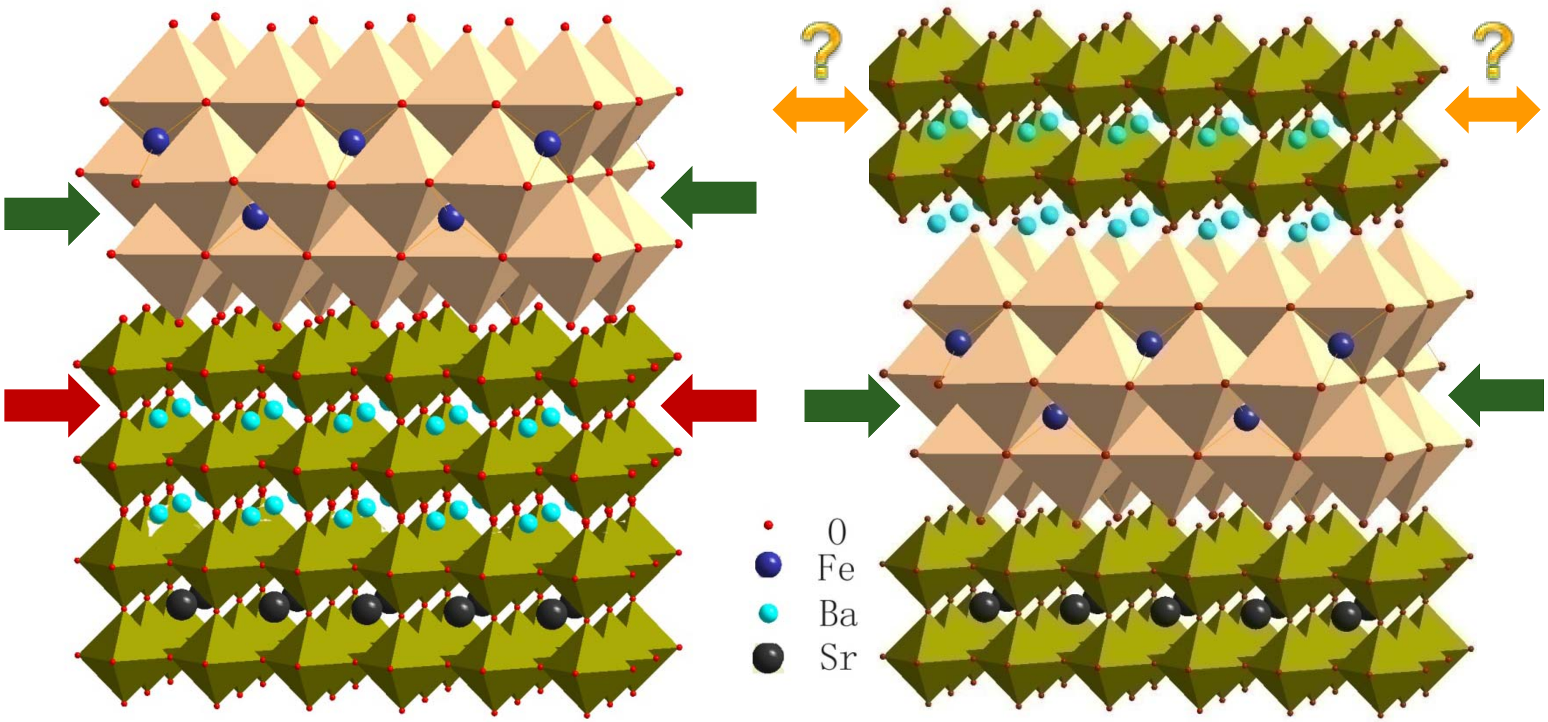




- 易于控制生长
  (PLD, sol-gel)
- 易于器件集成结构
- 抑止了漏电流



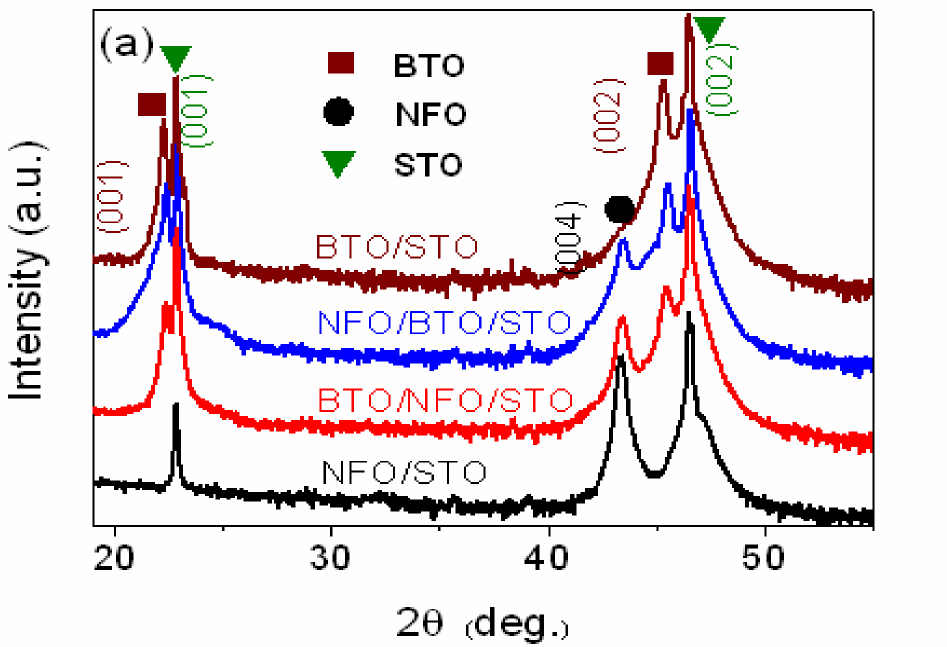
Horizontal heterosturcture



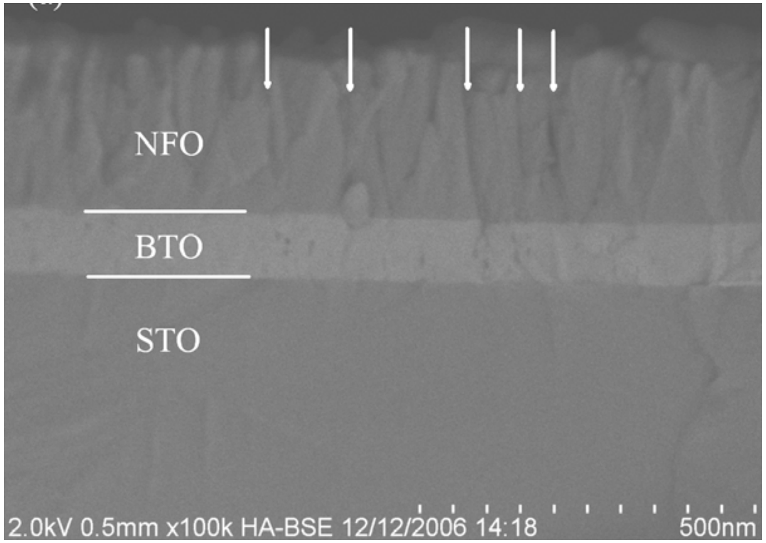
NFO/BTO/STO

BTO/NFO/STO

NFO-BTO on (001) STO by PLD

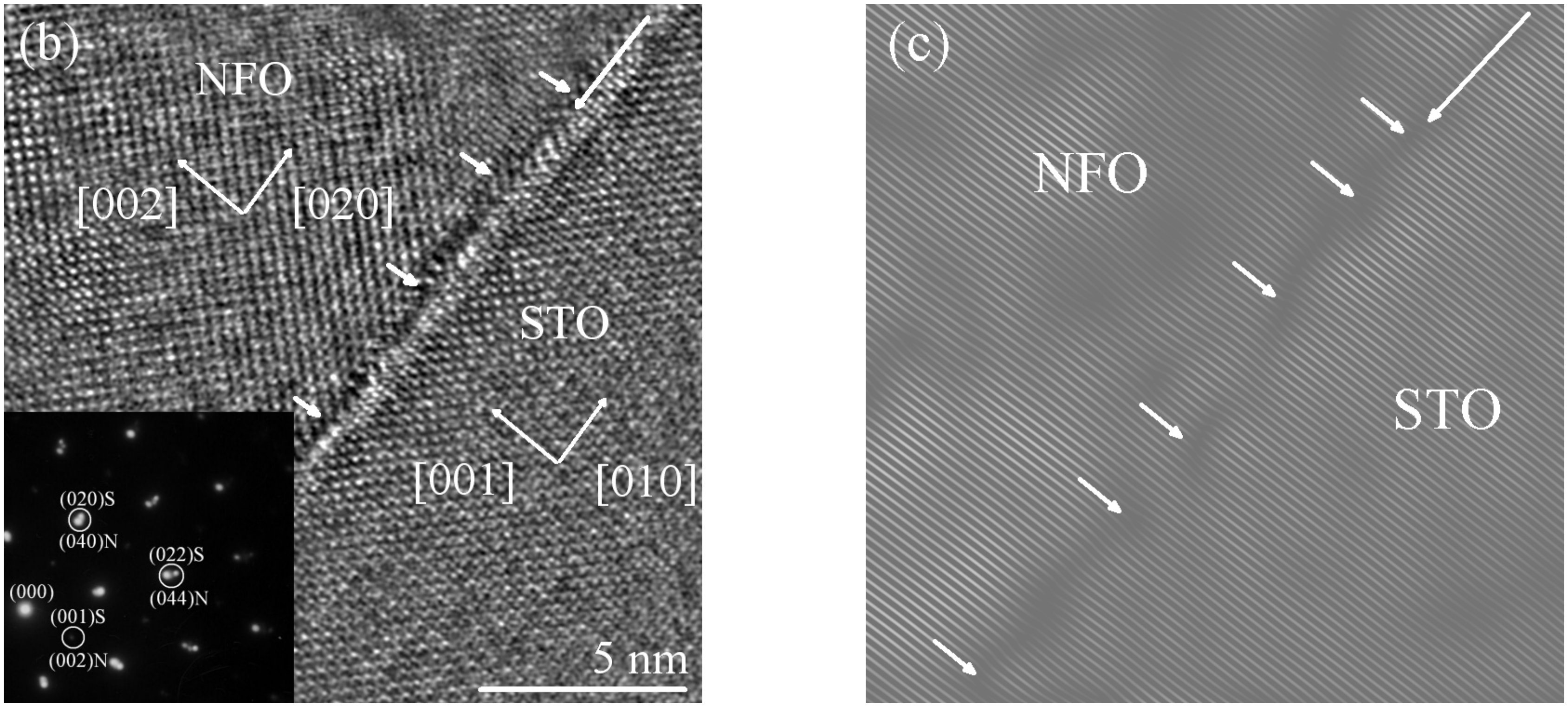


XRD patterns of composite and single phase films



Deng et al, *J. Appl. Phys*. **102**, 074114 **(2007)**

Dislocations in films



HRTEM(left) and inverse FFT(right) image for NFO-STO interface and SAED from both NFO and BTO layers of the BTO/NFO/STO film

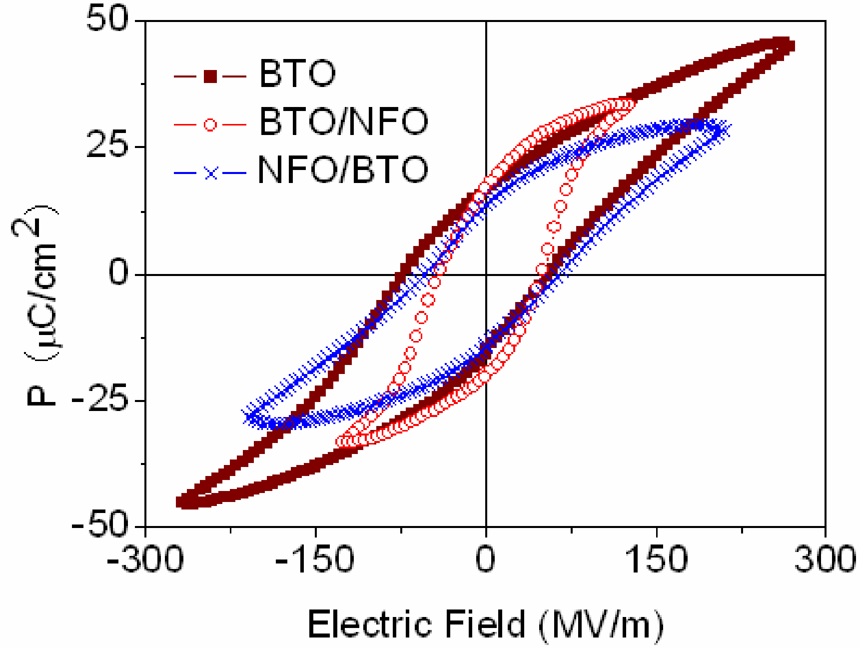
Strain state

	BTO		NFO	
	c(Å)	*△c/c(%)*	*a(Å)*	*△a /a(%)*
NFO/BTO	4.017	−0.52	8.331	−0.07
BTO/NFO	4.008	−0.75	8.324	−0.16
Bulk value	4.038	/	8.337	/

$\triangle c/c=(c-c^*)/c$ and $\triangle a/a=(a-a^*)/a$, where c^* and a^* are the lattice constants of the bulk single crystal

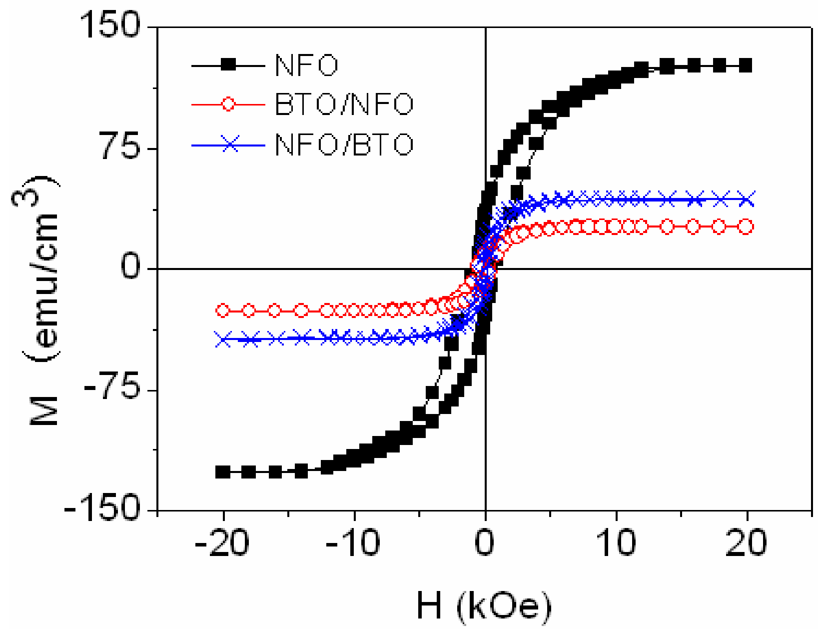
Ferroelectric hysteresis

	Ps μ C/cm²	P_r μ C/cm²	Ec MV/m
BTO	46	18	64
NFO/BTO	28	14	59
BTO/NFO	33	19	46

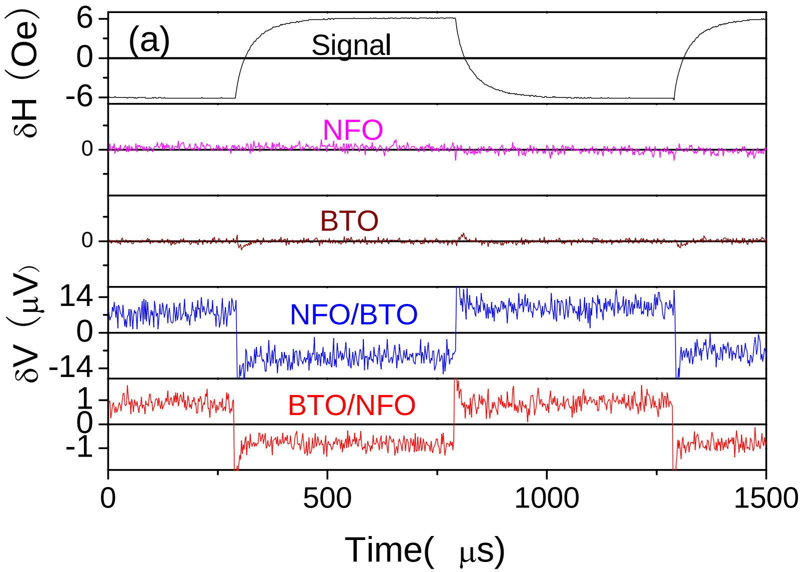


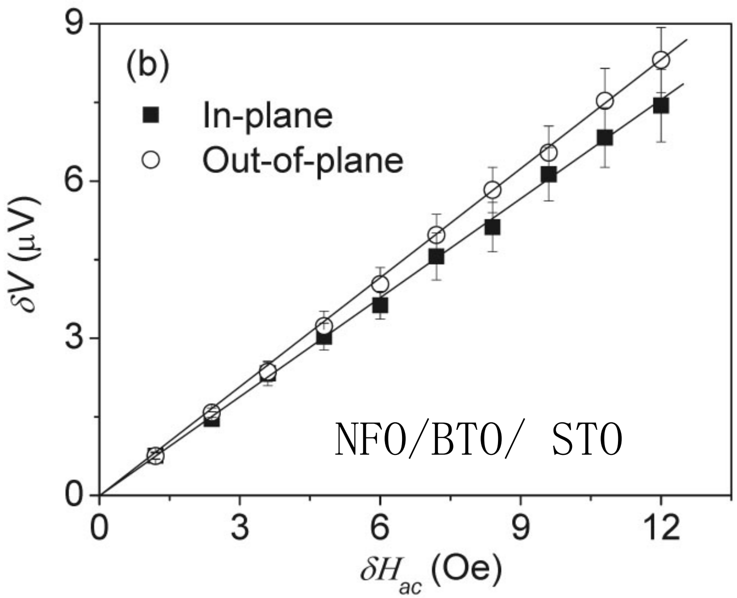
Ferromagnetic hysteresis

	Ms emu/cm³	Hc Oe
NFO	126	820
BTO/NFO	26	600
NFO/BTO	44	230



ME effect: 磁场 调控 电性

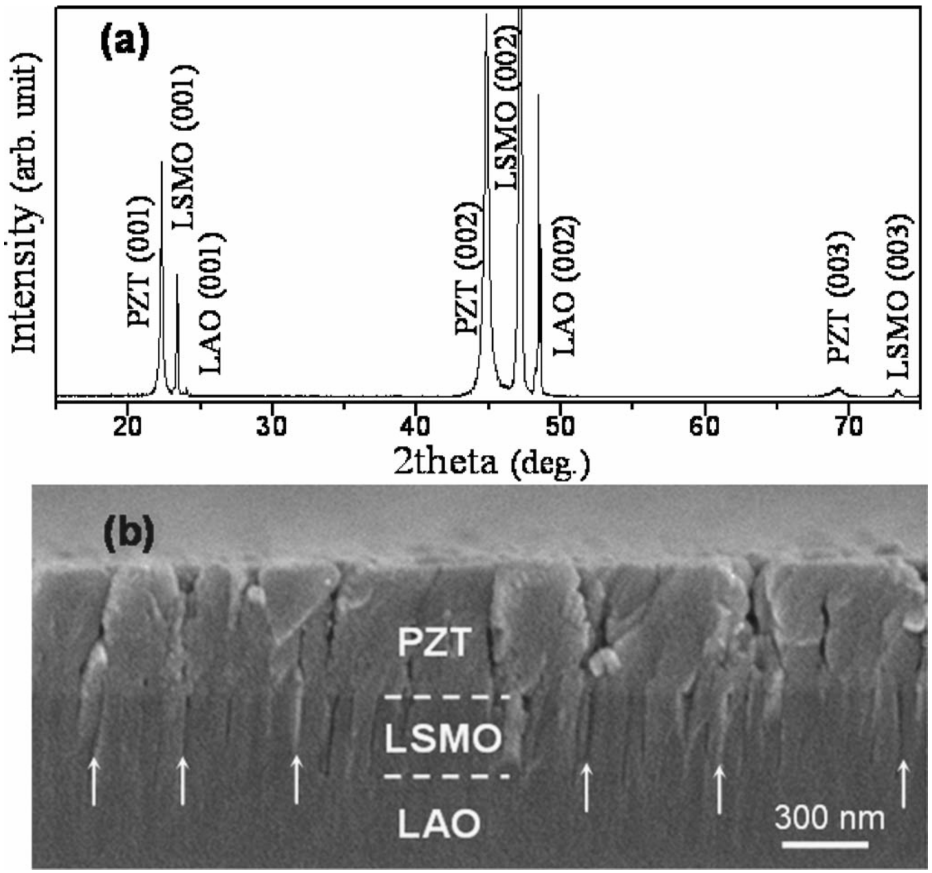


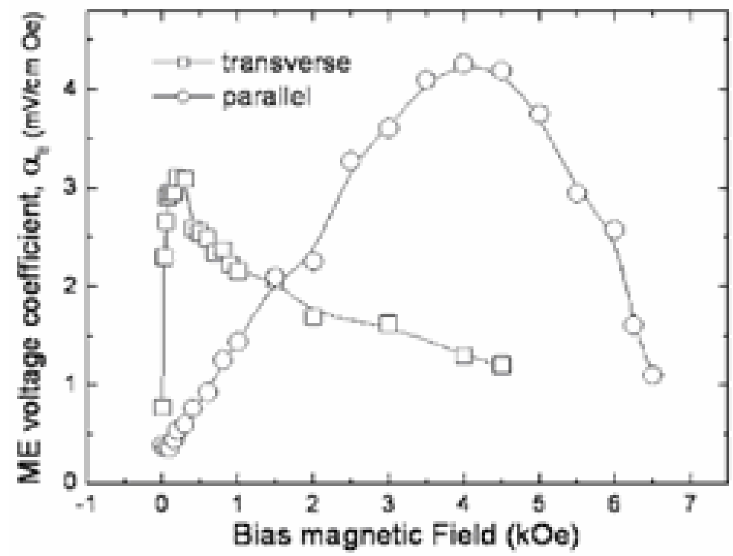


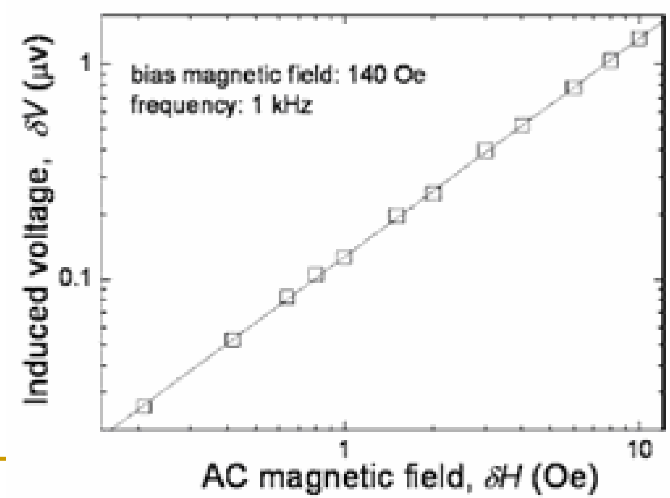
	In-plane(mV/cm Oe)	**Out-of-plane(mV/cm Oe)**
BTO/NFO	5.3	4.9
NFO/BTO	43.9	39.2

Deng et al, *J. Appl. Phys*. 102, 074114 **(2007); *Acta Mater*. 56**, 405 **(2008).**

PZT/LSMO on LAO by PLD

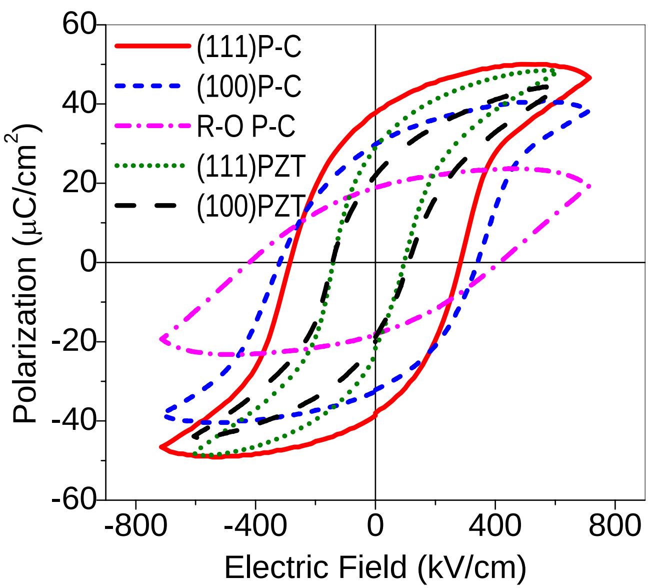


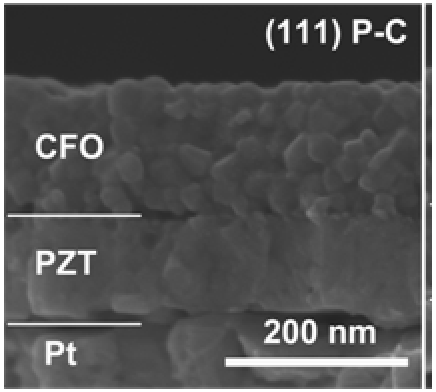


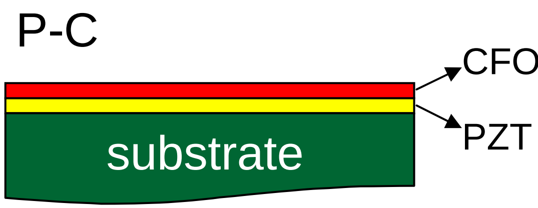


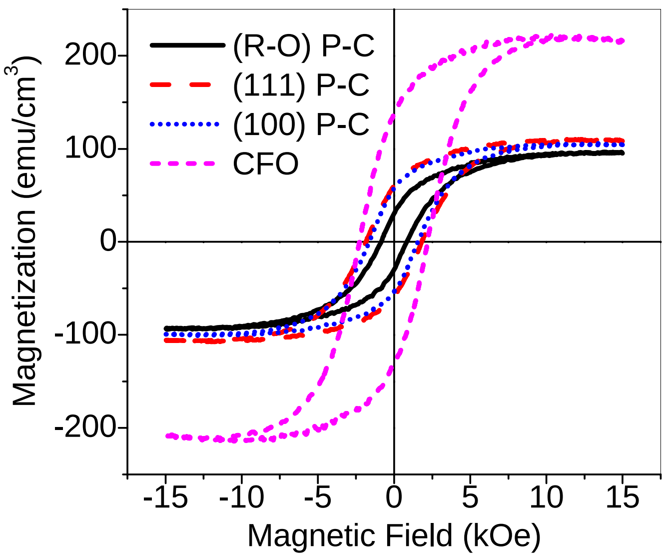
Ma *et al., Appl. Phys. Lett.*, 90, 152911 (2007)

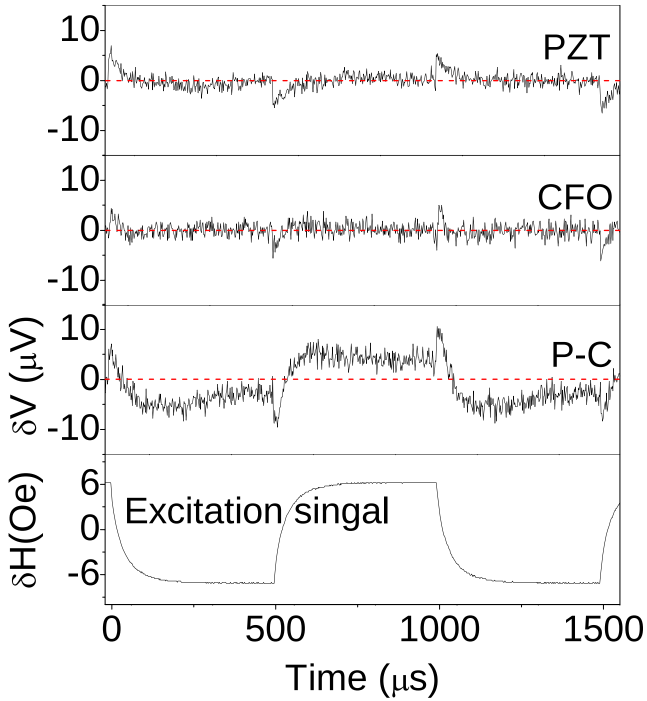
CFO/PZT on Pt/Si by Sol-gel







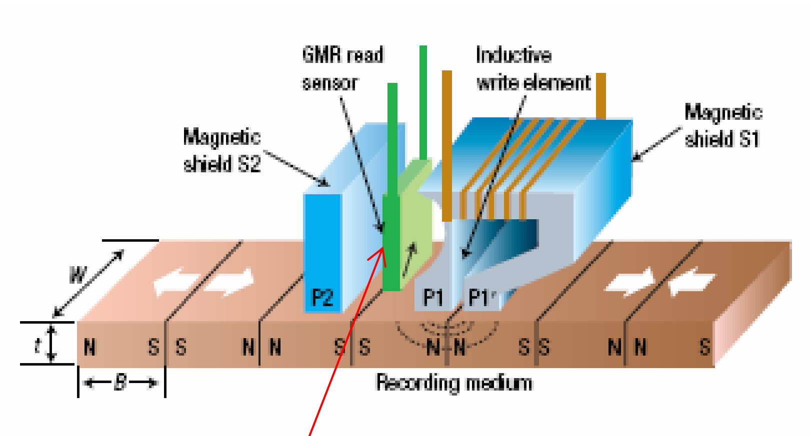




He et al, *J. Appl. Phys.* **103**, 034103 **(2008)**

磁场 调控 电

✓ 微磁场传感器：　读取磁头



MR磁头（有源磁头):

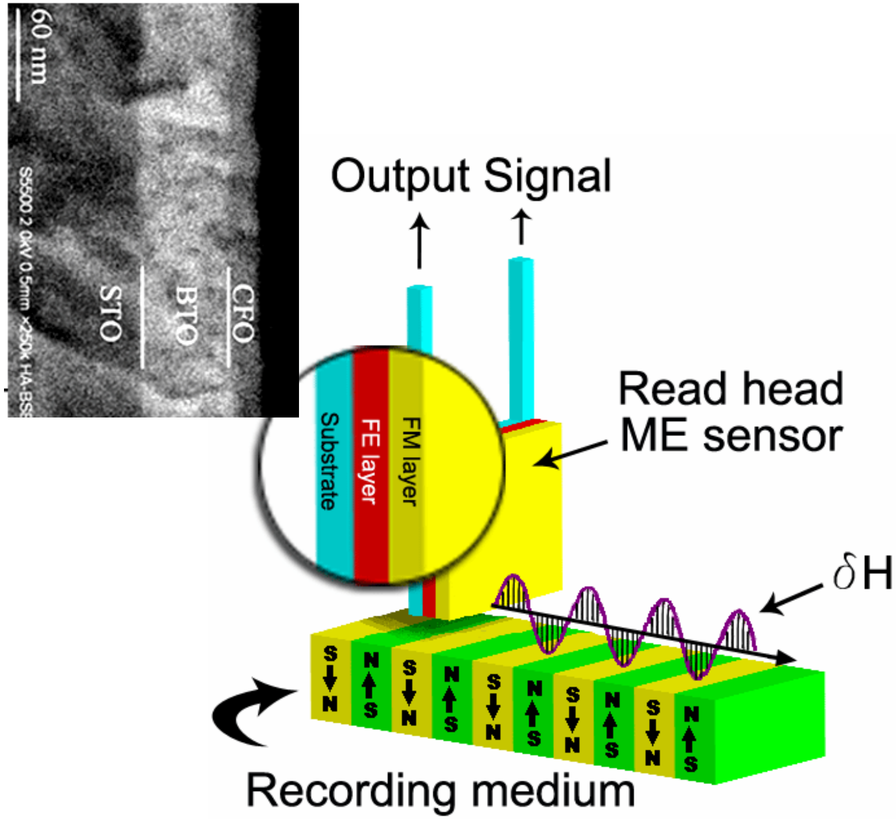
$\Delta V = I\,\Delta R(\delta H)$

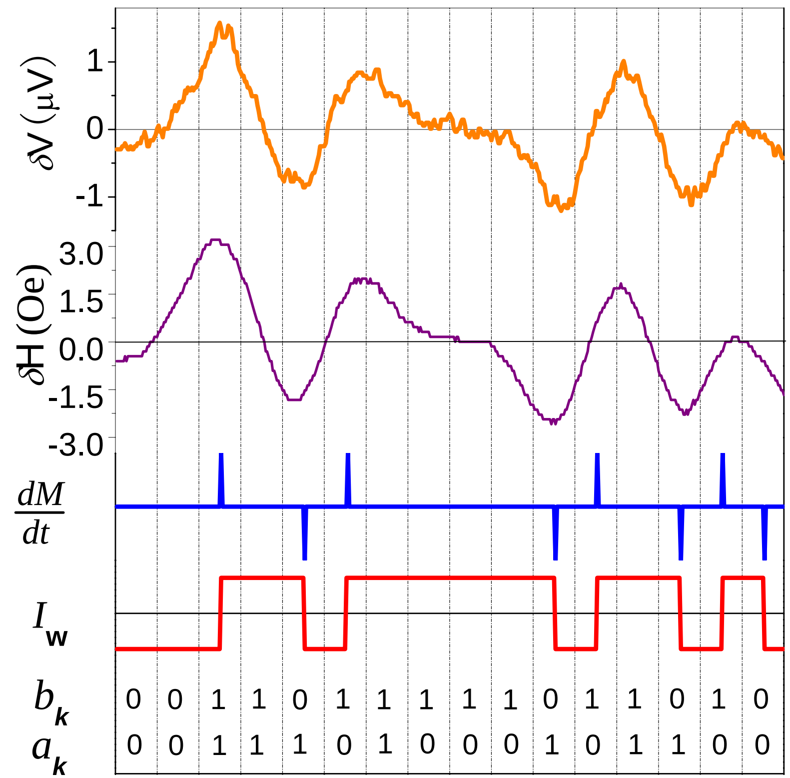
ME磁头（无源磁头):

$\Delta V = \alpha\,\delta H$

新型 ME 磁头

CFO/BTO on STO by PLD



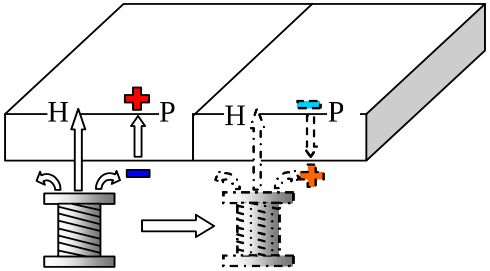


Zhang et al, *Appl. Phys. Lett.* 92, 152510 **(2008).**

电场 调控 磁性

✓自旋电子器件
✓存储器件

"电写磁读"

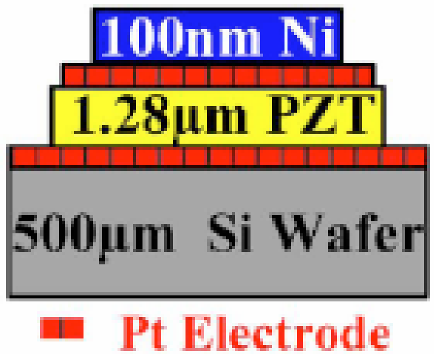


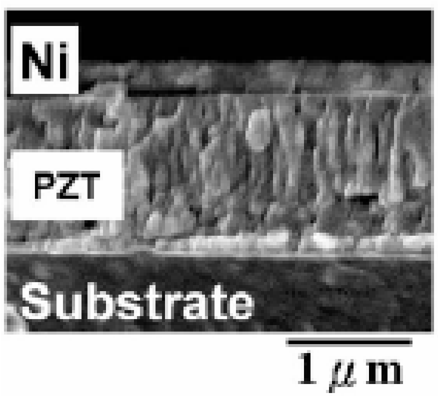
磁电储存器概念

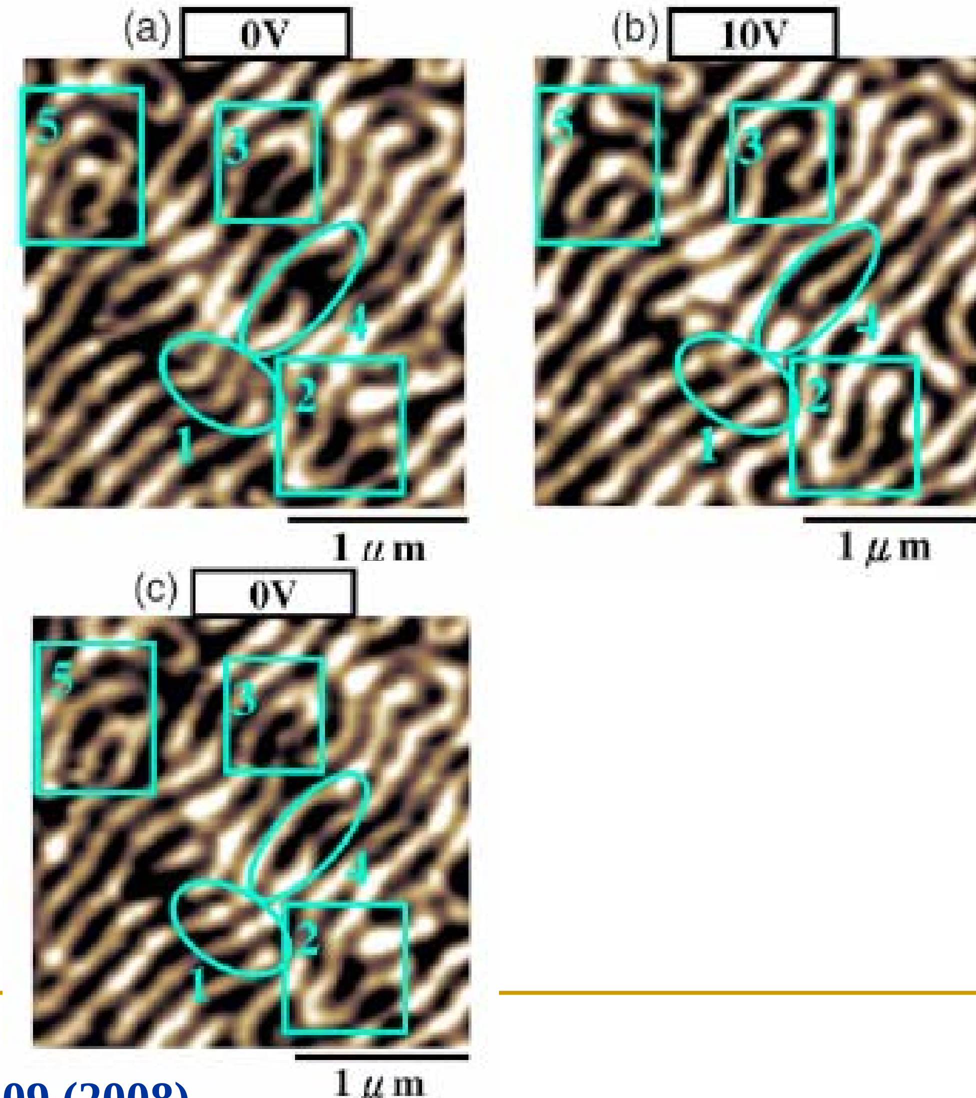
Eerenstein et al., ***Nature* 442,** 759 (2006)

ME effect: 电场 调控 磁性

Strain-Mediated 耦合机制



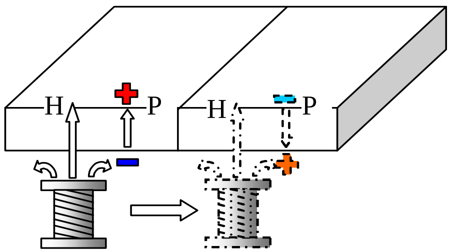




Chung et al., *Appl. Phys. Lett.* 92, 112509 (2008).

ME effect: 电场 调控 磁性

“电写磁读”



磁电储存器概念

Eerenstein et al., ***Nature* 442,** 759 (2006)

室温下，单相化合物 ？

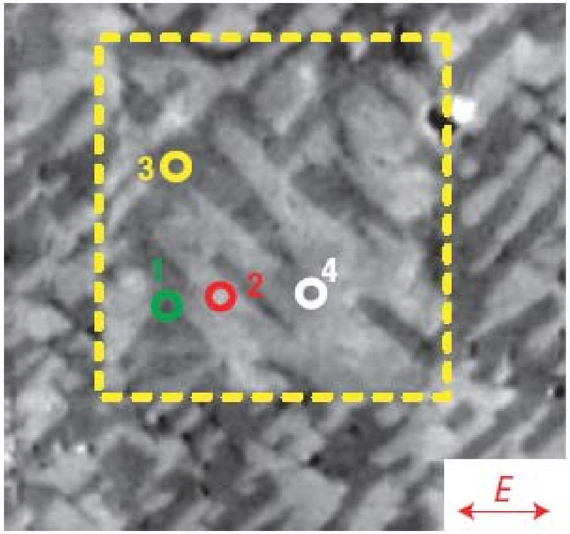
$BiFeO_3$：铁电－反铁磁 (FE-AFM)

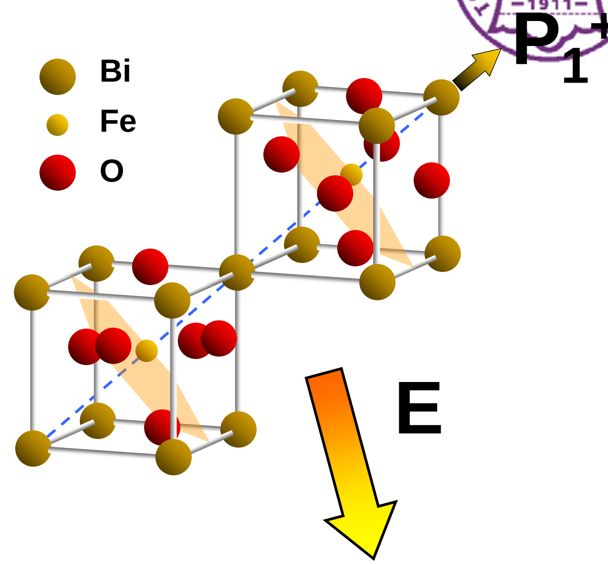
(1) 电场 $\xrightarrow{\text{FE 电畴switching}}$ AFM序变化

(2) AFM $\xrightarrow{\text{磁交换(钉扎)作用}}$ FM

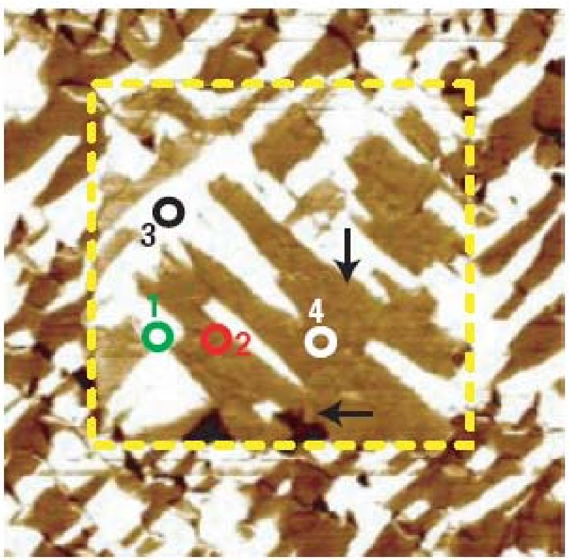
Electric Control of Antiferromagnetism

Photoemission Electron Microscopy

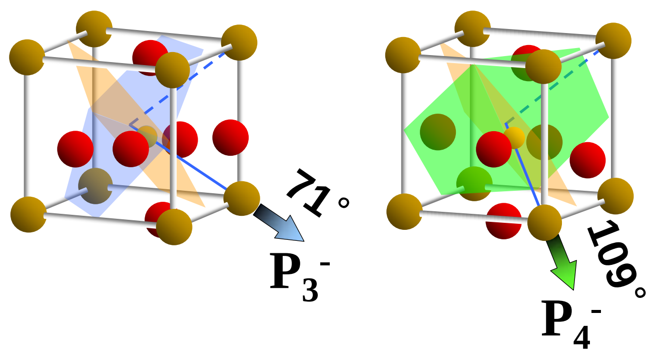




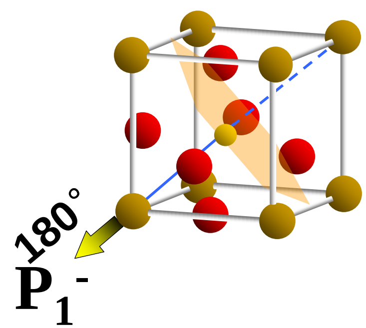
Piezoresponse Force Microscopy



Ferroelastic → Rotation of Magnetization Plane

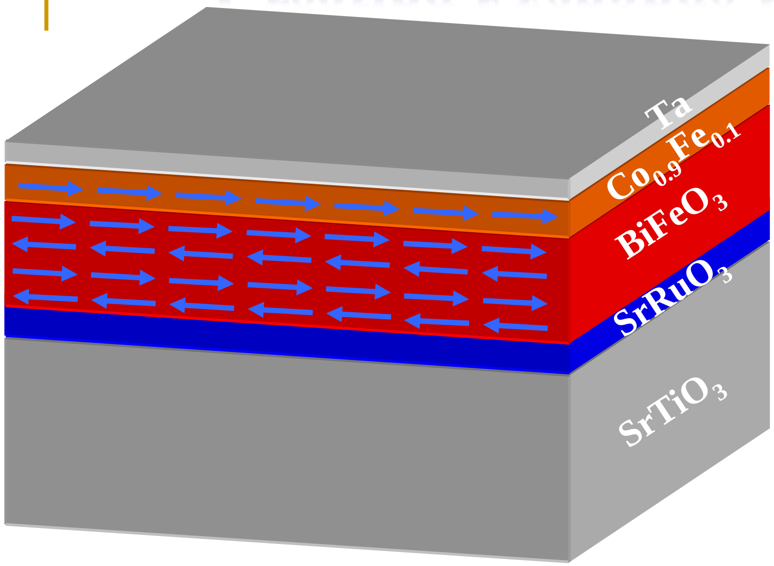


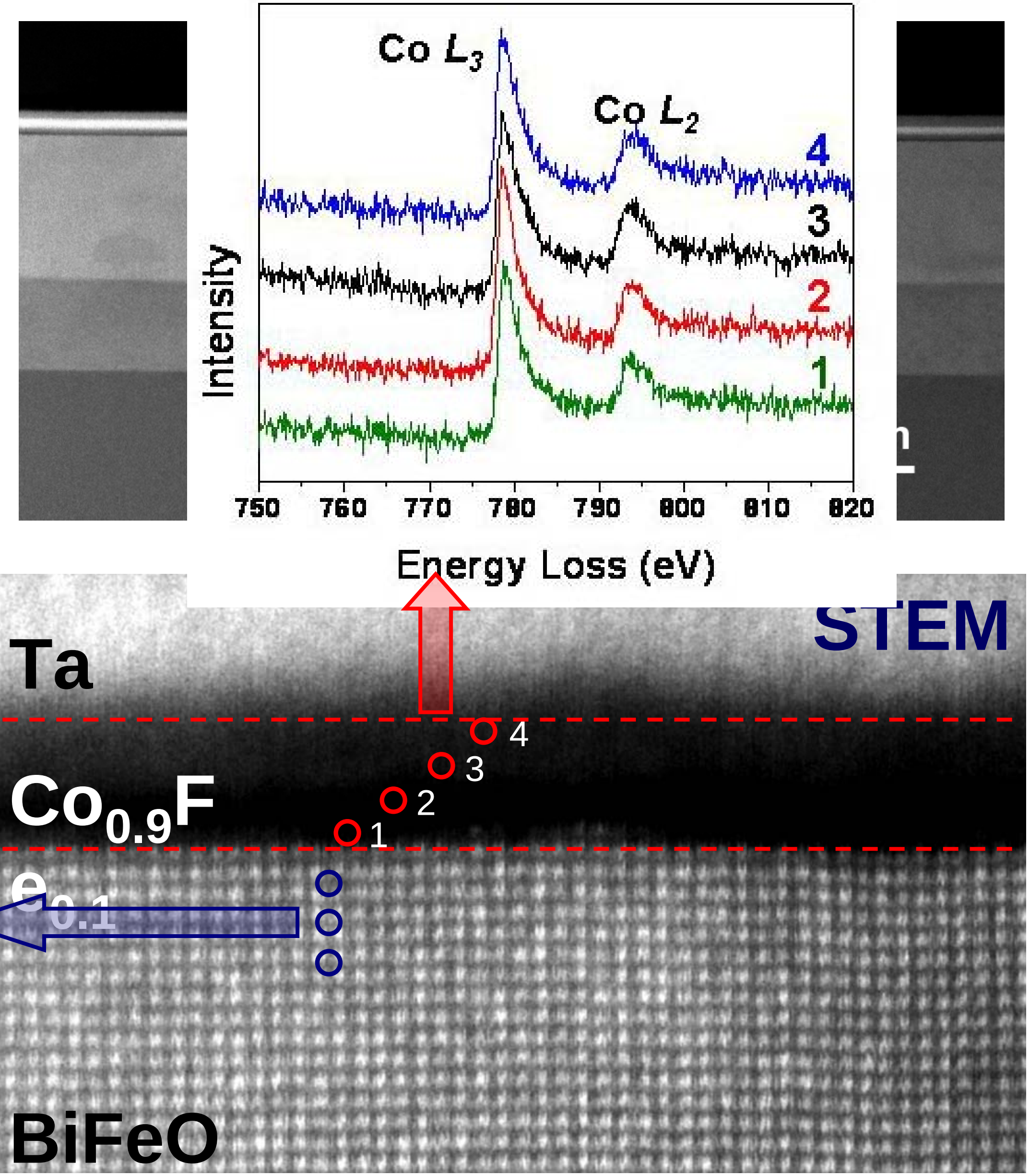
Ferroelectric → No Rotation of Magnetization Plane

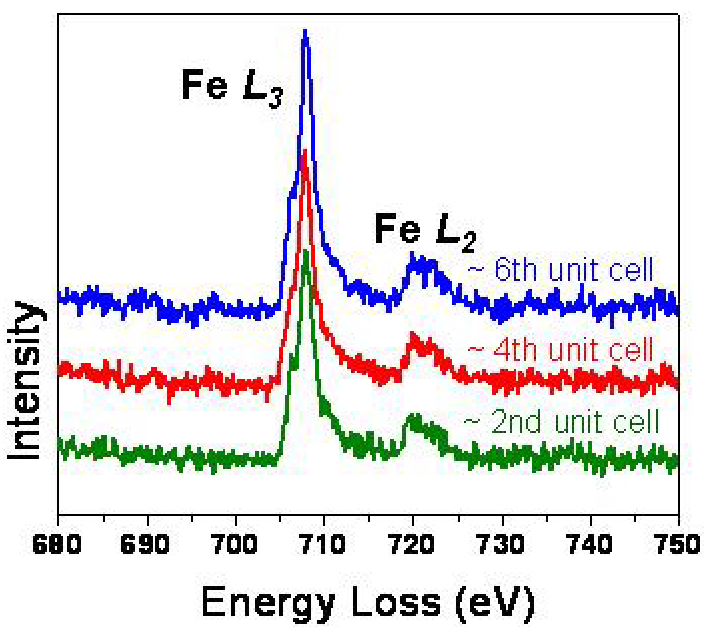


Zhao, *et al.*, *Nature Materials* 5, 823 (2006)

Creating Exchange Heterostructures

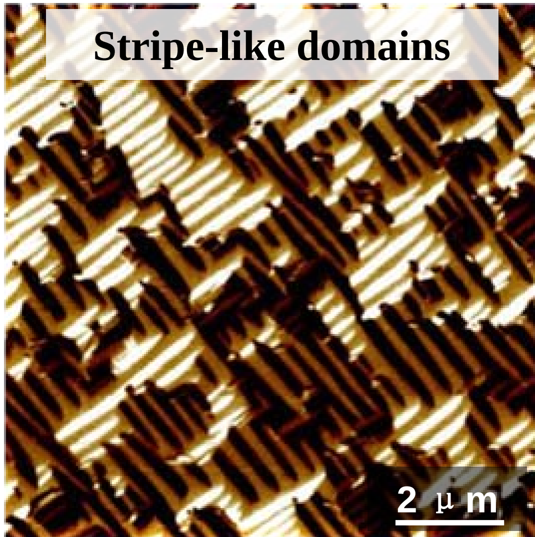




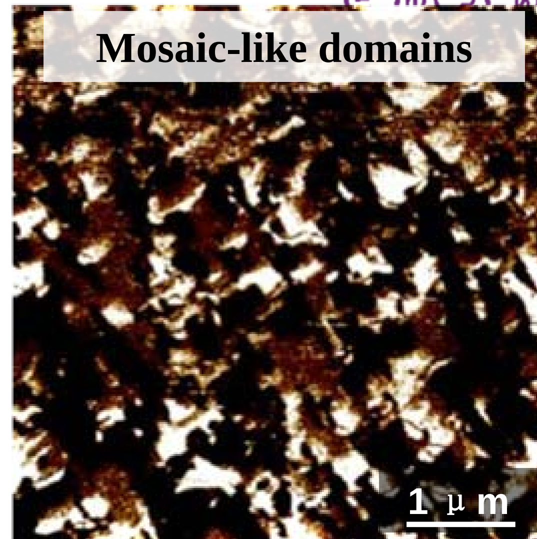


FE Domain Control of Exchange

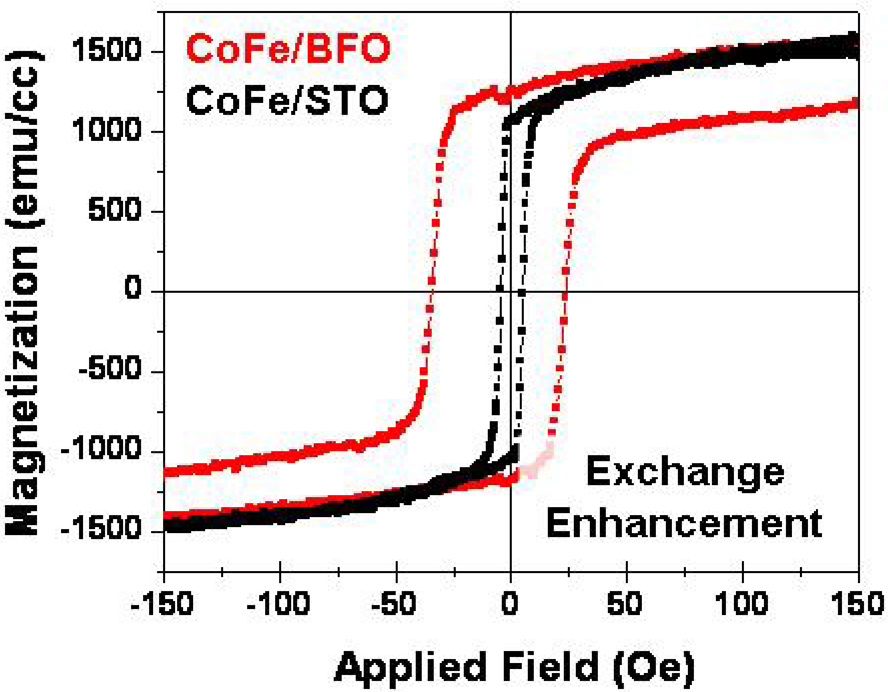
71° Domain Walls on (101) Planes

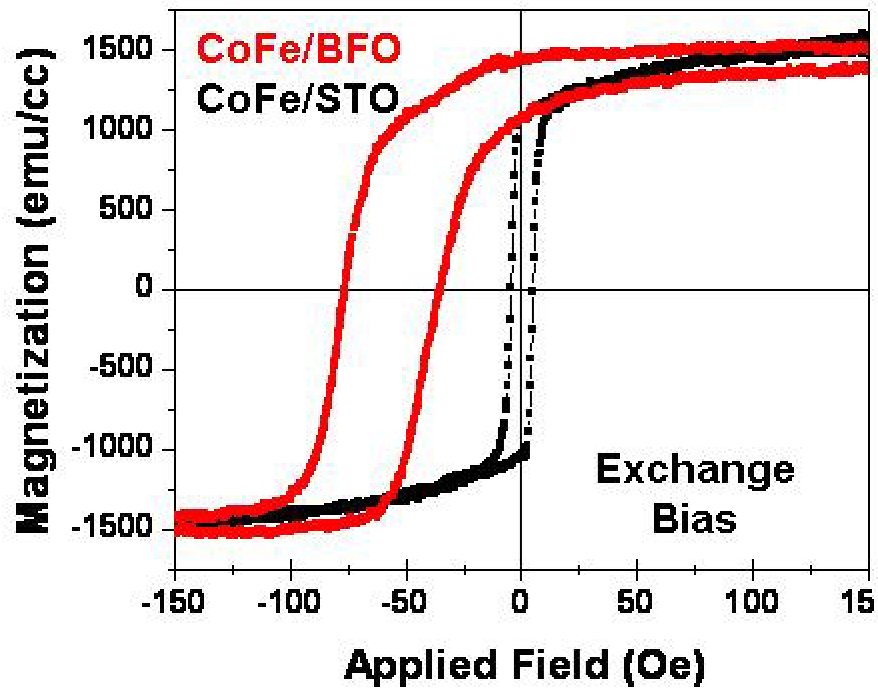


Streiffer, *et al.*, JAP **83**, 2742 (1998)



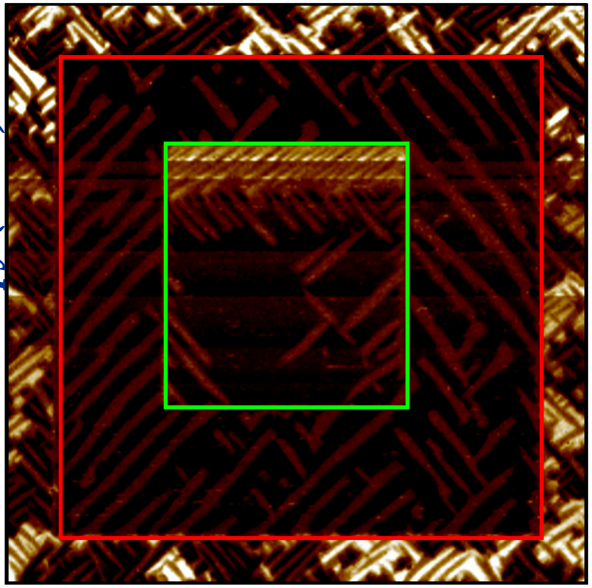
109° Domain Walls on (001) Planes



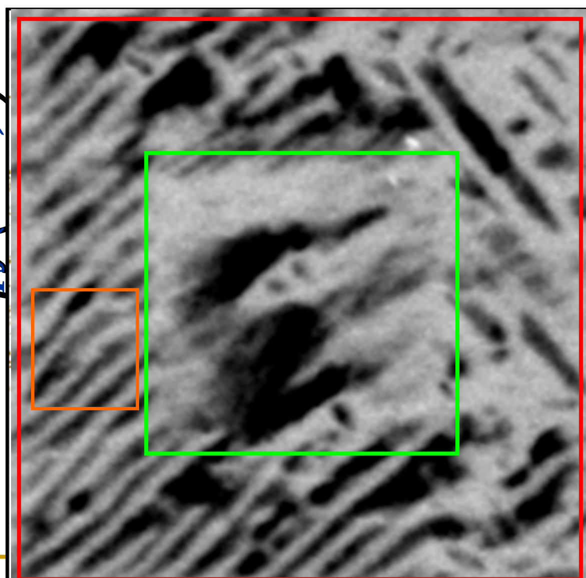


Electrical Control of Magnetism

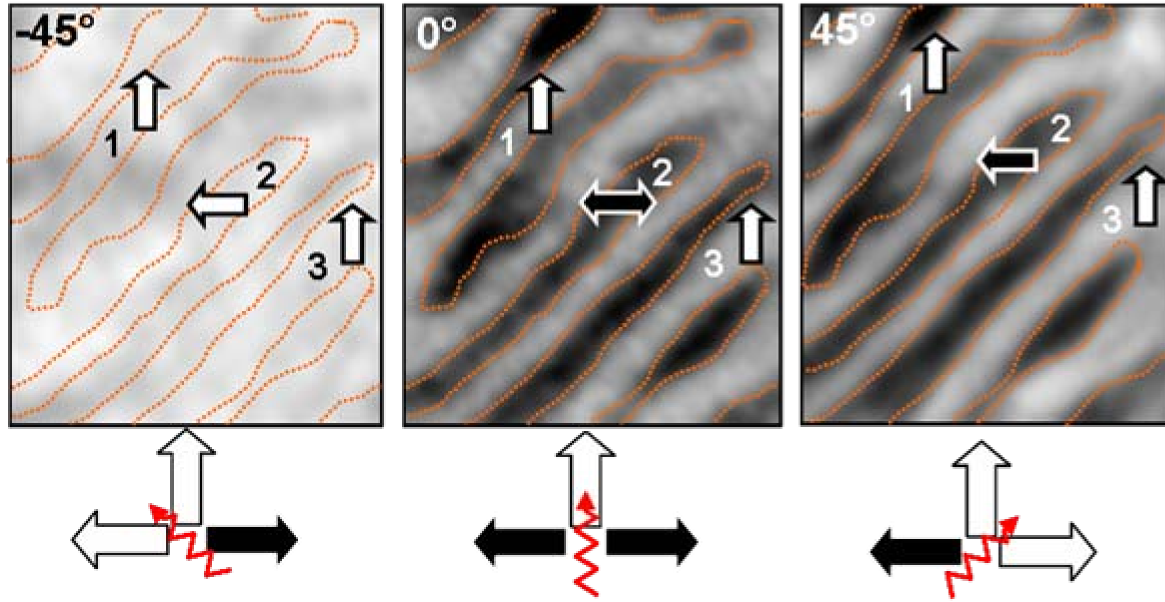
In-plane Piezoforce Microscopy (PFM)



Photoemission Electron Microscopy (PEEM)



(grey: spin up; dark: spin side-to-side)

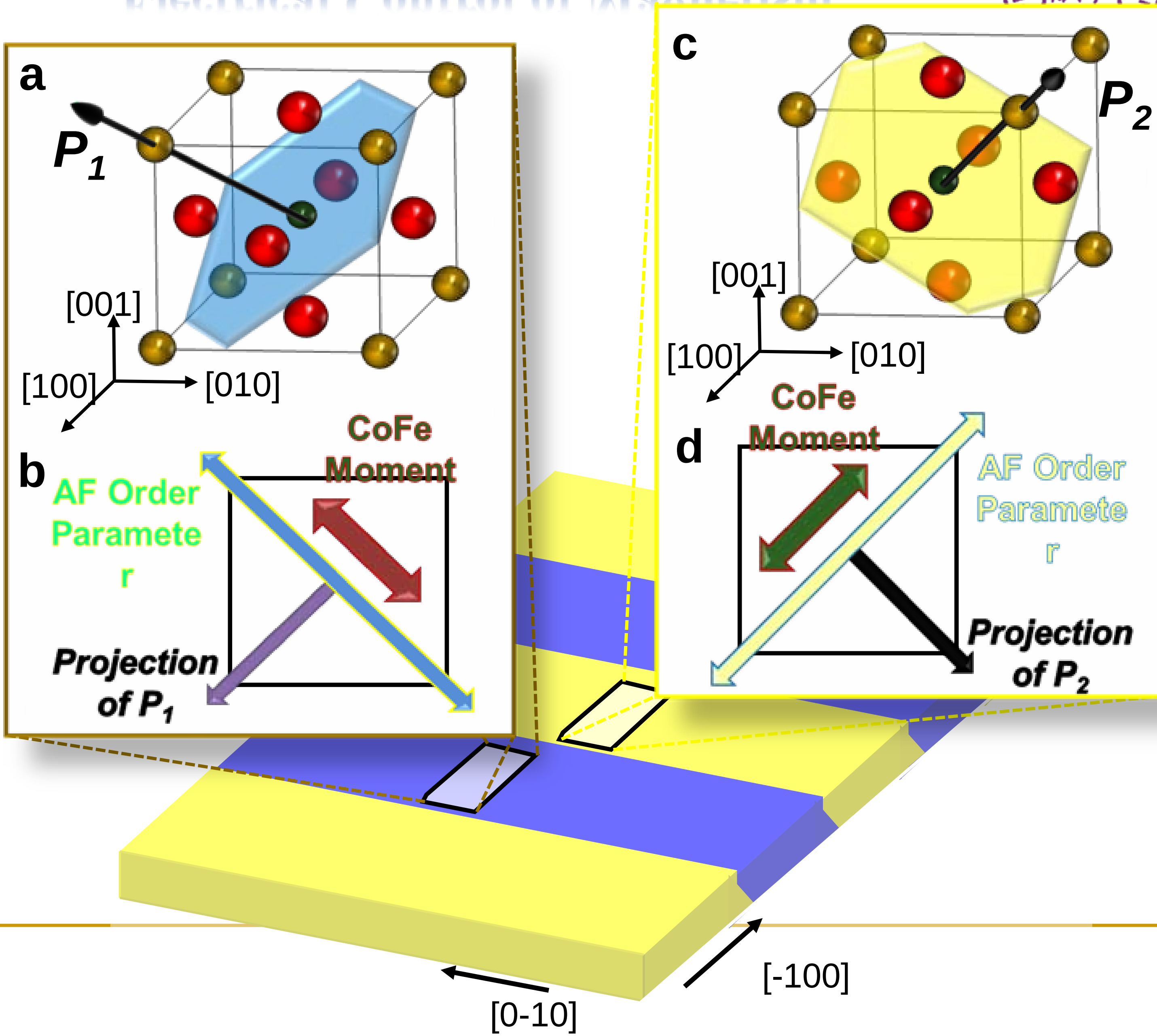


- Rotation of sample reveals true directions of CoFe spin alignment
- 90° Néel Walls
- M_{CoFe} // $\boldsymbol{L}_{BFO}$

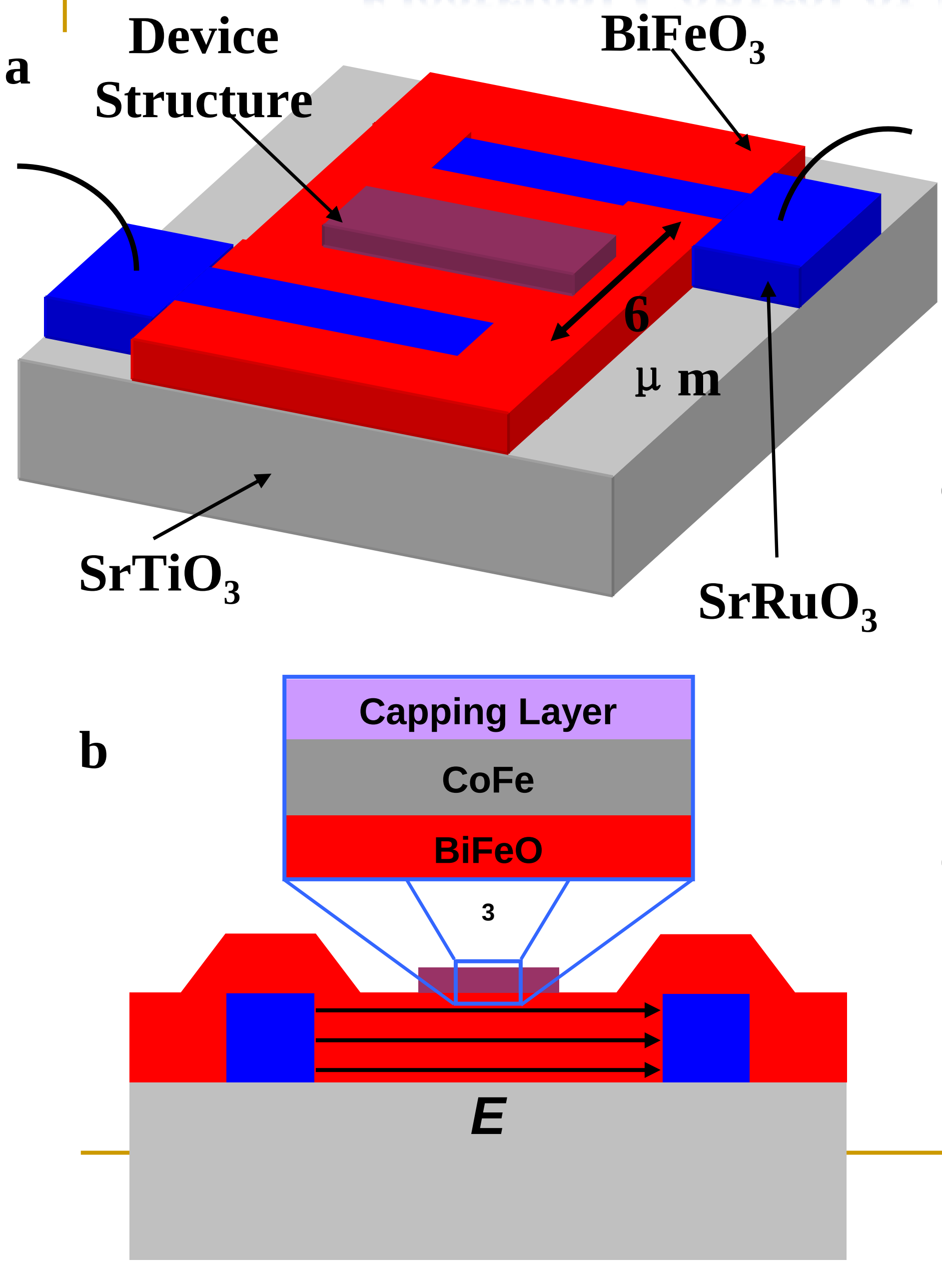
Chu *et al*. *Nature Materials*, 7 (2008).

Electrical Control of Magnetism

清華大學
Tsinghua University



Electrical Control of Magnetism

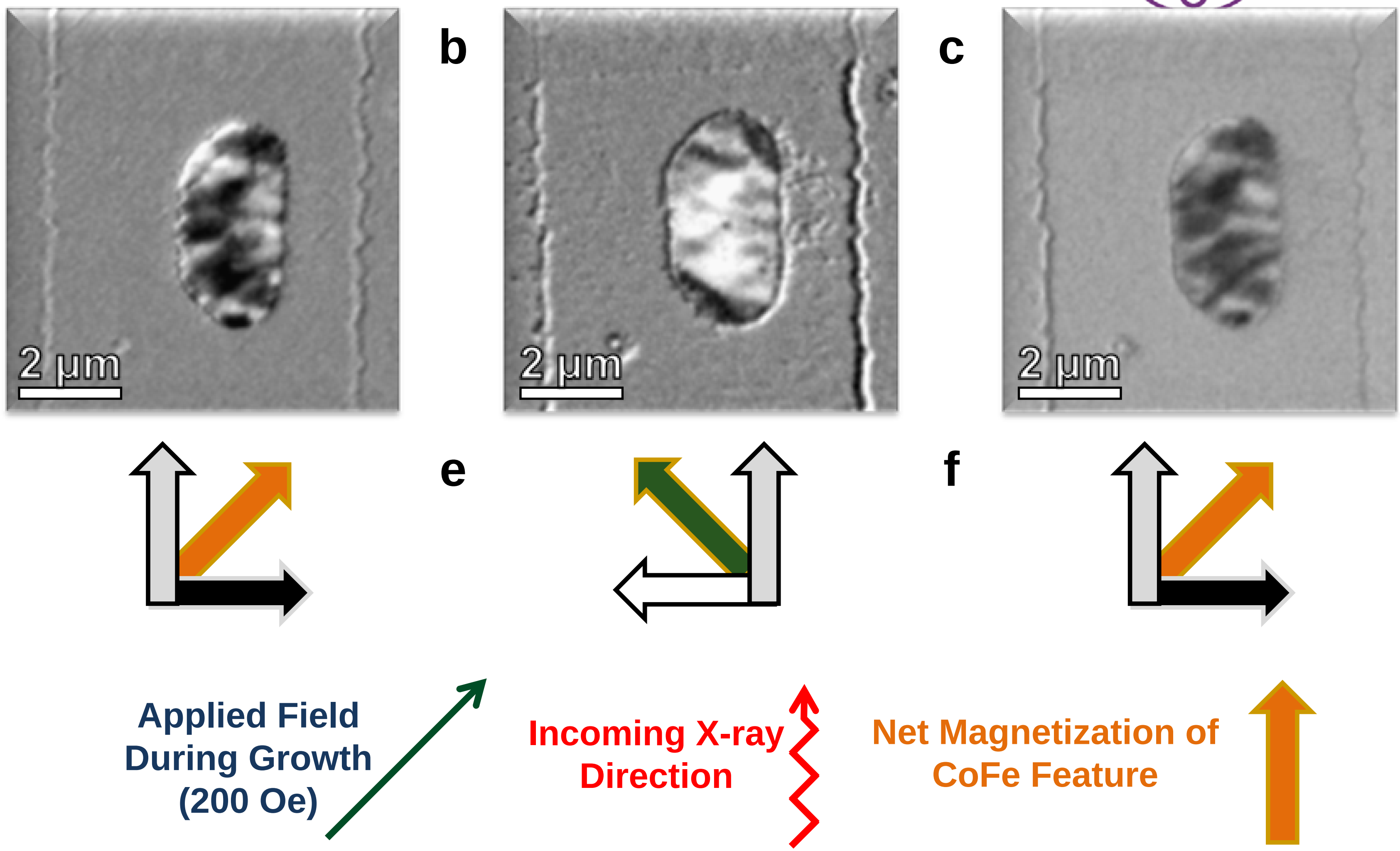


As Grown

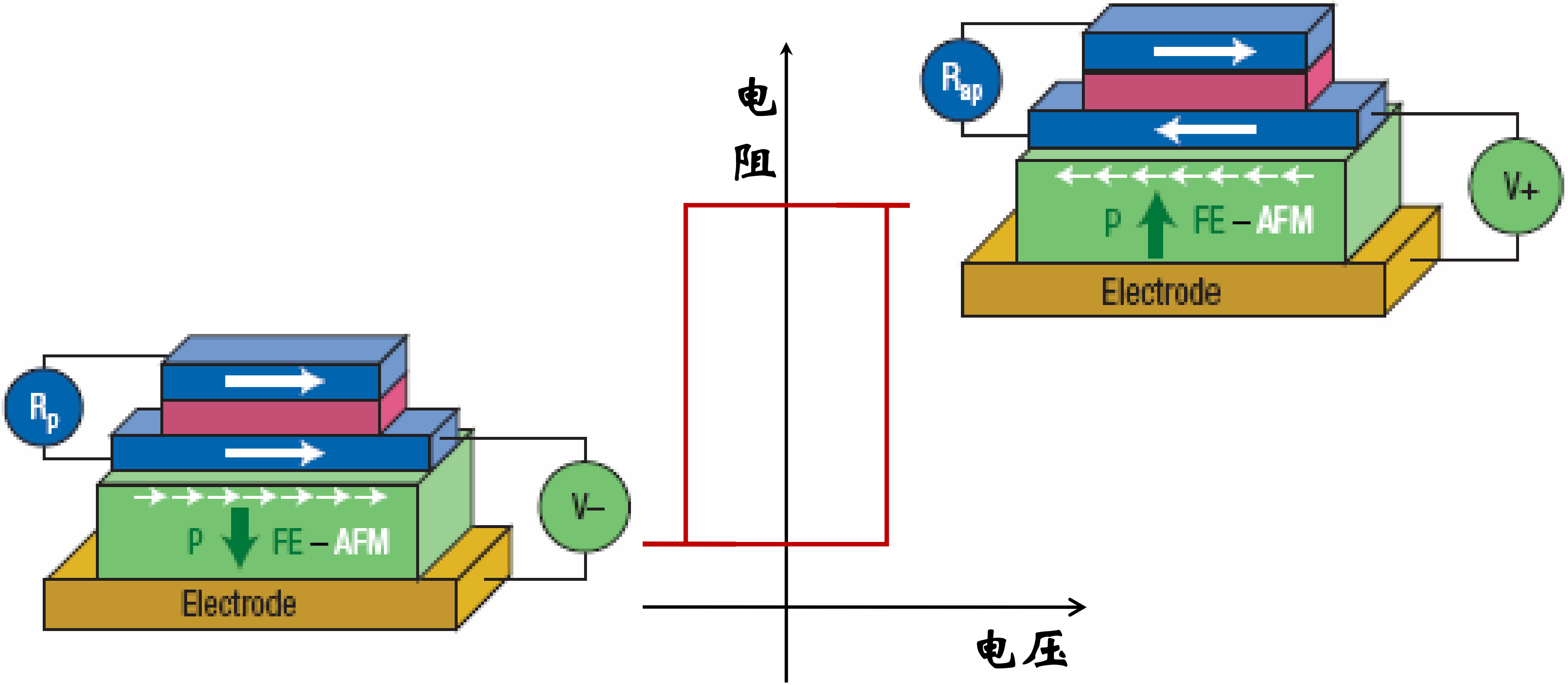
1st Electrical Switch

2nd Electrical Switch

Electrical Control of Magnetism



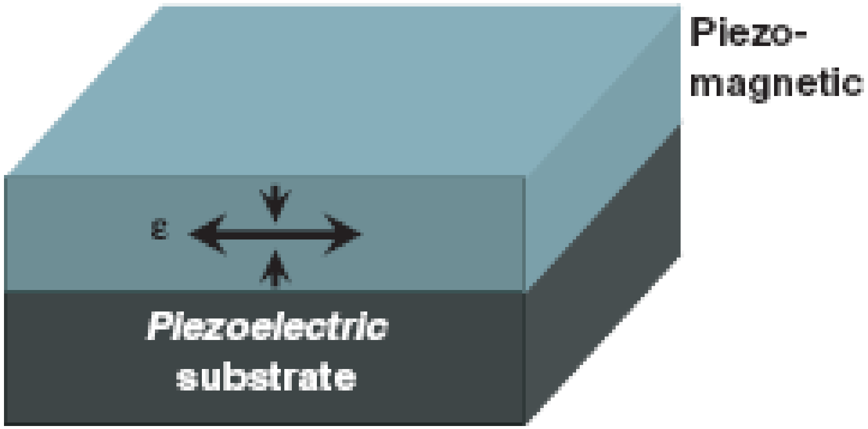
磁电 RAMs



Bibes et al., ***Nature Mater.*** 7, 425 (2008)

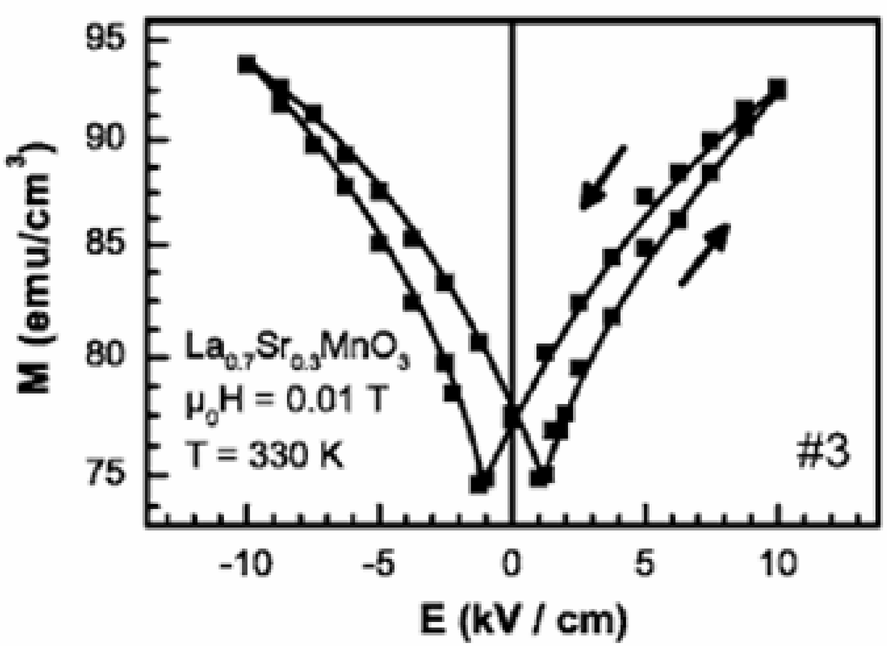
V、单层薄膜复合

电场 调控 磁性



铁磁薄膜/铁电单晶基片

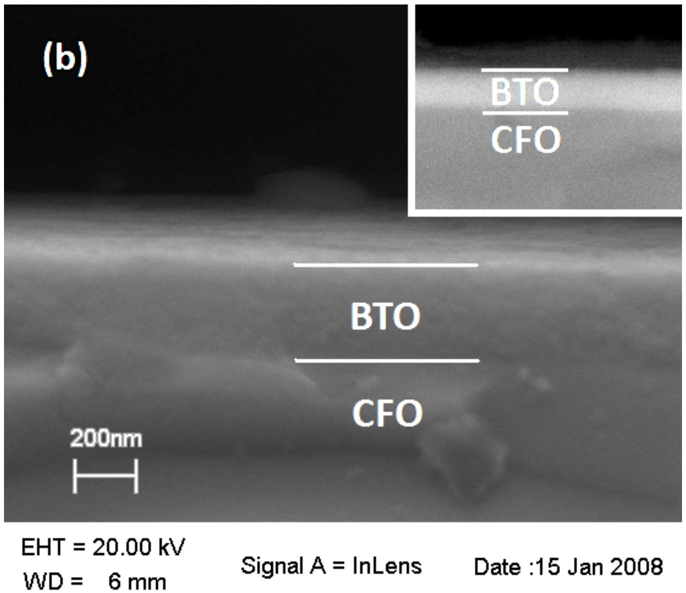
Strain-Mediated 耦合机制

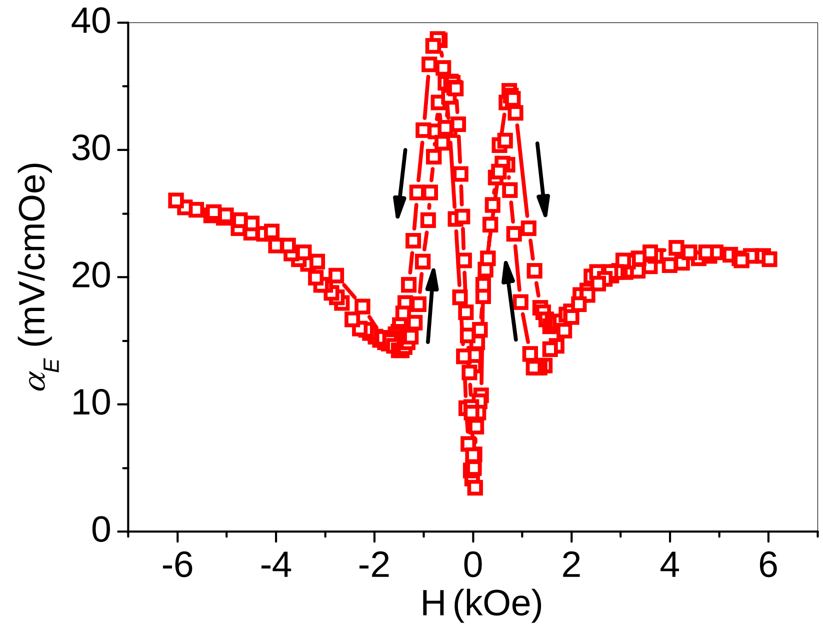


LSMO/PMN 单晶

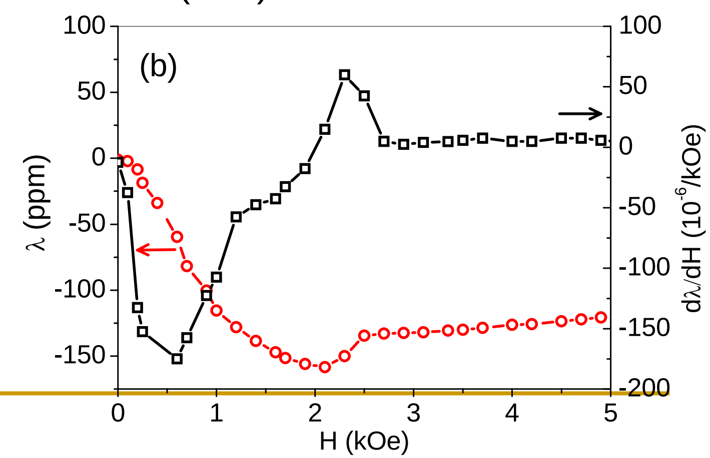
Dorr et al., *Phys. Rev. B*, 75, (2007)

磁场 调控 电性





BTO/CFO 陶瓷



Wang et al., *J. Appl. Phys*. in press (2008)

VI. 结 语

✓ on-chip integration. infant stage

- 器件应用导向的纳米生长控制：
  - (a) 不同结构外延生长控制
  - (b) 周期结构，磁电超晶格
- 概念、理解：
  - (a) 耦合新机制：其他机制？
    耦合动态问题(时间)：磁控电极化、电控磁性
  - (b) 纳米结构对磁电耦合的影响
  - (c) 尺寸效应
  - (d) 原子尺度界面耦合