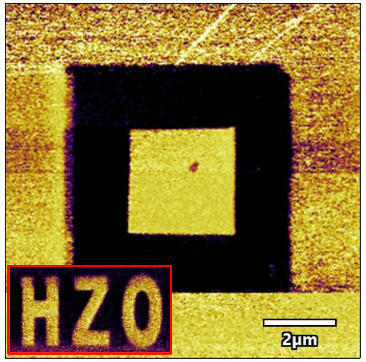
"la Caixa" Foundation

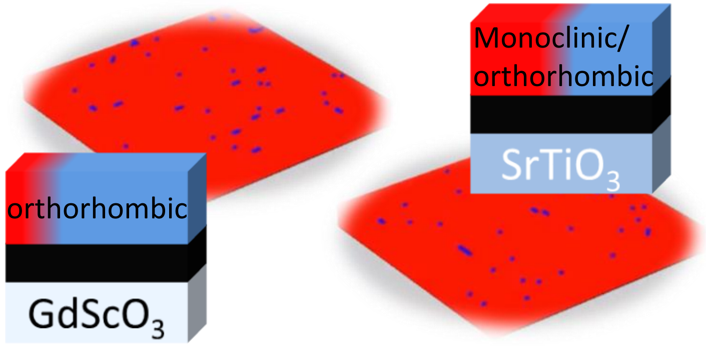
GOBIERNO DE ESPAÑA
MINISTERIO DE CIENCIA, INNOVACIÓN Y UNIVERSIDADES

Investigación
Programa
Ramón y Cajal

ICMAB
INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA
EXCELENCIA SEVERO OCHOA
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS



Worse might be better in ferroelectric HfO_2



T. Song, H. Tan,
F. Sánchez, Ignasi Fina
ignasifinamartinez@gmail.com
ifina@icmab.es
Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Barcelona, Spain

ICMAB
INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA
EXCELENCIA SEVERO OCHOA
CSIC
FOXEM

TWEET 2023, June 5th

@ICMAB

FOXEM Ferroelectric oxide films for energy and memory devices

SCOPE

Ferroelectric oxide films for energy and memory devices group (FOXEM) aims to develop high quality new ferroelectric materials compatible with industry to study their properties from a fundamental to a device level. Electronics Industry is facing several bottlenecks to sustain the increasing demand and necessity of new data storage, computation and communication devices. New materials are needed and CMOS-compatible ferroelectrics based in HfO2 are in the spotlight. We investigate epitaxial oxide thin films of these oxides as model systems to understand and improve the ferroelectric properties. Our activities involve growth, structural studies, advanced characterization of electrical properties and prototyping of conventional and emerging memory devices.

SELECTED WORKS

Ferroelectric (Hf,Zr,La)O_2 films

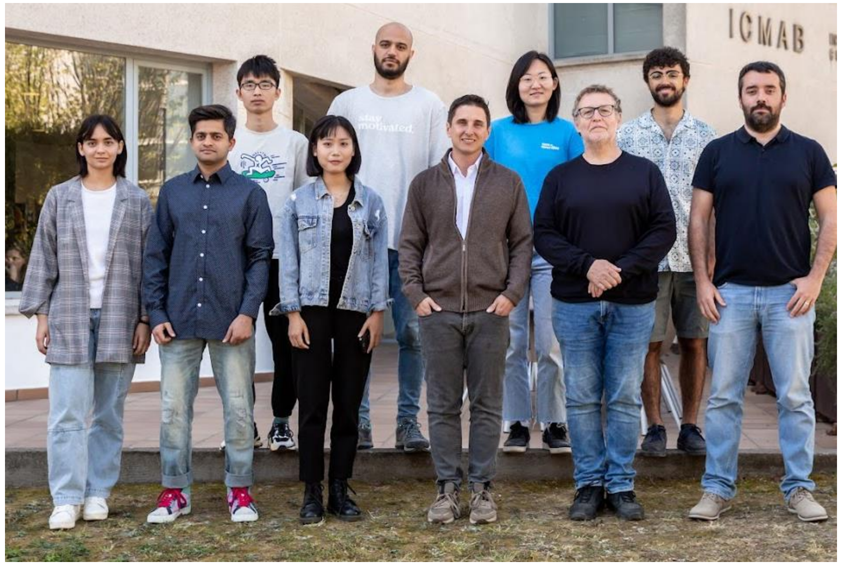
T. Song, S. Estandía, I. Fina, and F. Sánchez, Ferroelectric (Hf,Zr,La)O2 films. Applied Materials Today 29 (2022). https://doi.org/10.1016/j.apmt.2022.101661

Epitaxial Ferroelectric HfO_2 Films: Growth, Properties, and Devices

I. Fina and F. Sánchez, Epitaxial Ferroelectric HfO2 Films: Growth, Properties, and Devices. ACS Appl. Electron. Mater. 3, 1530 (2021). https://doi.org/10.1021/acsaelm.1c00110

Control of up-to-down/down-to-up light-induced ferroelectric polarization reversal

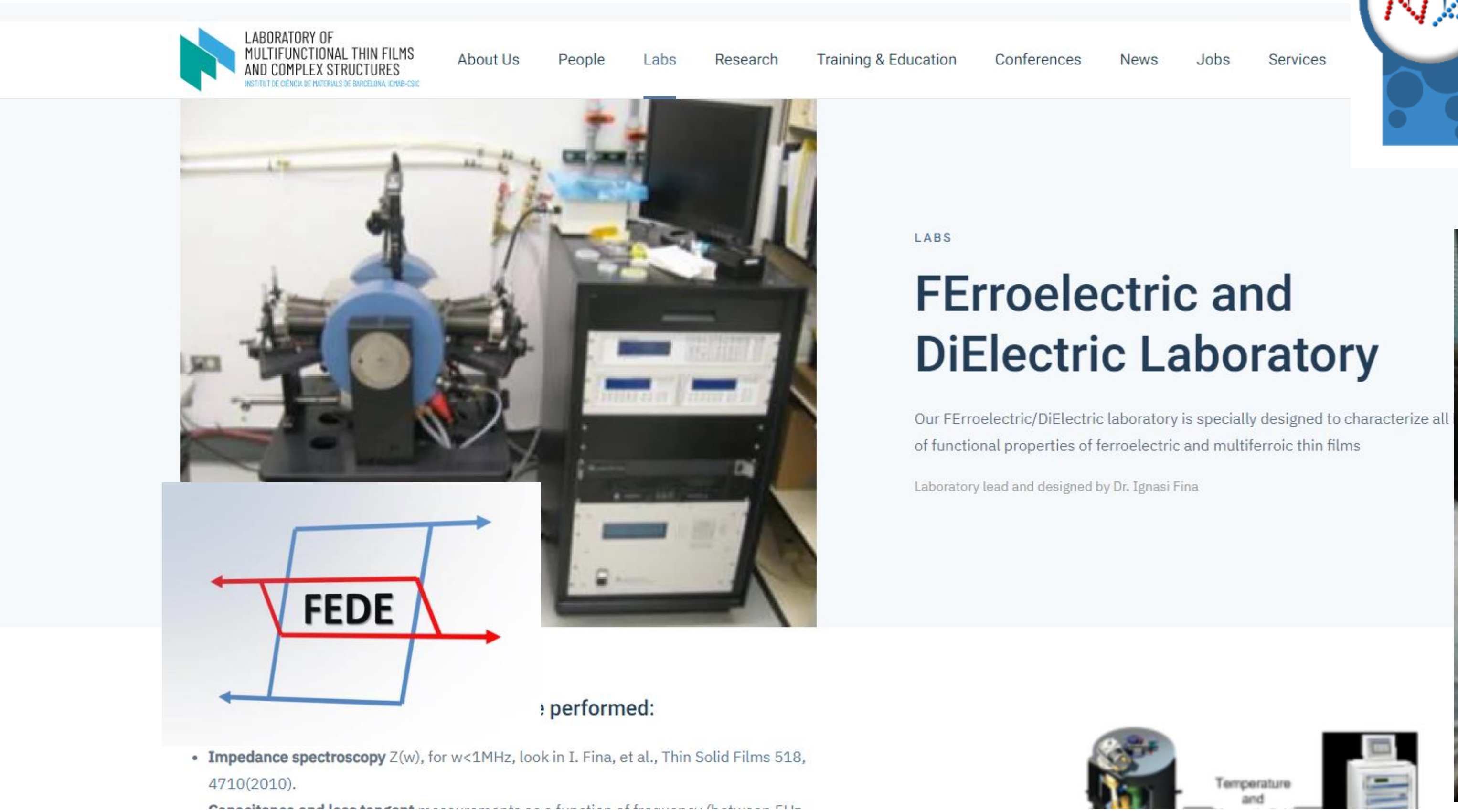
H. Tan, G. Castro, J. Lyu, P. Loza-Alvarez, F. Sánchez, J. Fontcuberta, and I. Fina, Control of up-to-down/down-to-up light-induced ferroelectric polarization reversal. Materials Horizons 9, 2345 (2022). https://doi.org/10.1039/d2mh00644h



https://foxem.icmab.es/

Ferroelectric and dielectric laboratory

nanoscience foundries & fine analysis
nffa.europe



LABORATORY OF MULTIFUNCTIONAL THIN FILMS AND COMPLEX STRUCTURES
INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA ICMAB-CSIC

About Us | People | Labs | Research | Training & Education | Conferences | News | Jobs | Services

LABS

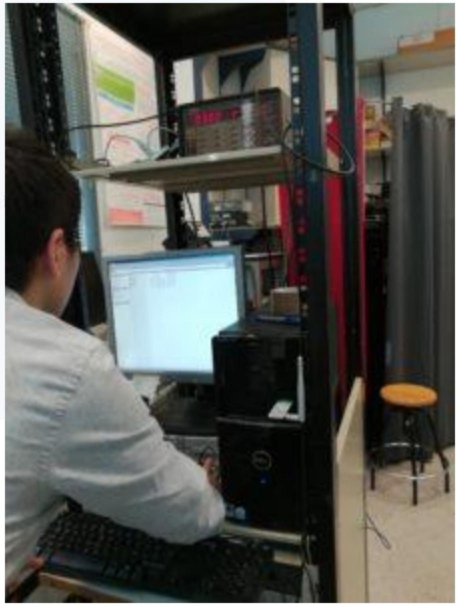
FErroelectric and DiElectric Laboratory

Our FErroelectric/DiElectric laboratory is specially designed to characterize all of functional properties of ferroelectric and multiferroic thin films

Laboratory lead and designed by Dr. Ignasi Fina

e performed:

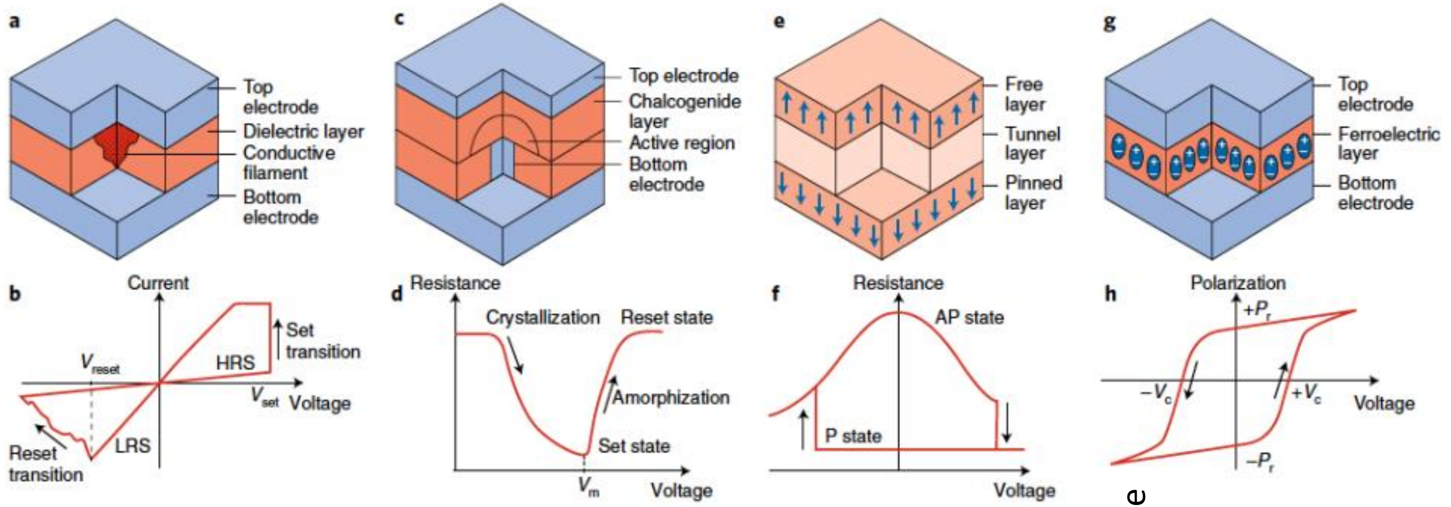
- **Impedance spectroscopy** Z(w), for w<1MHz, look in I. Fina, et al., Thin Solid Films 518, 4710(2010).



Introduction: Present and future for memristors

Current status

RRAM PCM STT-MRAM FeJ,FeFET

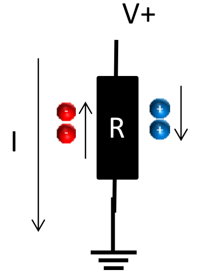


Current ↑ Current ↑ Current ↑ Displacive Current ↑

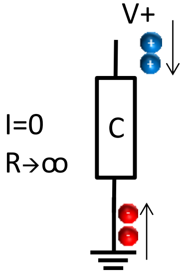
J. J. Yang *et al*, *Nat. Nanotechnol.* 2008.
R. Waser *et al*, *Adv. Mater.* 2009.
D. Ielmini *et al*, *Phase Transitions* 2011.
D. Ielmini et al., Nature Electronics

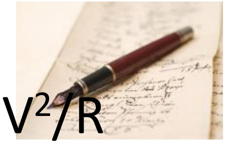
AnChen
IBM Research, San Jose, CA 95120, USA

Future?



V=IR
P=IV=V²/R=I2R



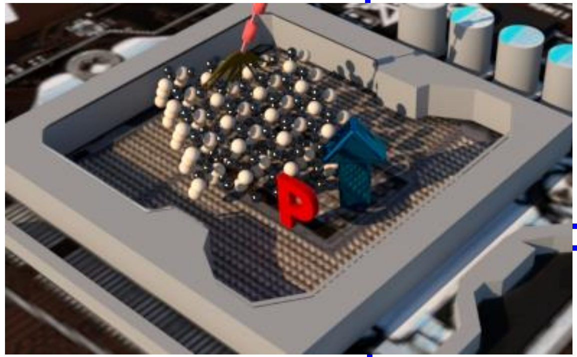


P=IV=V²/R
P=0

Ferroelectric means pure electronic effects

- Efficient
- Fast
- Reliable

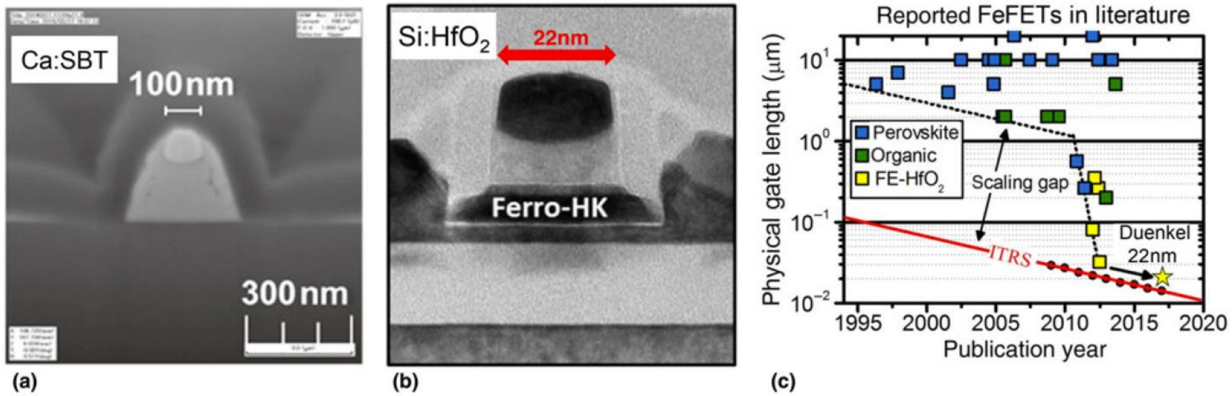
Introduction: Ferroelectric hafnium oxide



Ferroelectric FETs

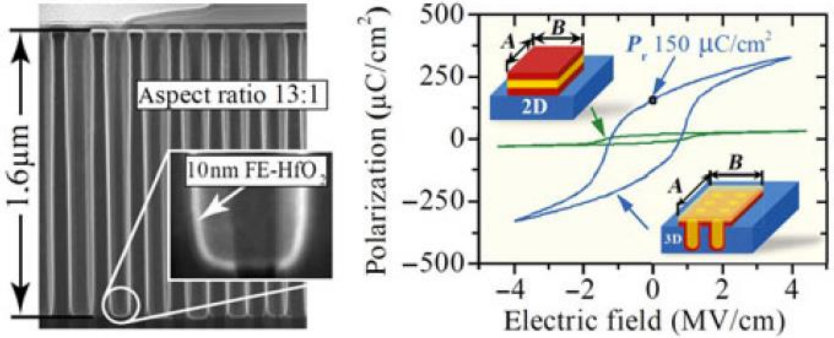
Perovskite

Doped HfO$_2$



REVIEW: Park et al., MRS Comm. **8**, 795 (2018)

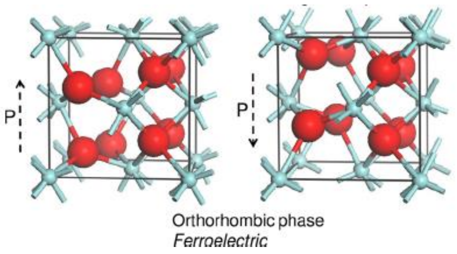
3D capacitors, t = 10 nm

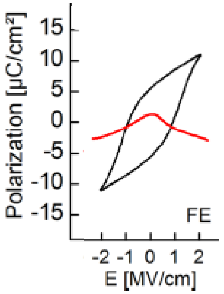


REVIEW: Park et al., MRS Comm. **8**, 795 (2018)

Introduction: ferroelectricity in hafnium oxide

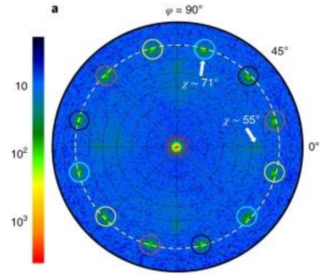
Polycrystalline doped HfO_2

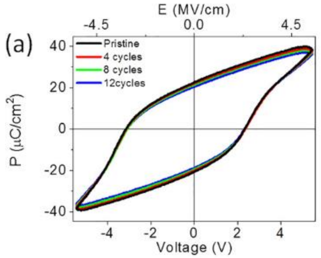




Orthorhombic phase **is** Ferroelectric

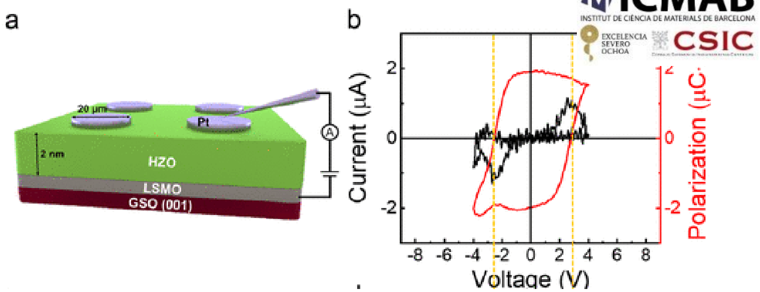
Epitaxial $Hf_{0.5}Zr_{0.5}O_2$

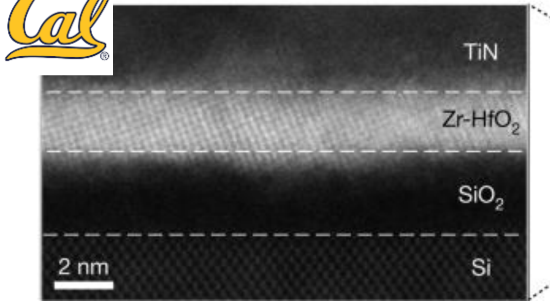


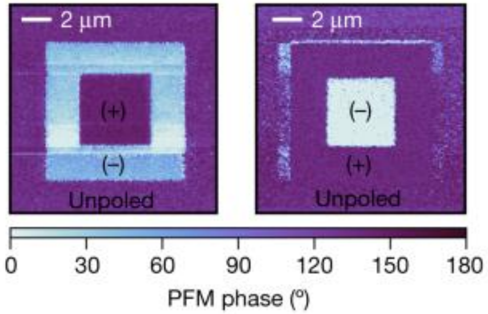


Y. Wei., ... B. Noheda. *Nature Materials* **17**, 1095–1100 (2018).
J.Lyu. **IF**, ..., F. Sánchez, Appl. Phys. Lett. 113, 082902 (2018);
ACS Applied Electronic Materials **1**, 220 (2019); Appl. Phys. Lett. In-print (2019).
Katayama, .., Funakubo APL **109**, 112901 (2016); Shimizu et al., Sci. Rep. **6**, 32931 (2016)

Ferroelectric response in epitaxial ultrathin films

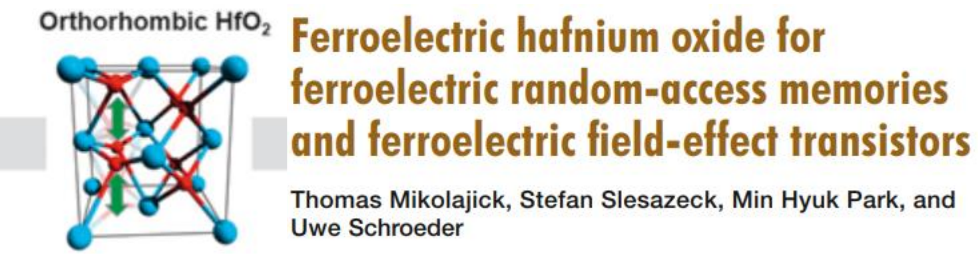






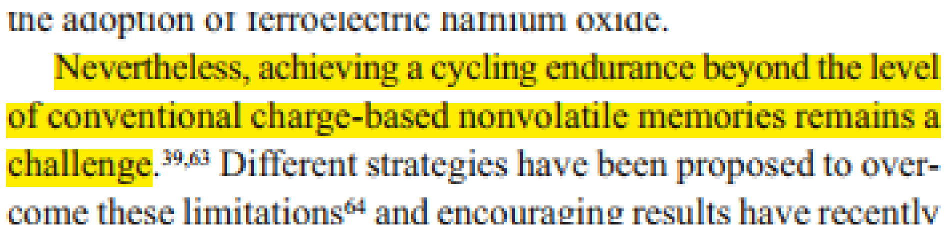
S. S. Cheema, et al., Nature 580, 478 (2020); Nature 604, 7904 (2022)
M.C. Sulzbach, IF, et al., ACS Applied Electronic Materials 3 (8), 3657-3666 (2021

Introduction: Ferroelectric hafnium oxide



Ferroelectric hafnium oxide for ferroelectric random-access memories and ferroelectric field-effect transistors

Thomas Mikolajick, Stefan Slesazeck, Min Hyuk Park, and Uwe Schroeder



the adoption of ferroelectric hafnium oxide.

Nevertheless, achieving a cycling endurance beyond the level of conventional charge-based nonvolatile memories remains a challenge.[39,63] Different strategies have been proposed to overcome these limitations[64] and encouraging results have recently

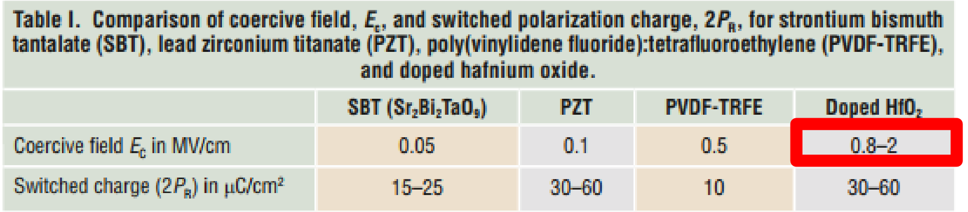
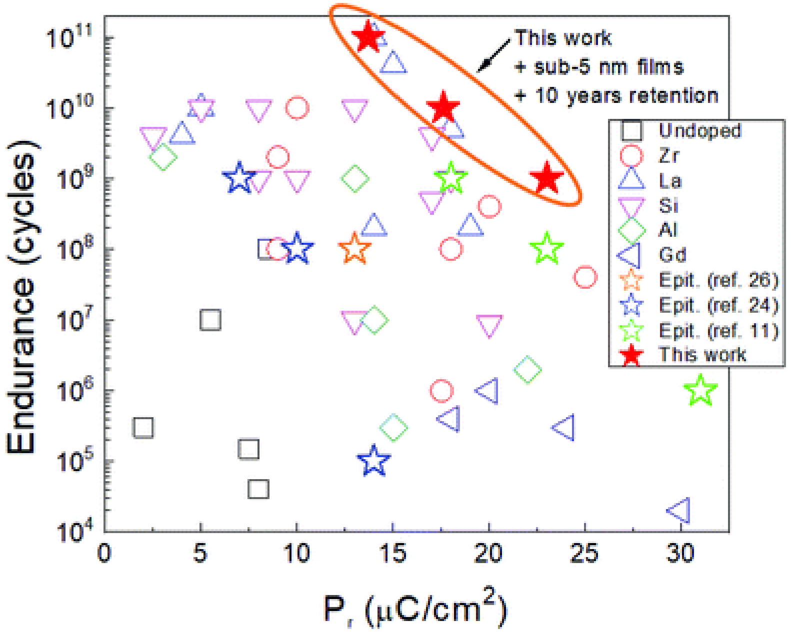


Table I. Comparison of coercive field, E_c, and switched polarization charge, $2P_R$, for strontium bismuth tantalate (SBT), lead zirconium titanate (PZT), poly(vinylidene fluoride):tetrafluoroethylene (PVDF-TRFE), and doped hafnium oxide.

	SBT ($Sr_2Bi_2TaO_9$)	PZT	PVDF-TRFE	Doped HfO_2
Coercive field E_c in MV/cm	0.05	0.1	0.5	0.8–2
Switched charge ($2P_R$) in µC/cm²	15–25	30–60	10	30–60

T. Mikolajick, et al. MRS Bull. 43, 340 (2018)

Polarization-endurance dilemma

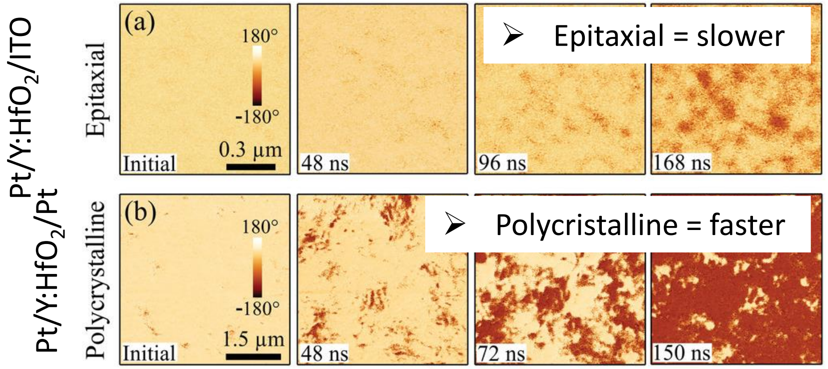


- Best endurance is NOT shown by films showing larger P_r

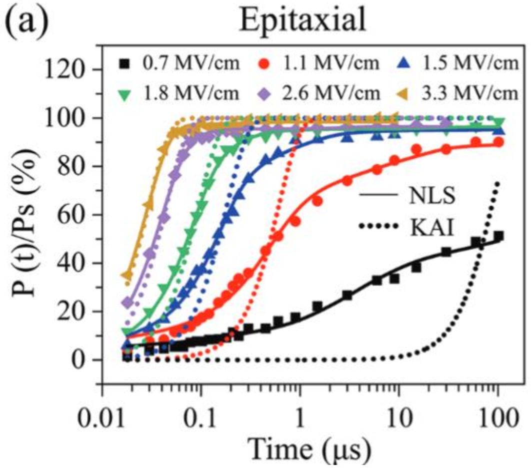
J. Lyu, …, IF, Sánchez, Nanoscale 12, 11280 (2020)

Introduction: switching dynamics in polycristalline film

Nucleation-limited switching model (NLS)

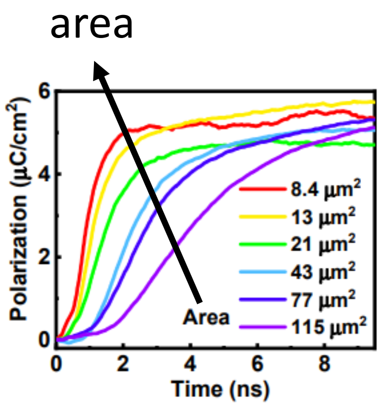


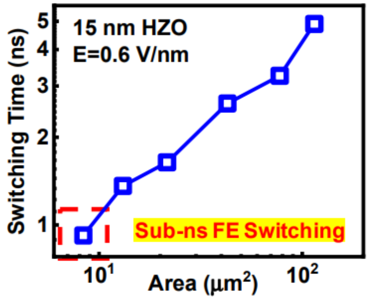
- ➢ Epitaxial = slower
- ➢ Polycristalline = faster



- ➢ As expected for a polycristalline film
- ➢ KAI model is not valid.

Subnanosecond switching speed (at least)

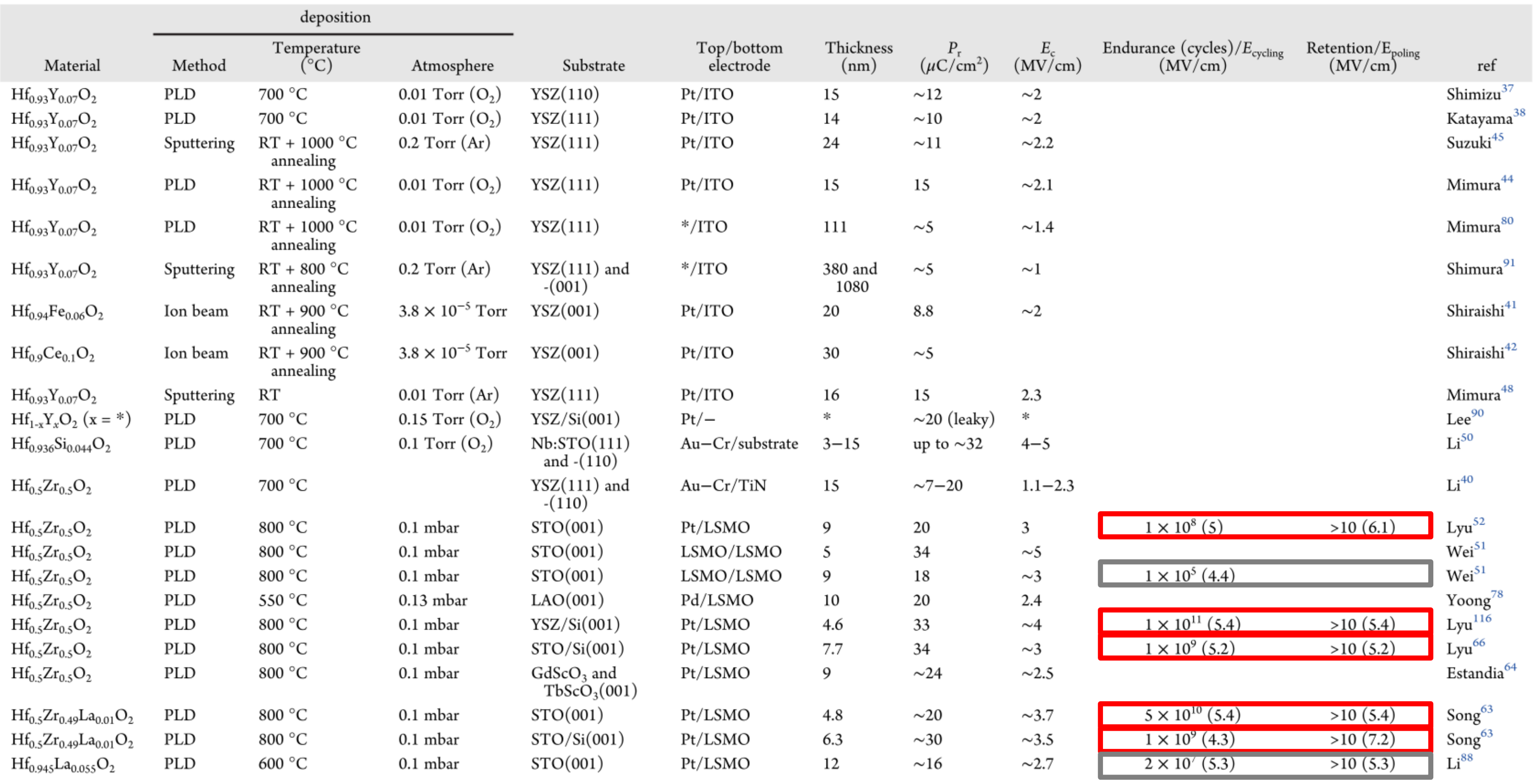




- ➢ 925 ps
- ➢ Important contribution of RC time
- ➢ Phase coexistance is present

P. Buragohain, et al, *Adv. Funct. Mater.*, 2022, **32**, 2108876.
X. Lyu et al., presented at the 2019 IEEE Int. Electron Devices Meeting (IEDM), 2019.
A. K. Tagantsev, et al, *Phys. Rev. B-Condens. Matter Mater. Phys.*, 2002, **66**, 1-6.
J. Y. Jo, et al, Phys. Rev. Lett., 2007, 99, 1–4.

Introduction: Epitaxial ferroelectric hafnium oxide



Material	deposition			Substrate	Top/bottom electrode	Thickness (nm)	P_r ($\mu C/cm^2$)	E_c (MV/cm)	Endurance (cycles)/$E_{cycling}$ (MV/cm)	Retention/E_{poling} (MV/cm)	ref
	Method	Temperature (°C)	Atmosphere								
$Hf_{0.93}Y_{0.07}O_2$	PLD	700 °C	0.01 Torr (O_2)	YSZ(110)	Pt/ITO	15	~12	~2			Shimizu[37]
$Hf_{0.93}Y_{0.07}O_2$	PLD	700 °C	0.01 Torr (O_2)	YSZ(111)	Pt/ITO	14	~10	~2			Katayama[38]
$Hf_{0.93}Y_{0.07}O_2$	Sputtering	RT + 1000 °C annealing	0.2 Torr (Ar)	YSZ(111)	Pt/ITO	24	~11	~2.2			Suzuki[45]
$Hf_{0.93}Y_{0.07}O_2$	PLD	RT + 1000 °C annealing	0.01 Torr (O_2)	YSZ(111)	Pt/ITO	15	15	~2.1			Mimura[44]
$Hf_{0.93}Y_{0.07}O_2$	PLD	RT + 1000 °C annealing	0.01 Torr (O_2)	YSZ(111)	*/ITO	111	~5	~1.4			Mimura[80]
$Hf_{0.93}Y_{0.07}O_2$	Sputtering	RT + 800 °C annealing	0.2 Torr (Ar)	YSZ(111) and -(001)	*/ITO	380 and 1080	~5	~1			Shimura[91]
$Hf_{0.94}Fe_{0.06}O_2$	Ion beam	RT + 900 °C annealing	3.8×10^{-5} Torr	YSZ(001)	Pt/ITO	20	8.8	~2			Shiraishi[41]
$Hf_{0.9}Ce_{0.1}O_2$	Ion beam	RT + 900 °C annealing	3.8×10^{-5} Torr	YSZ(001)	Pt/ITO	30	~5				Shiraishi[42]
$Hf_{0.93}Y_{0.07}O_2$	Sputtering	RT	0.01 Torr (Ar)	YSZ(111)	Pt/ITO	16	15	2.3			Mimura[48]
$Hf_{1-x}Y_xO_2$ (x = *)	PLD	700 °C	0.15 Torr (O_2)	YSZ/Si(001)	Pt/−	*	~20 (leaky)	*			Lee[90]
$Hf_{0.936}Si_{0.044}O_2$	PLD	700 °C	0.1 Torr (O_2)	Nb:STO(111) and -(110)	Au−Cr/substrate	3−15	up to ~32	4−5			Li[50]
$Hf_{0.5}Zr_{0.5}O_2$	PLD	700 °C		YSZ(111) and -(110)	Au−Cr/TiN	15	~7−20	1.1−2.3			Li[40]
$Hf_{0.5}Zr_{0.5}O_2$	PLD	800 °C	0.1 mbar	STO(001)	Pt/LSMO	9	20	3	1×10^8 (5)	>10 (6.1)	Lyu[52]
$Hf_{0.5}Zr_{0.5}O_2$	PLD	800 °C	0.1 mbar	STO(001)	LSMO/LSMO	5	34	~5			Wei[51]
$Hf_{0.5}Zr_{0.5}O_2$	PLD	800 °C	0.1 mbar	STO(001)	LSMO/LSMO	9	18	~3	1×10^5 (4.4)		Wei[51]
$Hf_{0.5}Zr_{0.5}O_2$	PLD	550 °C	0.13 mbar	LAO(001)	Pd/LSMO	10	20	2.4			Yoong[78]
$Hf_{0.5}Zr_{0.5}O_2$	PLD	800 °C	0.1 mbar	YSZ/Si(001)	Pt/LSMO	4.6	33	~4	1×10^{11} (5.4)	>10 (5.4)	Lyu[116]
$Hf_{0.5}Zr_{0.5}O_2$	PLD	800 °C	0.1 mbar	STO/Si(001)	Pt/LSMO	7.7	34	~3	1×10^9 (5.2)	>10 (5.2)	Lyu[66]
$Hf_{0.5}Zr_{0.5}O_2$	PLD	800 °C	0.1 mbar	$GdScO_3$ and $TbScO_3$(001)	Pt/LSMO	9	~24	~2.5			Estandia[64]
$Hf_{0.5}Zr_{0.49}La_{0.01}O_2$	PLD	800 °C	0.1 mbar	STO(001)	Pt/LSMO	4.8	~20	~3.7	5×10^{10} (5.4)	>10 (5.4)	Song[63]
$Hf_{0.5}Zr_{0.49}La_{0.01}O_2$	PLD	800 °C	0.1 mbar	STO/Si(001)	Pt/LSMO	6.3	~30	~3.5	1×10^9 (4.3)	>10 (7.2)	Song[63]
$Hf_{0.945}La_{0.055}O_2$	PLD	600 °C	0.1 mbar	STO(001)	Pt/LSMO	12	~16	~2.7	2×10^7 (5.3)	>10 (5.3)	Li[88]

- ICMAB systematic studies on endurance and retention are unique.
- Other reported results are far from the best performance of ICMAB films

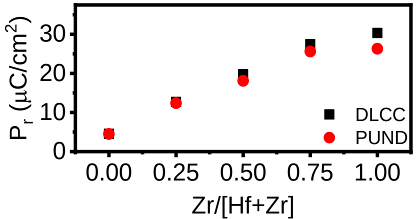
Review: Fina and Sánchez,
ACS Applied Electronic Materials 3, 1530 (2021)

Introduction: Epitaxial ferroelectric hafnium oxide, taxonomy

Strategies to improve functional properties in epitaxial films

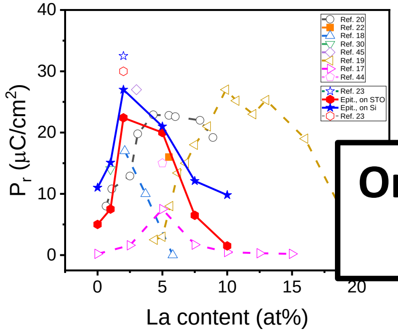
1 **Doping**

Zr doping



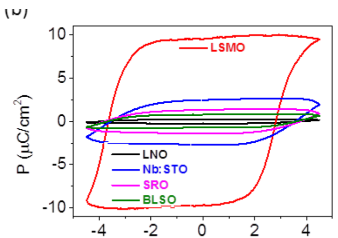
Orthorhombic Tetragonal

La doping



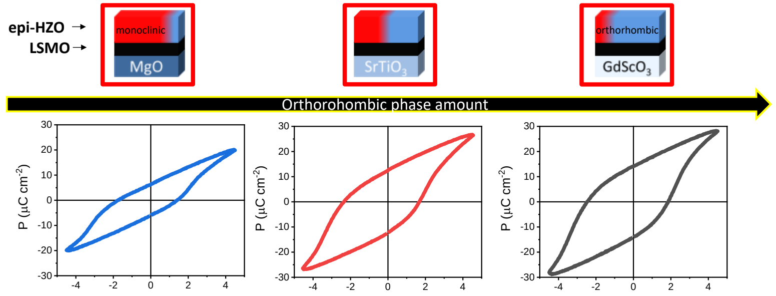
Orthorhombic Cubic

2 **Electrode selection**



Orthorhombic Monoclinic

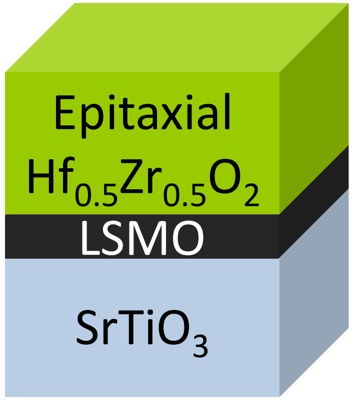
3 **Epitaxial stress**



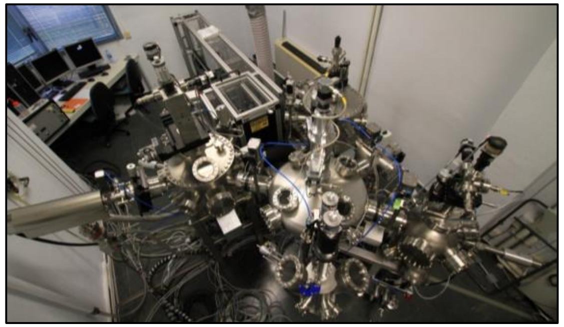
Orthorhombic - Monoclinic

Kiguchi et al.,. J. Ceram. Soc. Jpn. 124, 689 (2016)
Mimura et al., Jpn. J. Appl. Phys. 59, SGGB04 (2020)
Shimizu et al., Appl. Phys. Lett. 2015, 107 (3), 032910
Müller et al, Nano Lett. 2012, 12, 4318−4323
Kozodaev, et al., J. Appl. Phys. 125, 034101 (2019)

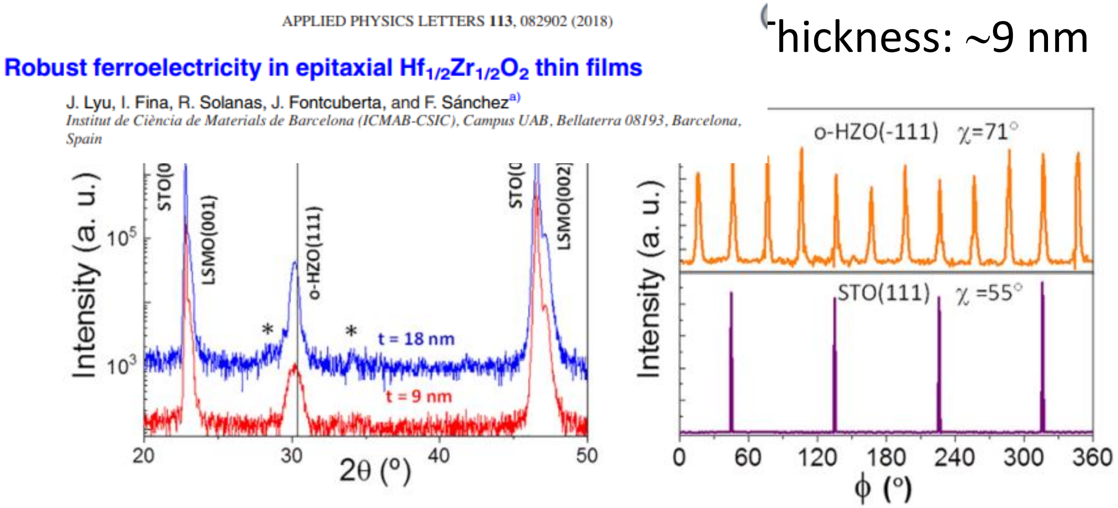
Introduction: ferroelectricity in epitaxial HZO (**homemade**)



Epitaxial heterostructures fabricated by PLD in a single process



PLD Lab at ICMAB



APPLIED PHYSICS LETTERS **113**, 082902 (2018)

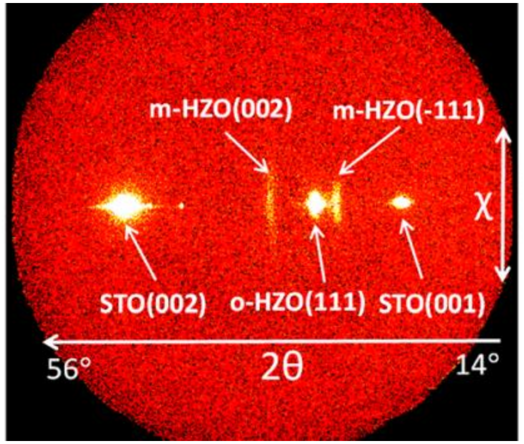
Robust ferroelectricity in epitaxial $Hf_{1/2}Zr_{1/2}O_2$ thin films

J. Lyu, I. Fina, R. Solanas, J. Fontcuberta, and F. Sánchez[a)]

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra 08193, Barcelona, Spain

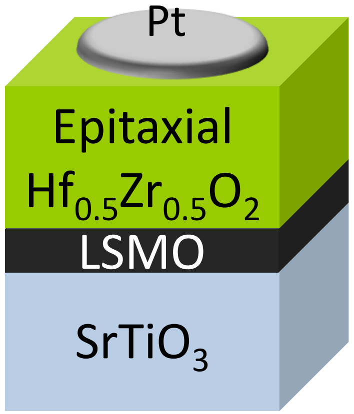
hickness: ~9 nm

Lyu, IF, …. F. Sánchez
Appl. Phys. Lett. 113, 082902 (2018)

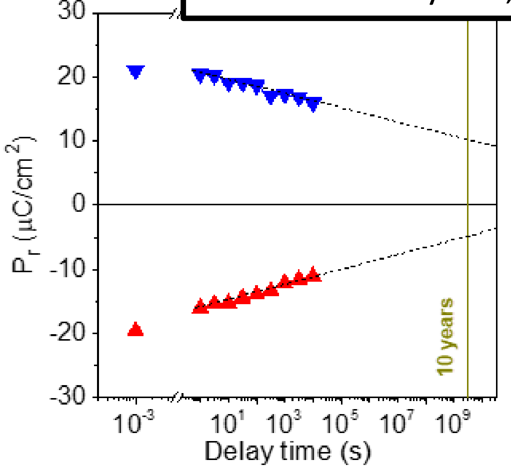


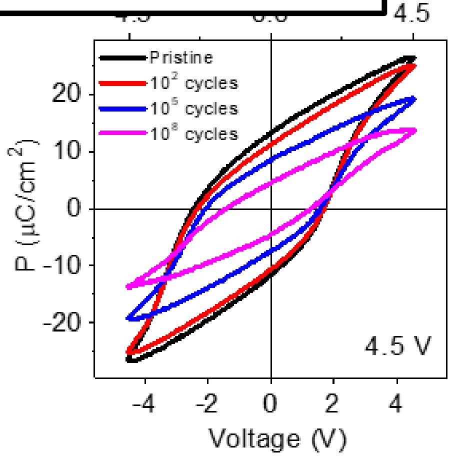
- High quality materials
- Sharp interfaces

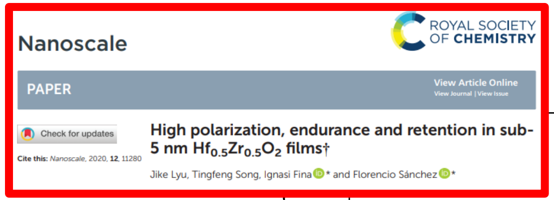
Introduction: ferroelectricity in epitaxial HZO (**homemade**)



Retention >10 years; endurance > 10^8 cycles







Nanoscale

ROYAL SOCIETY OF CHEMISTRY

PAPER

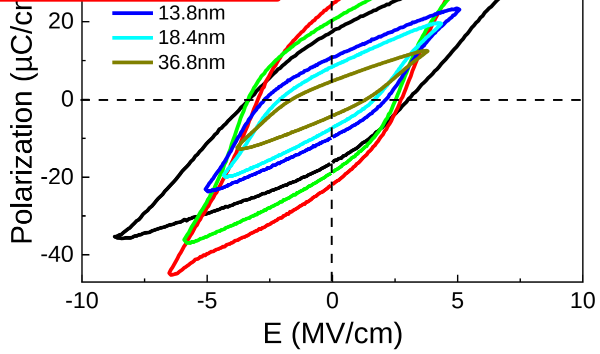
View Article Online
View Journal | View Issue

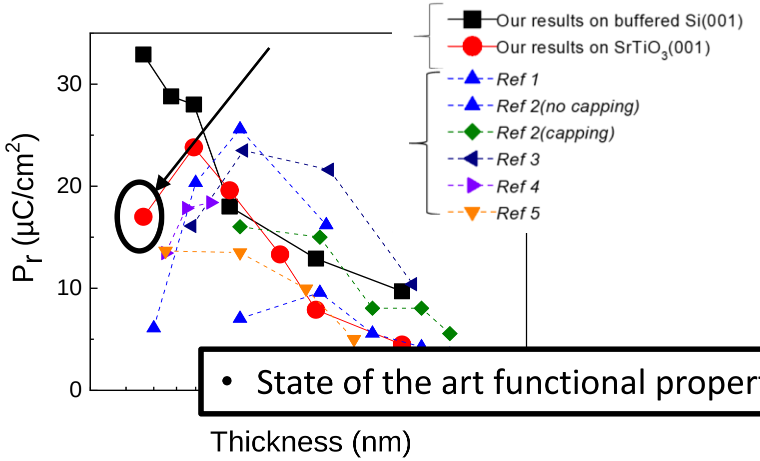
Check for updates

Cite this: *Nanoscale*, 2020, **12**, 11280

High polarization, endurance and retention in sub-5 nm $Hf_{0.5}Zr_{0.5}O_2$ films†

Jike Lyu, Tingfeng Song, Ignasi Fina* and Florencio Sánchez*





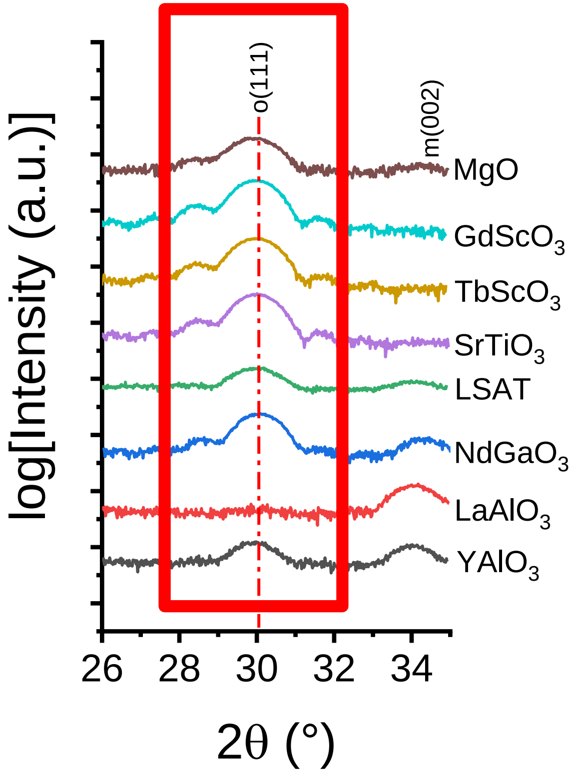
- State of the art functional properties

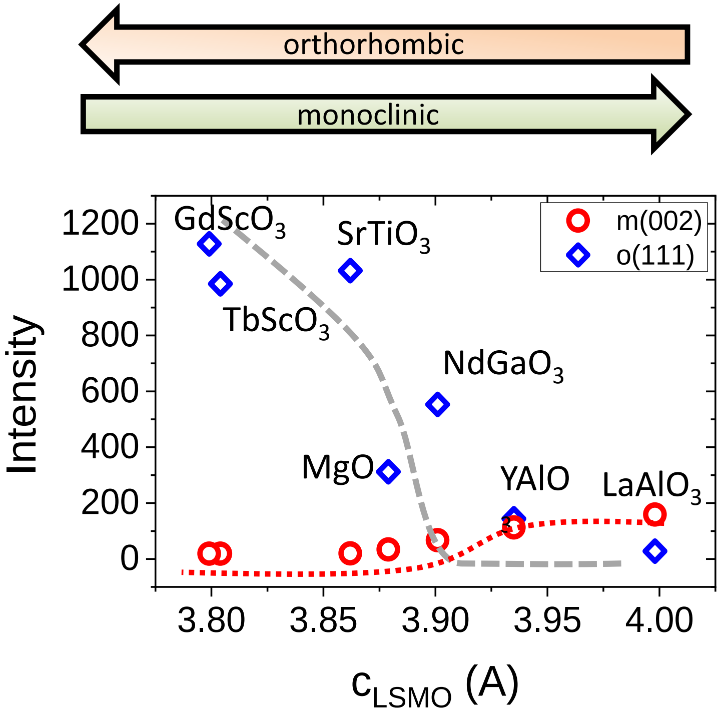
J. Lyu, IF,… et al., APL **113**, 082902 (2018); ACS Appl. Electron. Mater. **1**, 220 (2019); Nanoscale 12, 11280 (2020)

Results: tunning of orthorhombic phase in epitaxial LHO (**PLD films**)

- All films are relaxed
- There are not variations of lattice parameters depending on the substrate
- You can't change the phase by strain

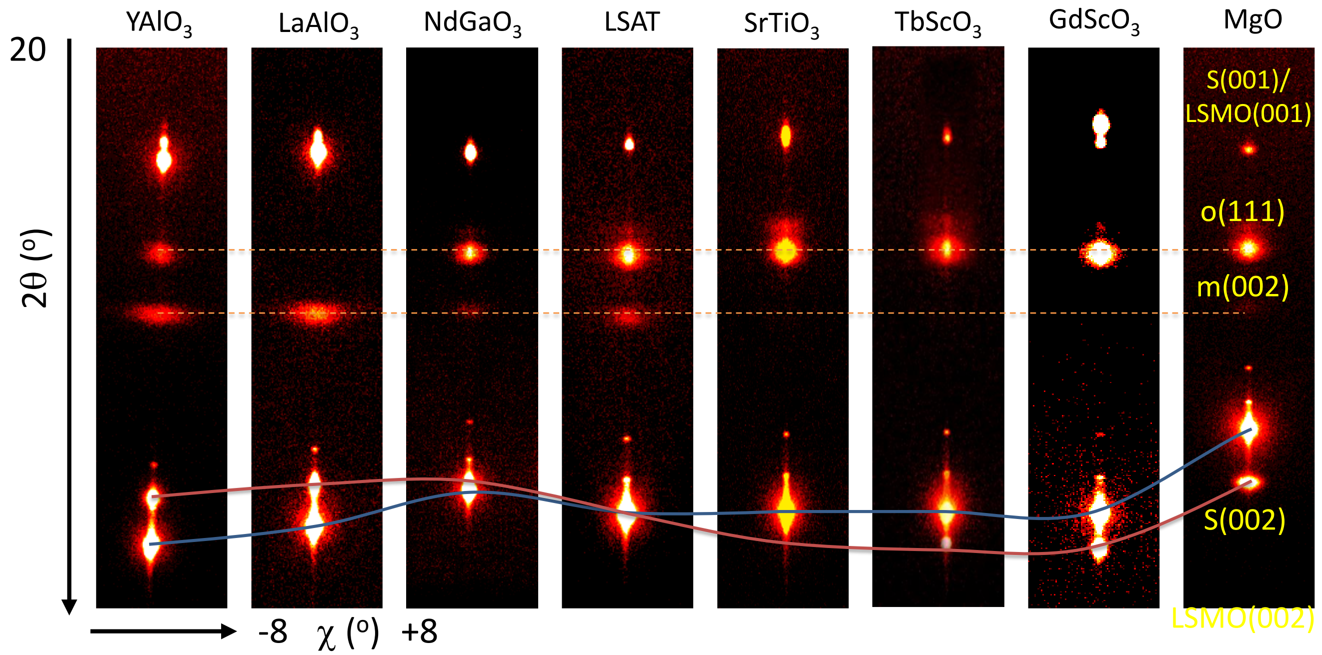
- The orthorhombic phase ratio depends on the selected substrate





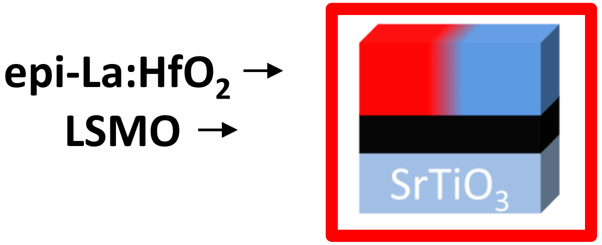
Results: tunning of orthorhombic phase in epitaxial LHO (**PLD films**)

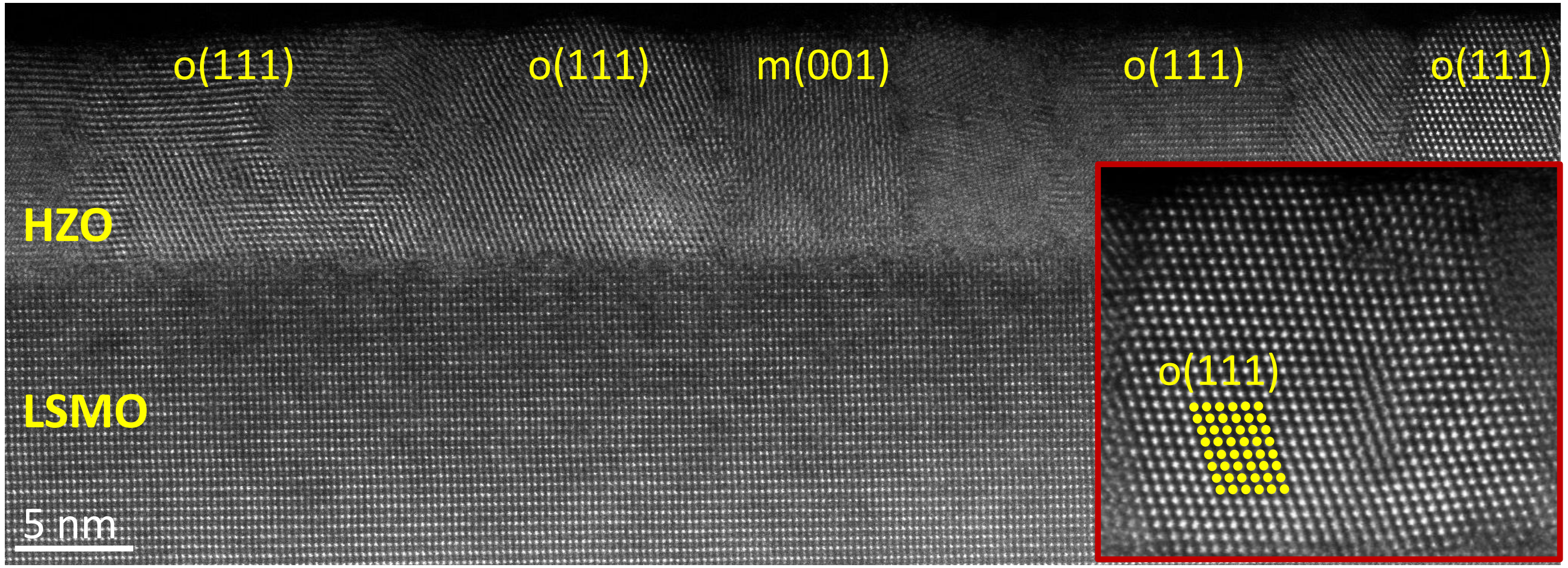
Orthorohombic phase amount



Substrate in-plane pseudo-cubic or cubic lattice parameter

Results: tunning of orthorhombic phase in epitaxial LHO (**PLD films**)

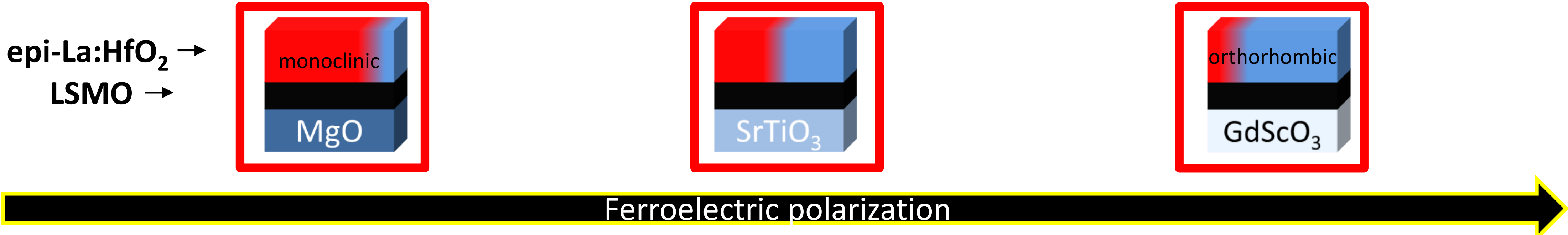


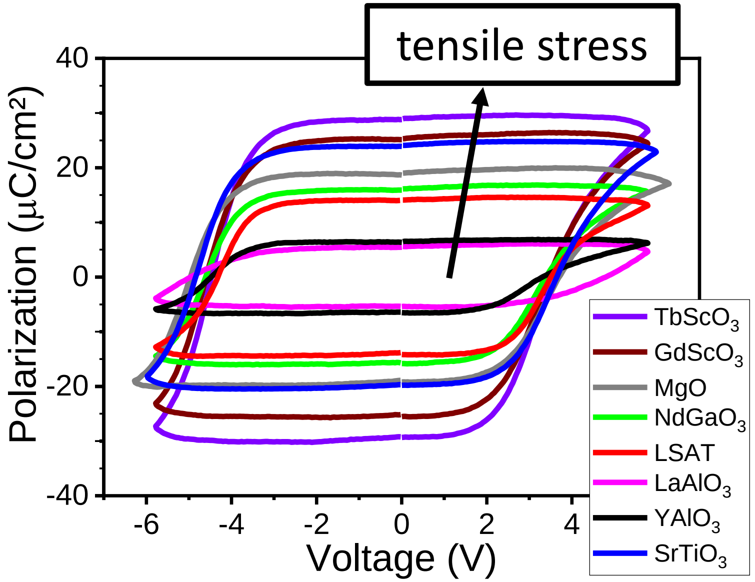


Coexistance of monoclinic (001) and orthorhombic (111) grains

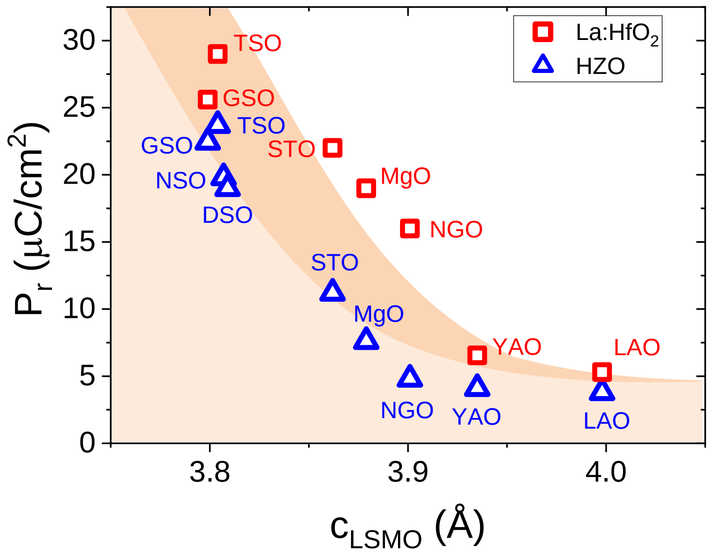
Collaboration S Estandia, J Gazquez

Results: tunning of orthorhombic phase in epitaxial LHO (**PLD films**)



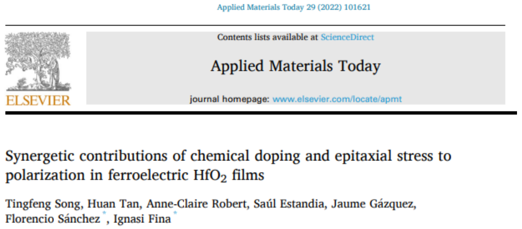


Zr doping produce similar effect



La doping → Greater Polarization

Results: strain/stress



Applied Materials Today 29 (2022) 101621

Contents lists available at ScienceDirect

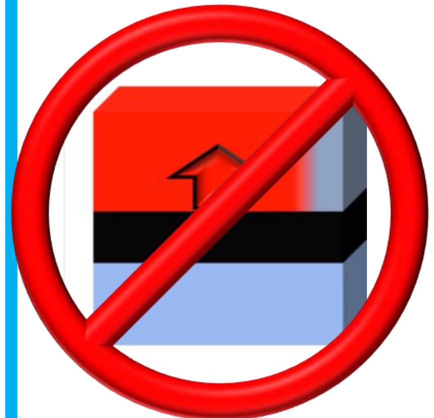
Applied Materials Today

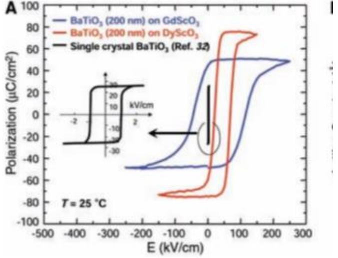
journal homepage: www.elsevier.com/locate/apmt

Synergetic contributions of chemical doping and epitaxial stress to polarization in ferroelectric HfO_2 films

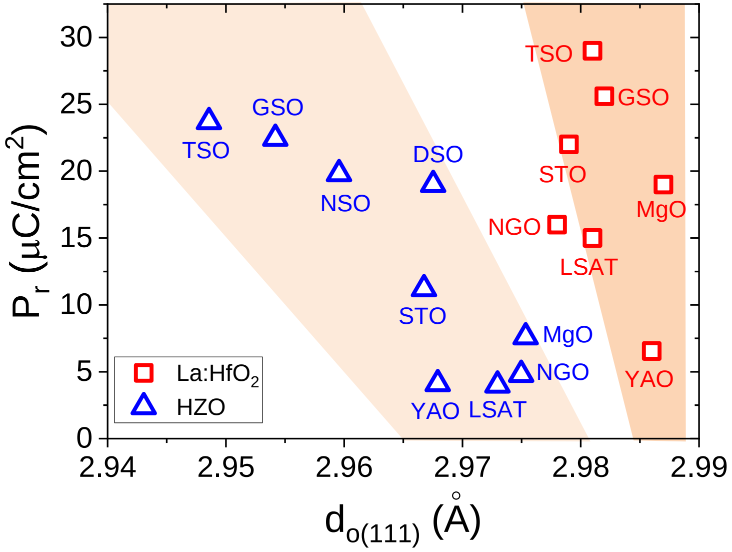
Tingfeng Song, Huan Tan, Anne-Claire Robert, Saúl Estandia, Jaume Gázquez, Florencio Sánchez *, Ignasi Fina *

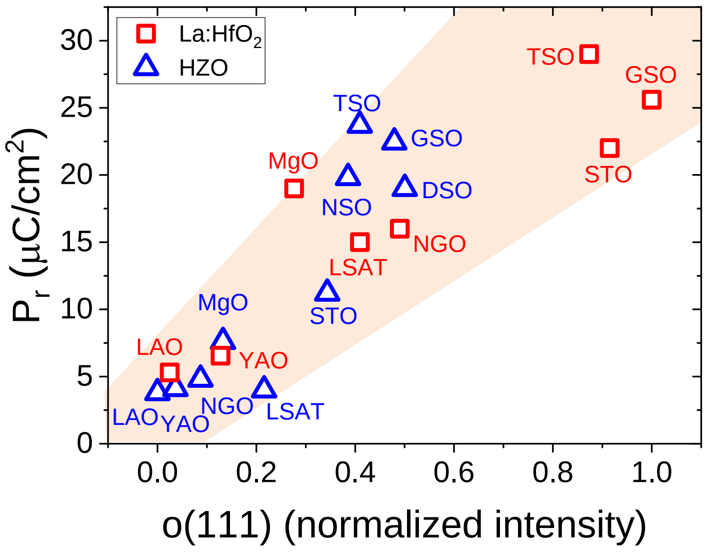
Song, …, IF.
Applied Materials Today 29, 101621





Choi, et al., Science 306.5698 (2004): 1005-1009.



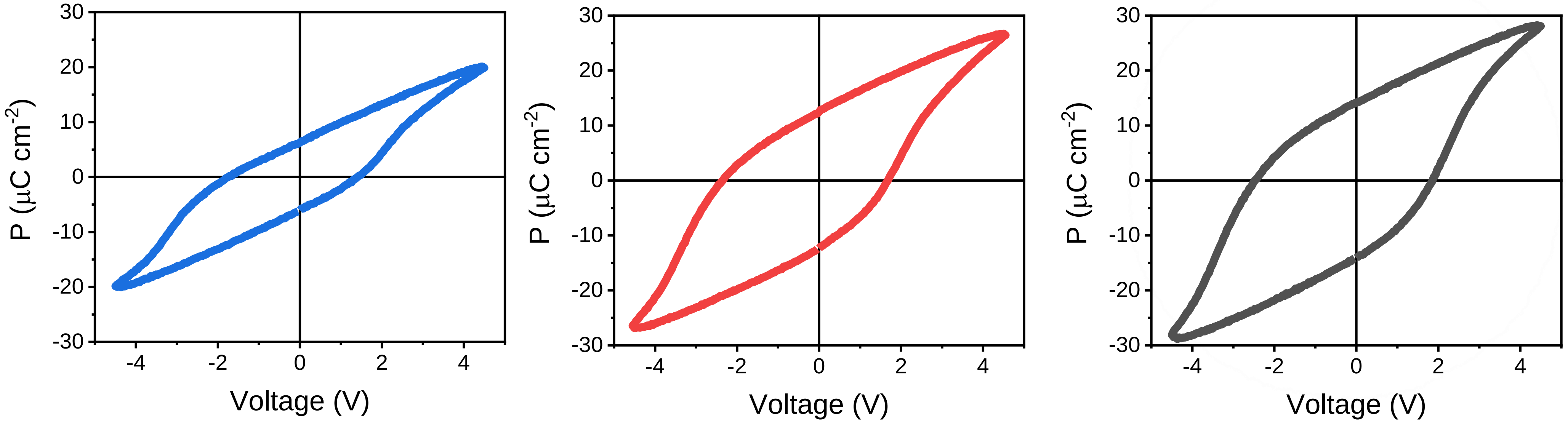


- No strain effects for different samples

- Dependence on orthorhombic phase ratio amount prevails

Results: polarization dependence on orthorhombic phase amount

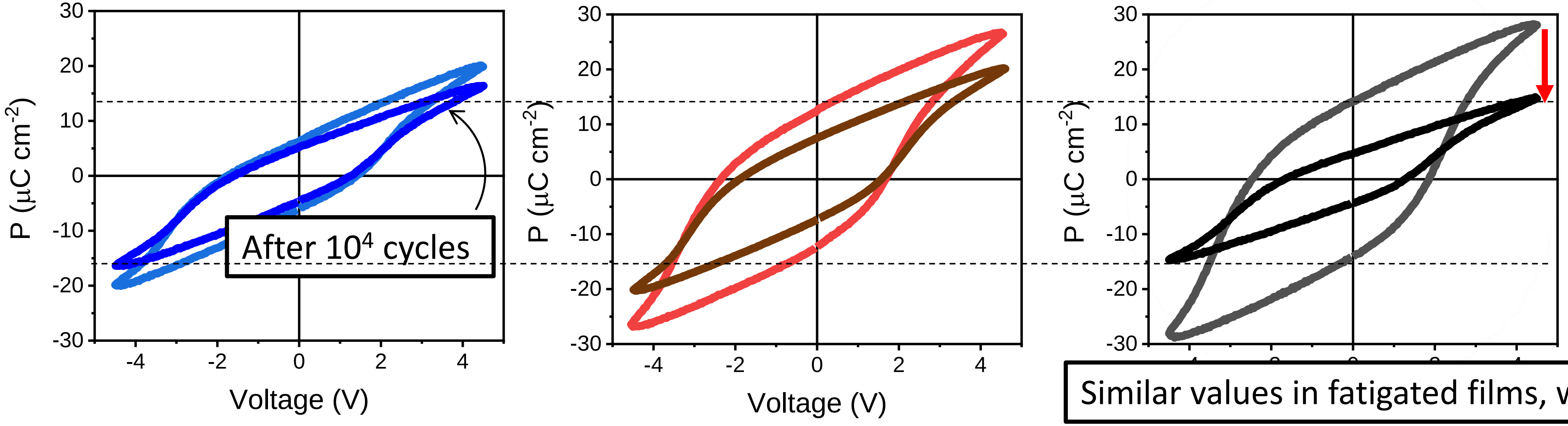
Orthorohombic phase amount



Ferroelectric polarization

Results: fatigue dependence on orthorhombic phase amount

Orthorohombic phase amount



After 10^4 cycles

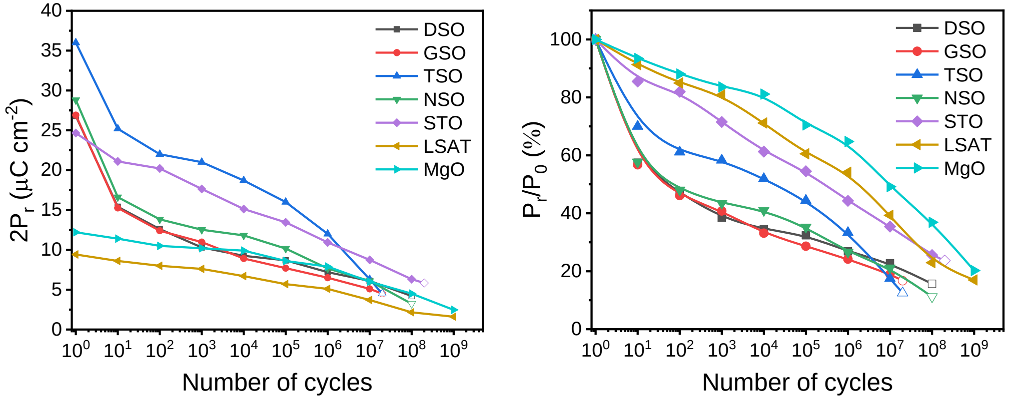
Similar values in fatigated films, why?

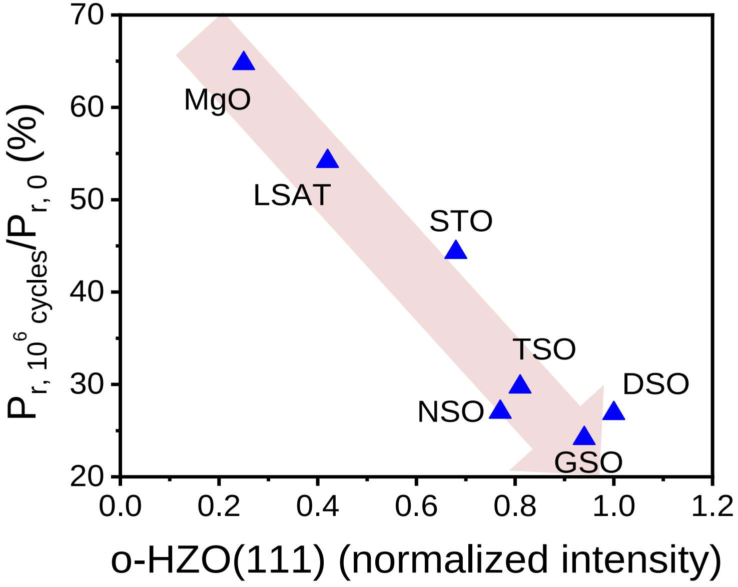
Ferroelectric polarization

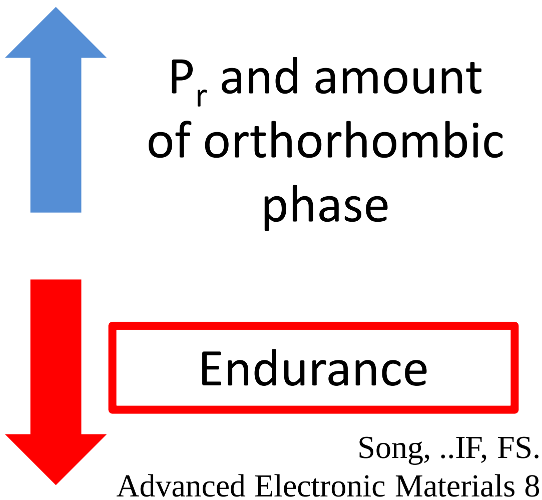
Fatigue

Results: fatigue dependence on orthorhombic phase amount

Similar results are reproduced using a wide variety of substrates





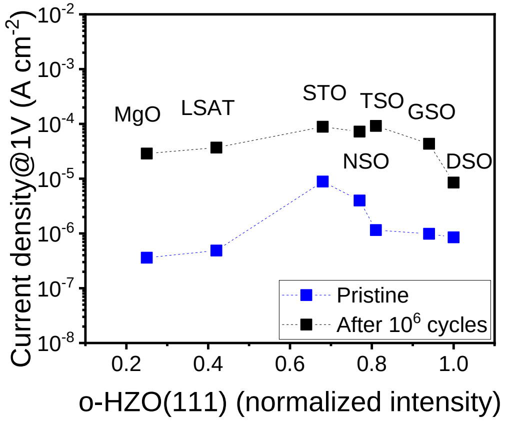


P_r and amount of orthorhombic phase

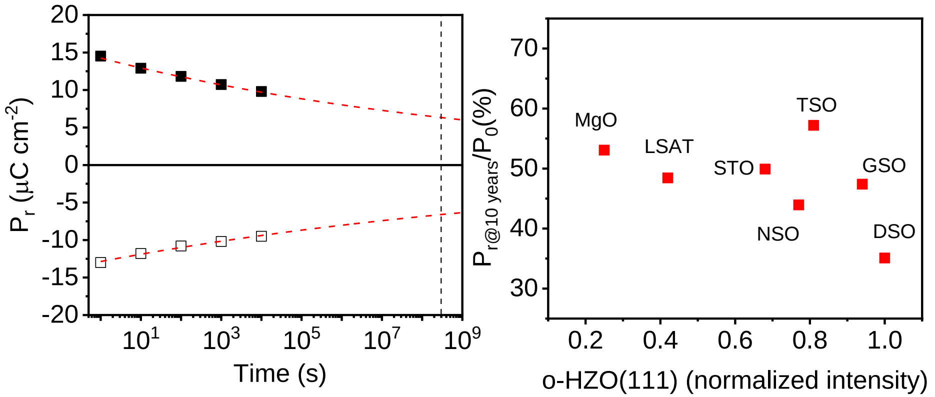
Endurance

Song, ..IF, FS.
Advanced Electronic Materials 8, 2100420 (2022)

Important influence of leakage is disregarded

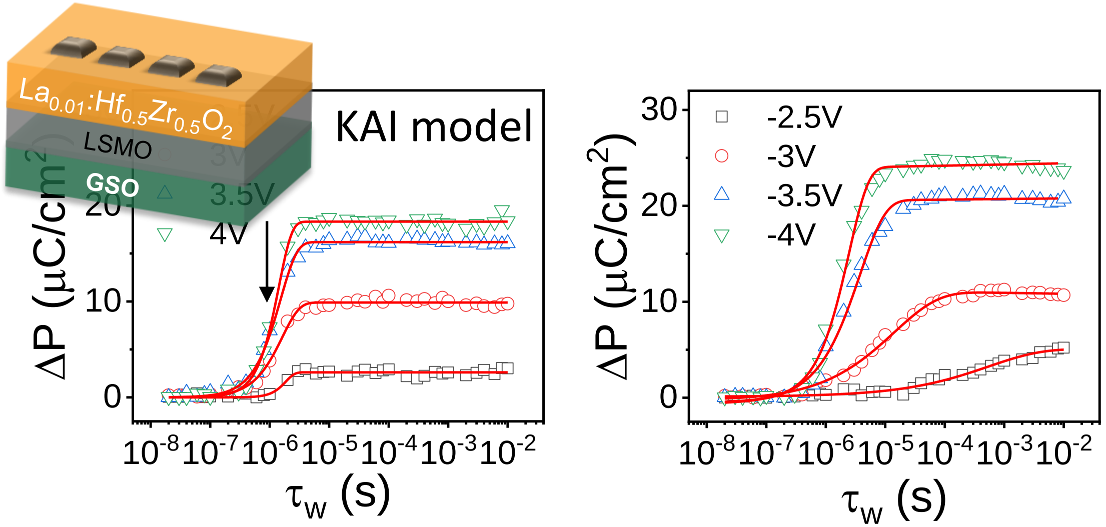


Retention is not importantly affected



Results: switching dynamics

Almost phase pure orthorhombic films

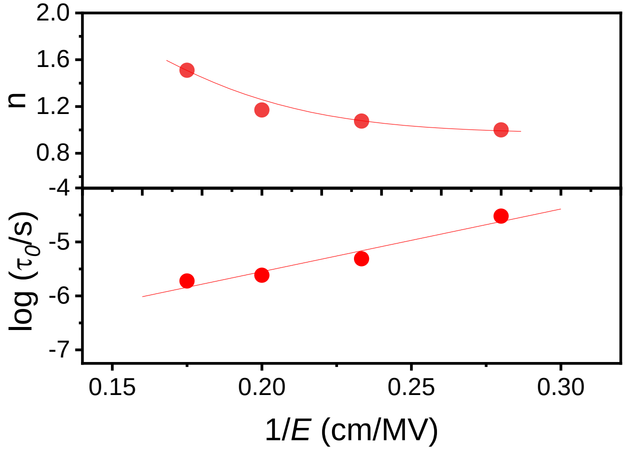


La:HZO/LSMO//GSO

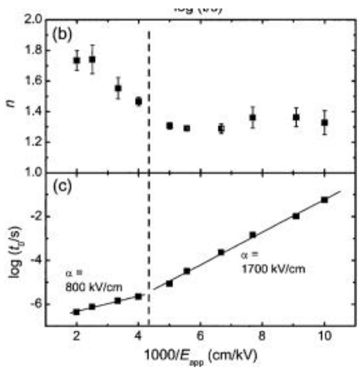
- For both polarities switching time is slow 1.4μs
- For both polarities n > 1

$$P(t)\,/\,P_s = 1 - \exp\left[-(t\,/\,t_0)^n\right],$$

Dependence on electric field



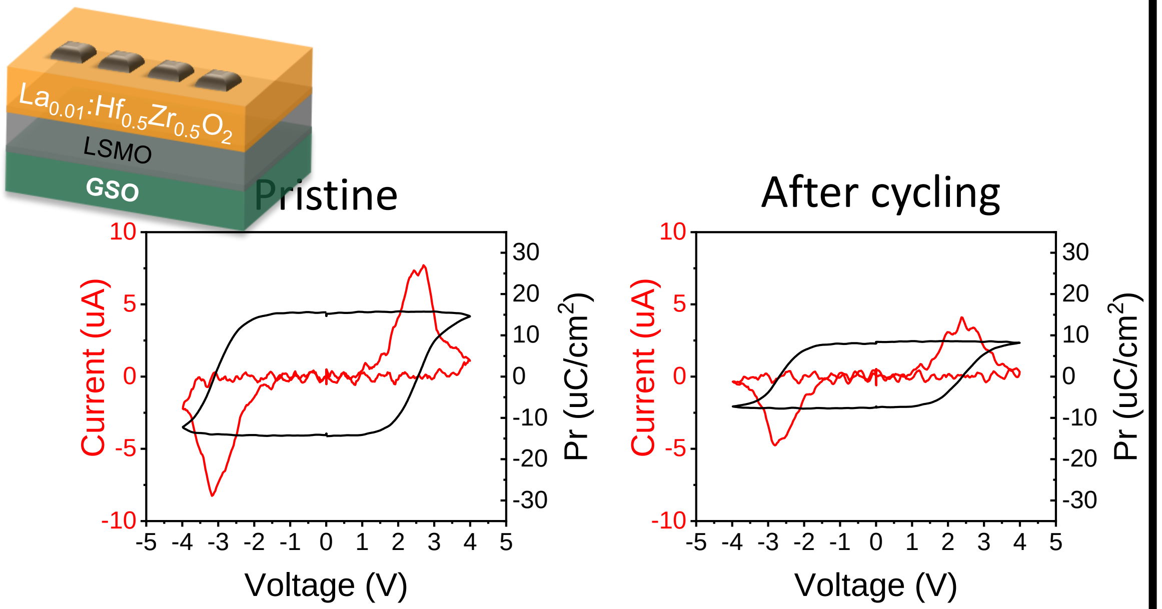
- As found in PZT switching time shortens with electric field and n decreases.
- <u>KAI is valid for all fields</u>



Y. W. So *et al.*, Appl. Phys. Lett. **86**, 092905 (2005).

Results: effect of fatigue

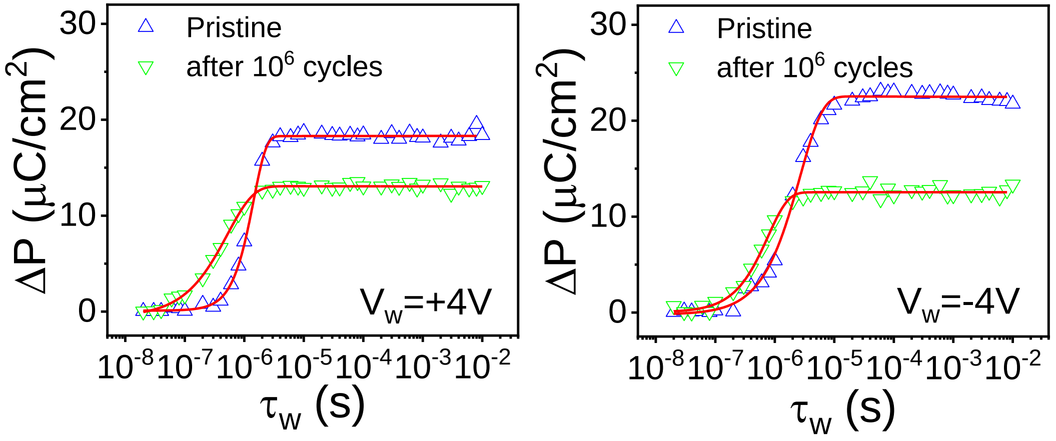
Fatigue effect on polarization



- ➢ After 10^6 cycles polarization decreases by ≈33%

T. Song, et al., Advanced Electronic Materials 8 (1), 2100420 (2022)
M. Peˇsi´c et al., Adv. Funct. Mater. 26, 4601 (2016).
E. D. Grimley et al., Adv. Electron. Mater. 2, 1600173 (2016).

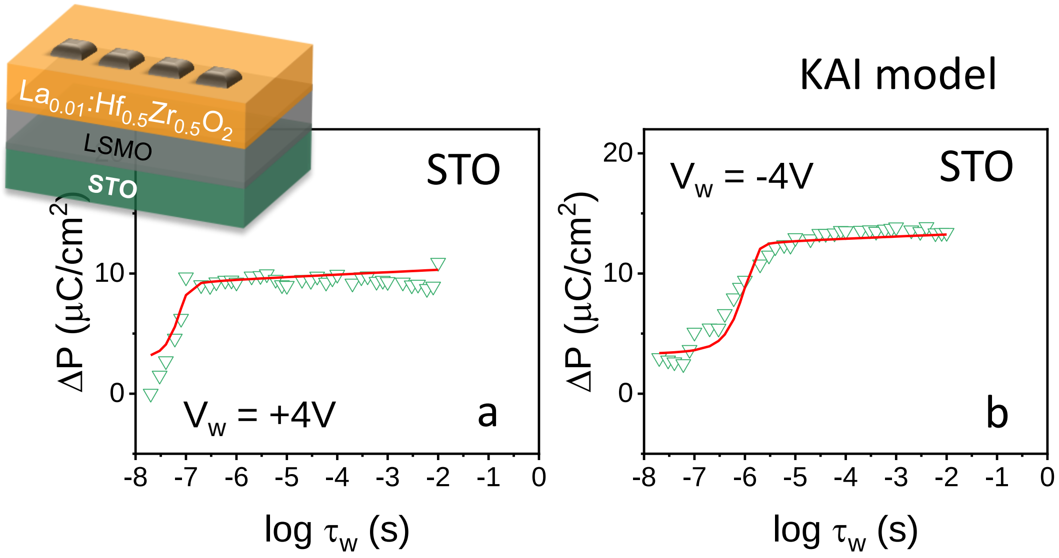
Fatigue effect on switching time



- ➢ After 10^6 cycles switching time decreases by ≈60%
- ➢ KAI is still valid

Results: switching dynamics

Mix phase pure orthorhombic films



KAI model

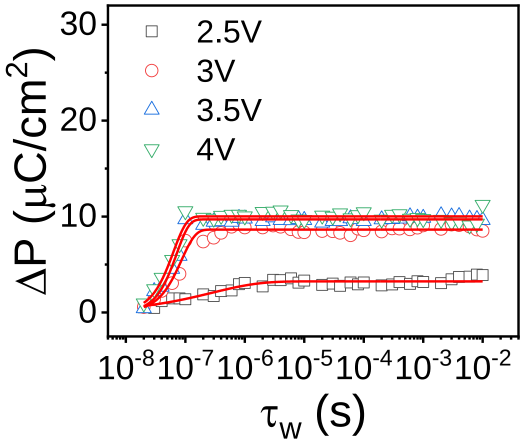
La:HZO/LSMO//STO

- Fitting is not bad
- n<1 = Unrealistic value

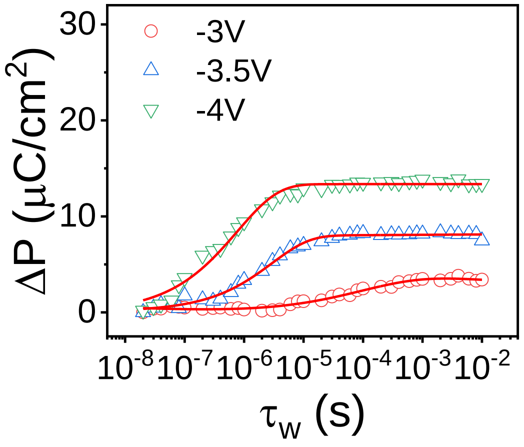
Results: switching dynamics

Mix phase pure orthorhombic films

Limited by RC



NLS model



La:HZO/LSMO//STO

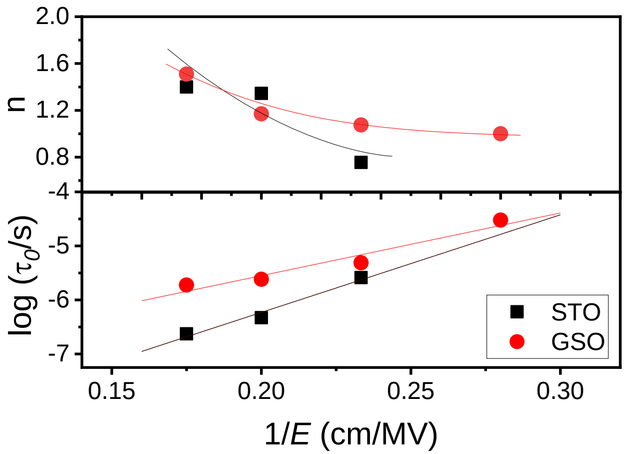
- ➢ Fitting with is not bad
- ➢ n values are >1
- ➢ For positive voltage switching dependence is limited by RC time

NLS model

$$\Delta P(t) = 2P_r \int_{-\infty}^{\infty} \left[1 - \exp\{-(t/t_0)^n\}\right] F(\log t_0)\, d(\log t_0)$$

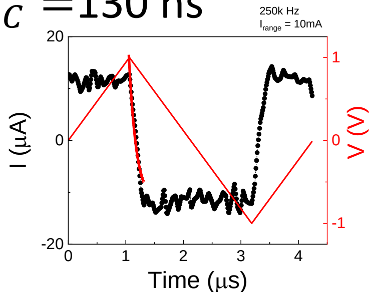
$$F(\log t_0) = \frac{A}{\pi}\left[\frac{w}{(\log t_0 - \log t_1)^2 + w^2}\right]$$

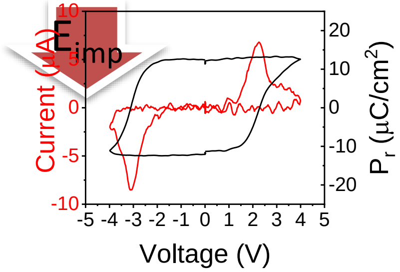
Dependence on electric field (for negative V)



RC time constant (for positive V)

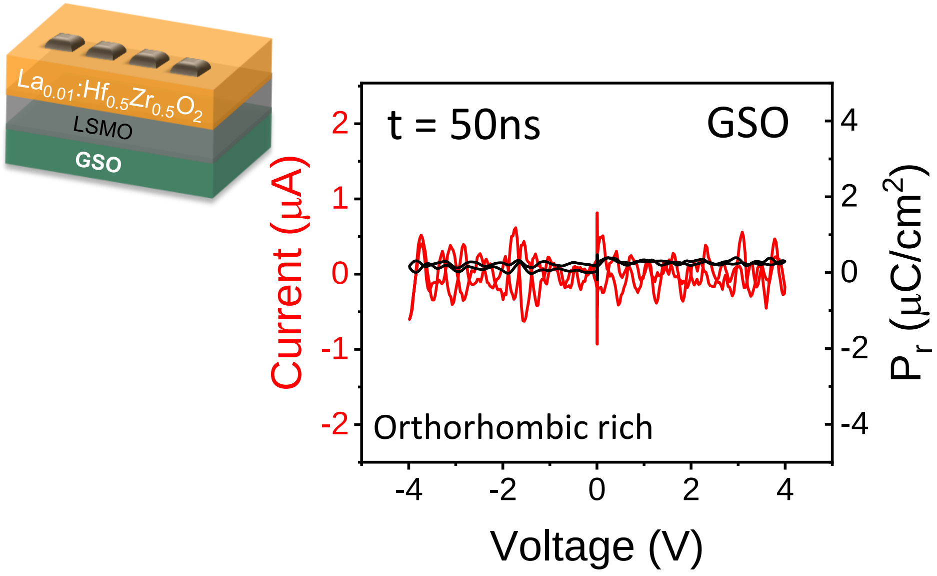
τ_{RC} =130 ns

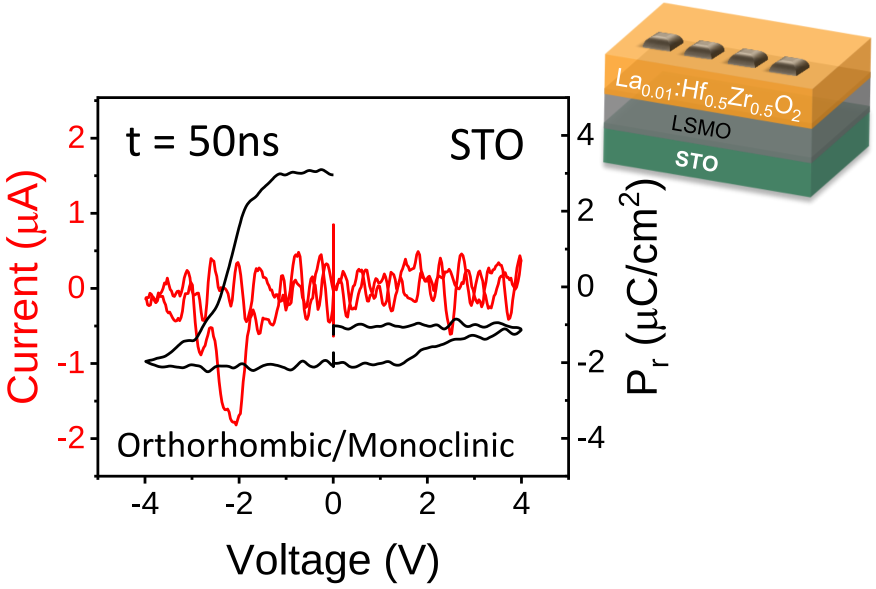




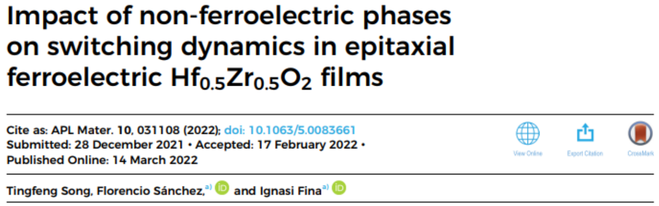
Results: in brief…

Mix phase film shows switched polarization using the same pulse width than the phase pure film





Results: Scenario

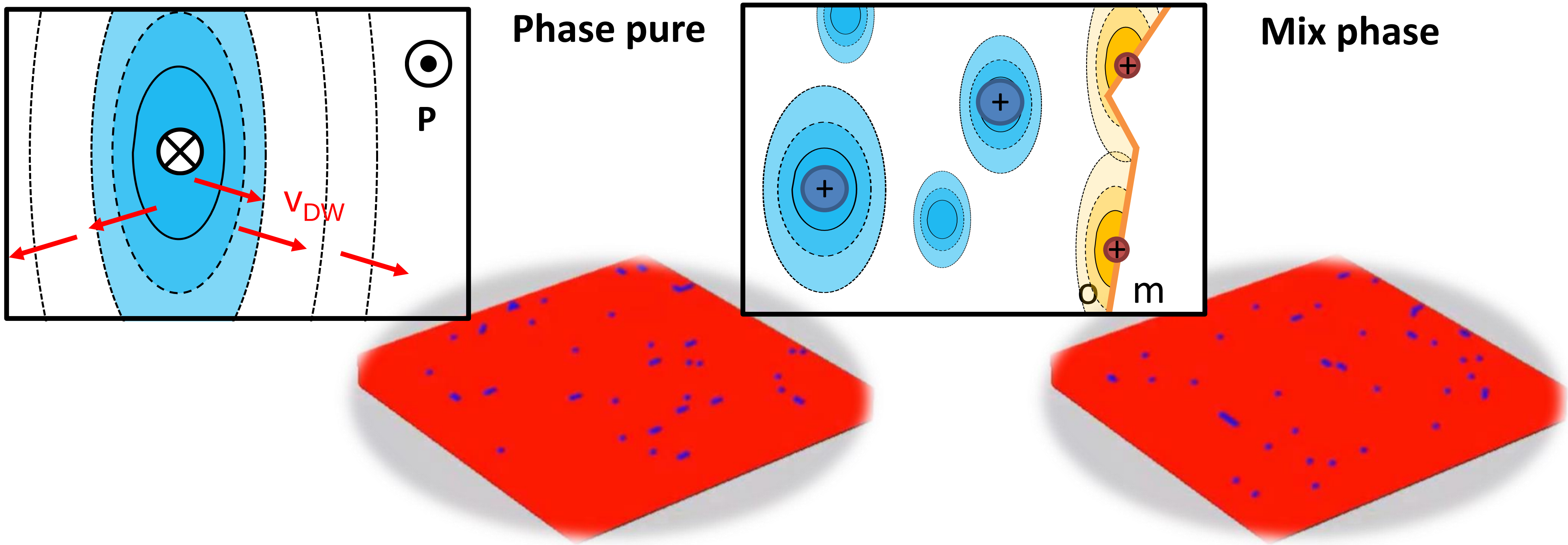


Impact of non-ferroelectric phases on switching dynamics in epitaxial ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ films

Cite as: APL Mater. 10, 031108 (2022); doi: 10.1063/5.0083661
Submitted: 28 December 2021 • Accepted: 17 February 2022 •
Published Online: 14 March 2022

Tingfeng Song, Florencio Sánchez,[a] and Ignasi Fina[a]

Song,…, IF
APL Materials 10 (3), 031108



Phase pure

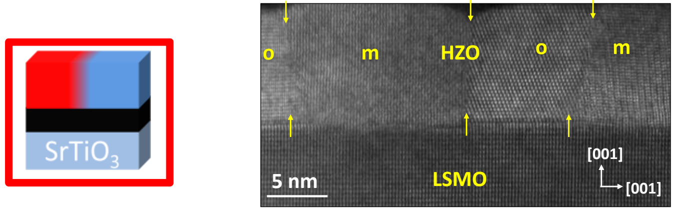
Mix phase

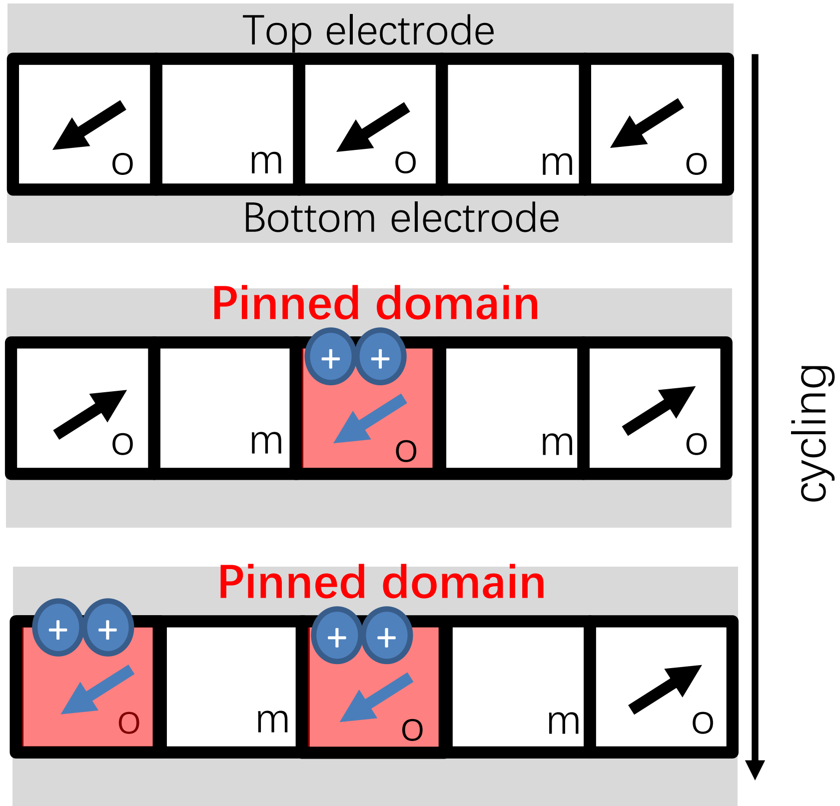
- ➢ The absence of defects/non-polar phase favors 2D domain growth.
- ➢ In films on STO (coexisting orthorhombic/monoclinic phases), charged defects/incoherent grain boundary help on the initiation of the nucleation.

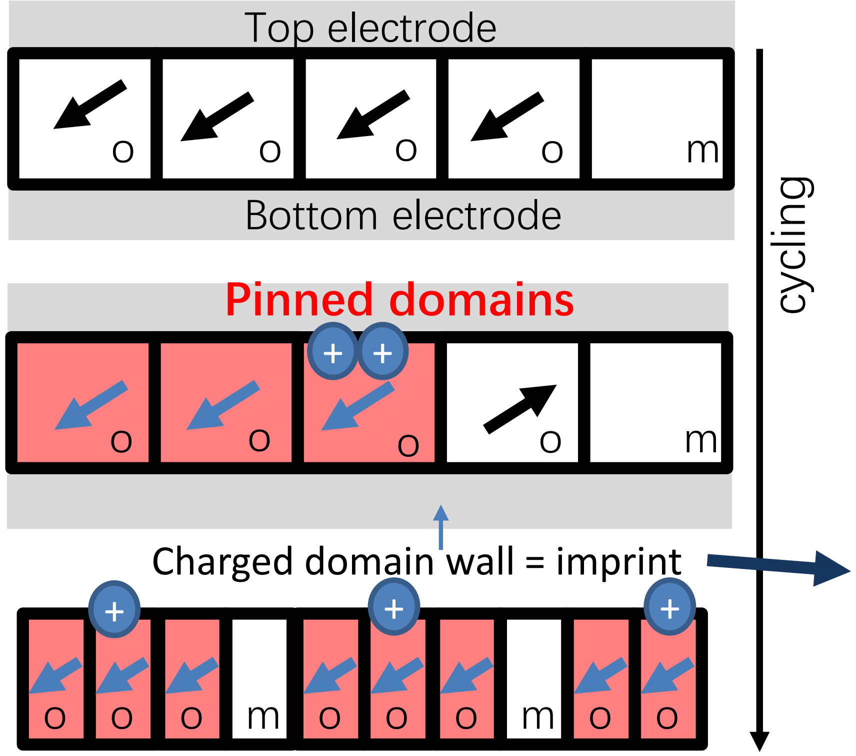
M. D. Glinchuk et al., J. Alloys Compd. 830, 153628 (2020).
P. Nukala et al., Science 372, 630 (2021).

Scenario: monoclinic grains are buffers for pinning propagation

Grainy nature of epitaxial and polycrystalline films

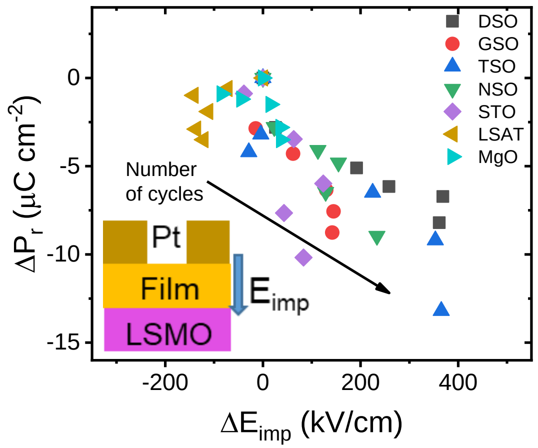






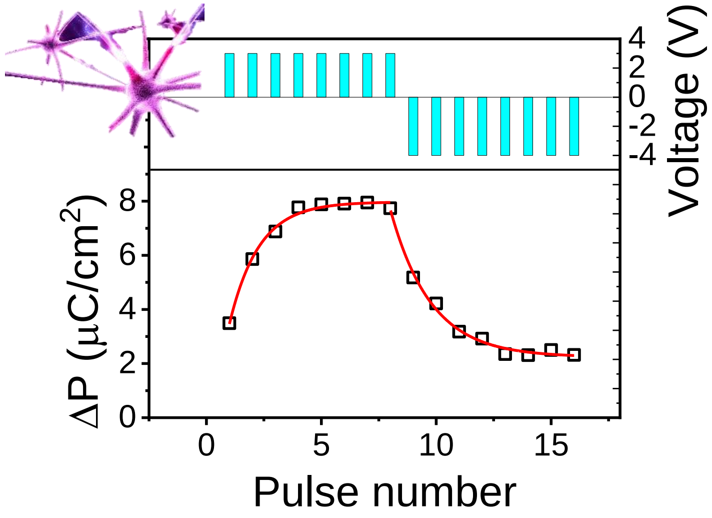
Assuming
- Oxygen vacancies
- At Pt/HZO interface

Imprint ant P reduction

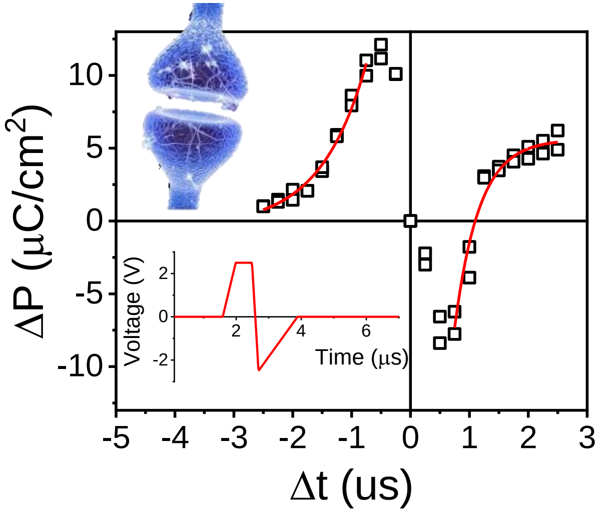


TWEET 2023, June 5th

Beyond: neuromorphic-like behavior



50 ns pulse, +3V/-4V
Exponential coefficients of potentiation/depression, 1.2/1.8



750 ns
Shifted along ΔP (imprint)

Asymmetric Hebbian learning rule

$$\boxed{\Delta\omega = Ae^{-\frac{\Delta t}{\tau}}}$$

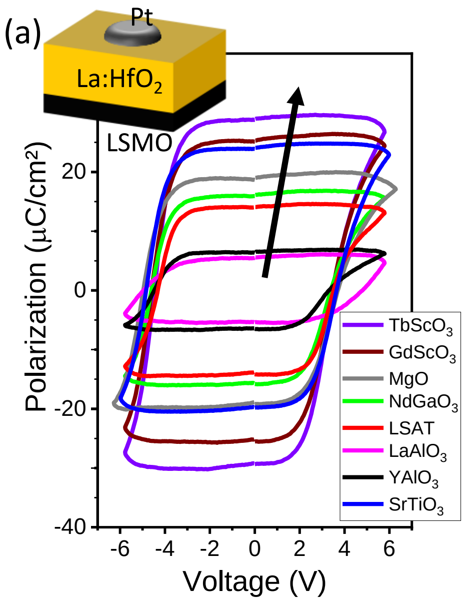
τ is the time constant of a STDP function

	Δt > 0	**Δt < 0**
[1]	$6.53\mu s$	$9.28\mu s$
[2]	$35\mu s$	$22\mu s$
This work	$0.8\mu s$	$0.4\mu s$

1.H. Y. Yoong et al., Adv. Funct. Mater. 28, 1806037 (2018).
2.B. Max et al., ACS Appl. Electron. Mater. 2, 4023 (2020). 15U.

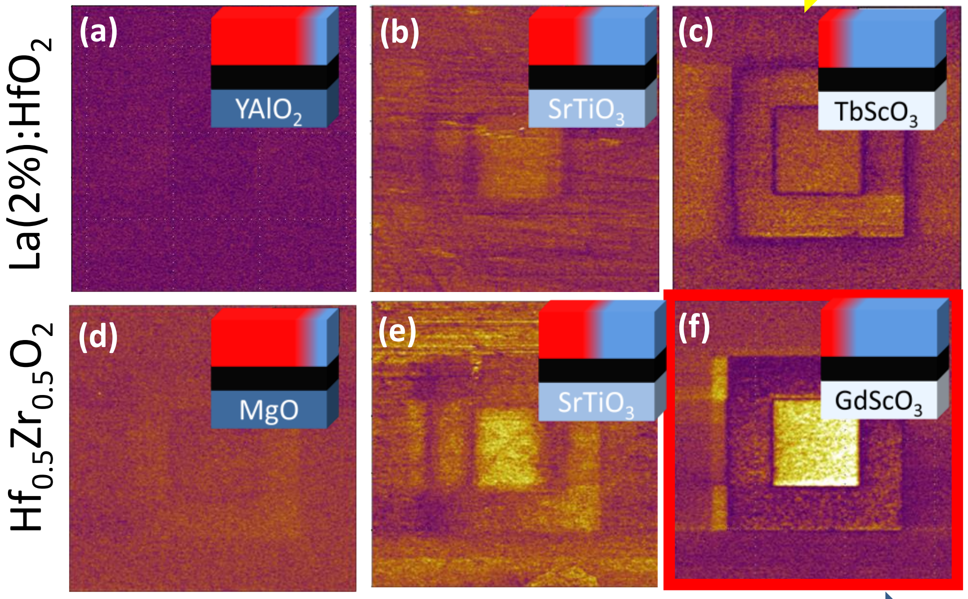
- Long term potentiation/depression and STPD characteristics at the shortest pulse time
- Both are non symmetric due to the defects

Beyond: Piezoelectric response

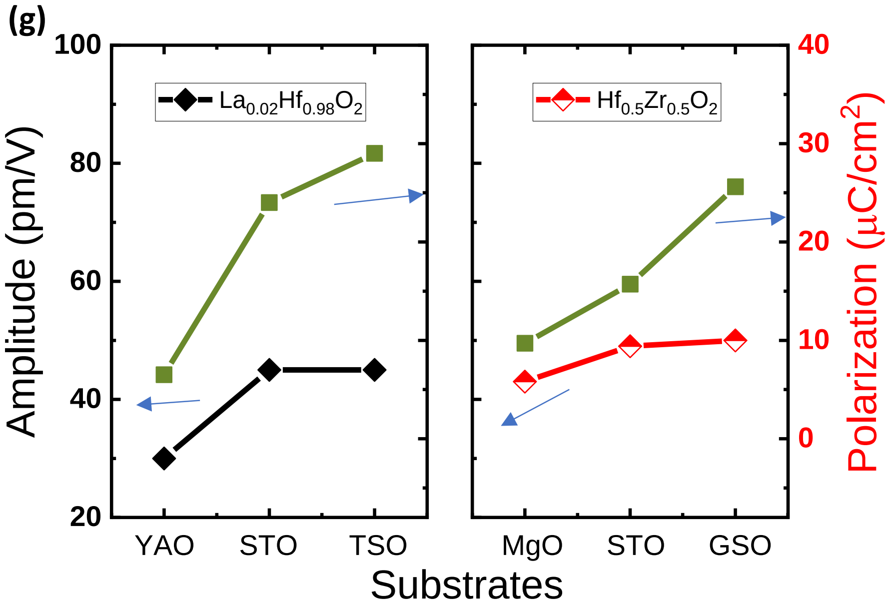


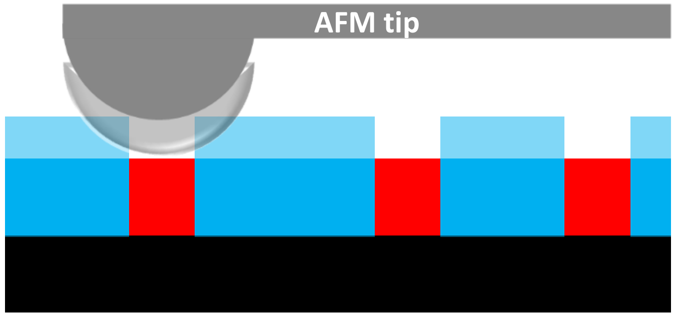
Amplitude piezo response

Orthorohombic phase amount



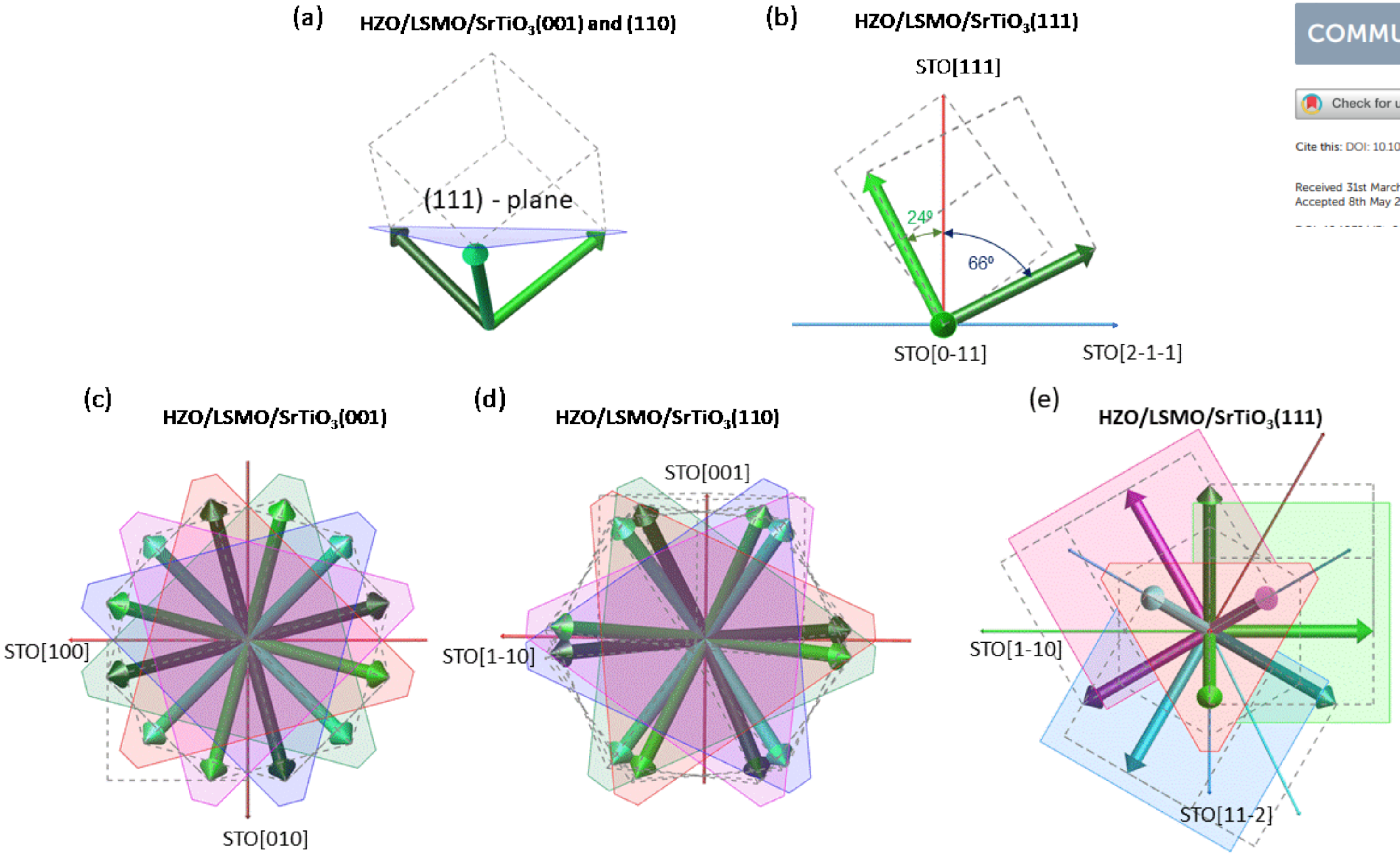
Brighter

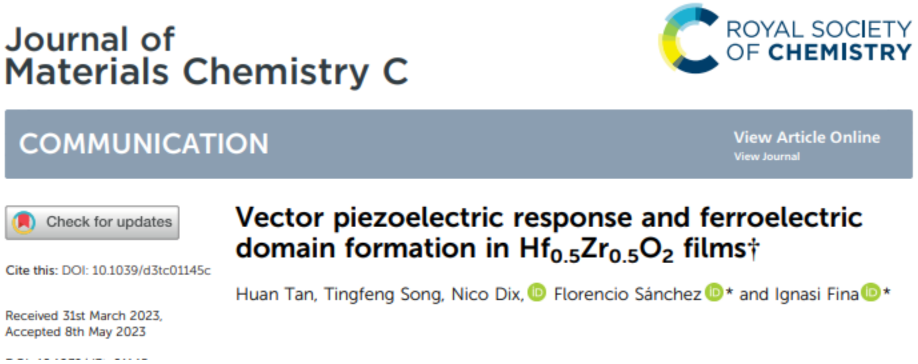




- ➢ Orthorhombic phase shows larger piezoresponse
- ➢ Piezoresponse saturates due to tip size effect

Beyond: Piezoelectric response




Journal of
Materials Chemistry C

ROYAL SOCIETY
OF CHEMISTRY

COMMUNICATION

Cite this: DOI: 10.1039/d3tc01145c

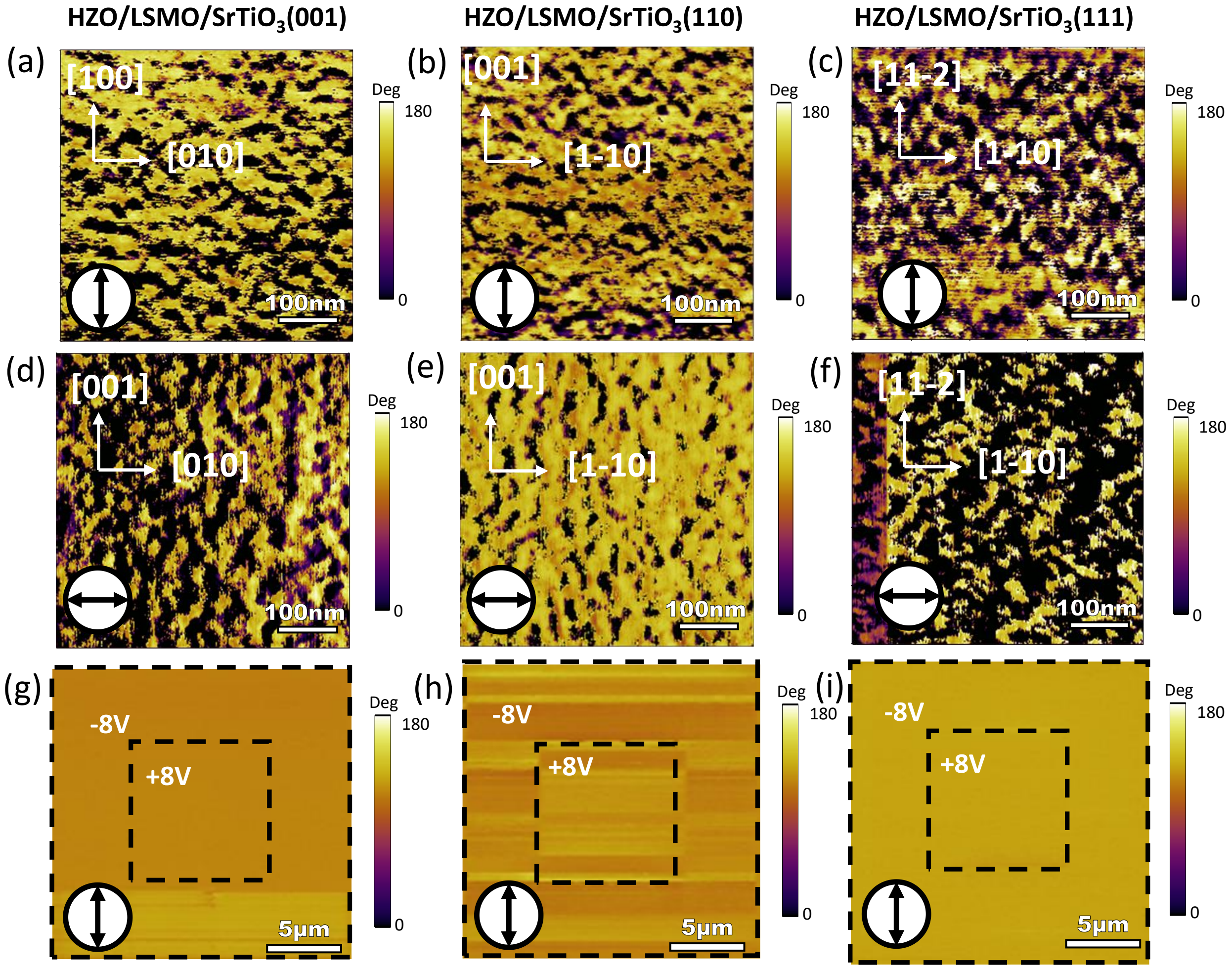
Received 31st March 2023,
Accepted 8th May 2023

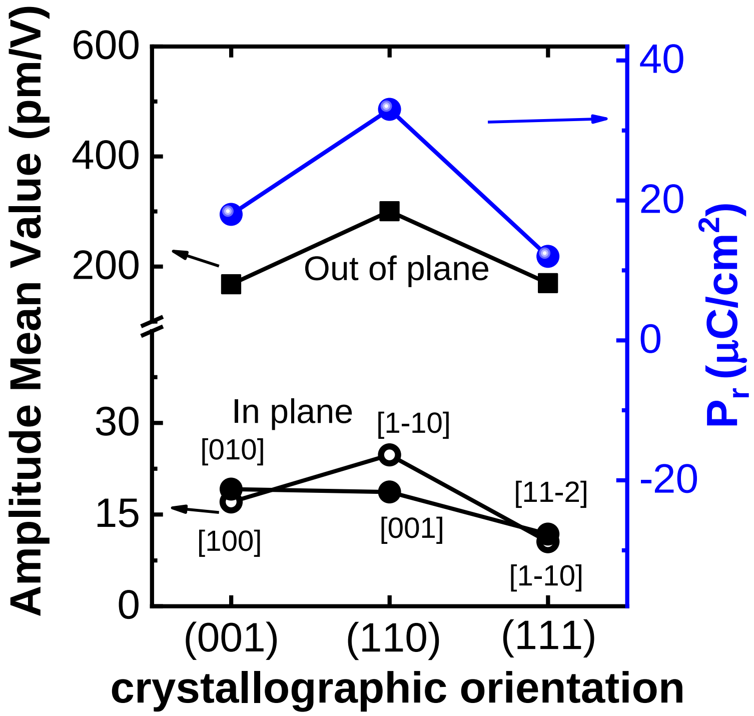
Vector piezoelectric response and ferroelectric domain formation in Hf$_{0.5}$Zr$_{0.5}$O$_2$ films†

Huan Tan, Tingfeng Song, Nico Dix, Florencio Sánchez* and Ignasi Fina*

Tan, …IF, 10.1039/D3TC01145C (Communication)
J. Mater. Chem. C, 2023, Advance Article
Song, …IF,
Nanoscale 14, 2337 (2020)
Journal of Materials Chemistry C 10, 8407

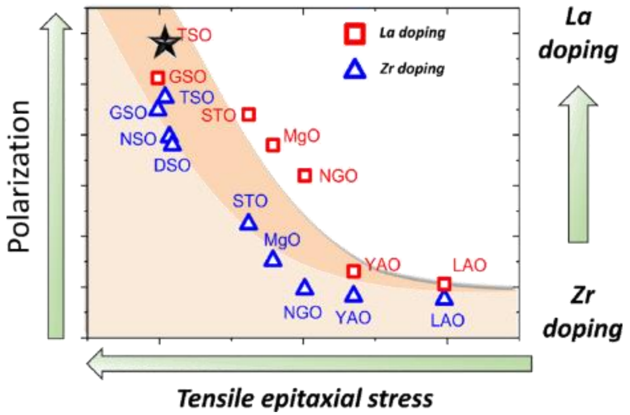
Beyond: Piezoelectric response

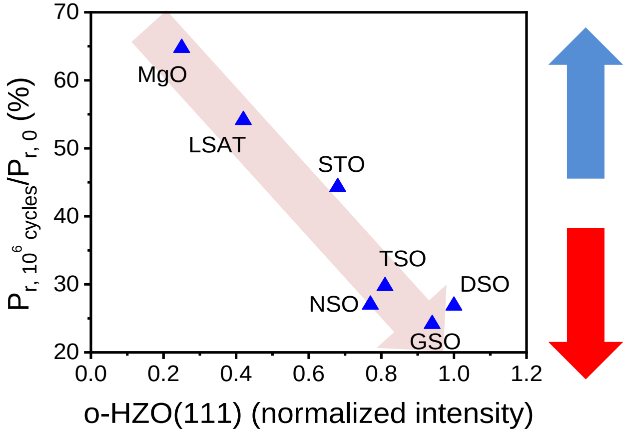




Conclusions

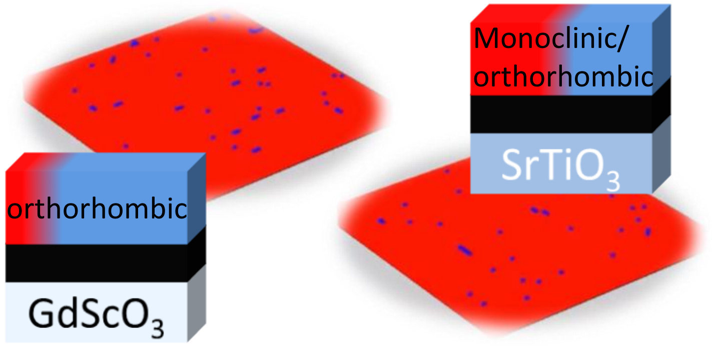
Ferroelectric polarization depends on orthorhombic phase amount (negligible strain effects)





Endurance is not better in single-phase films

Faster switching is observed in films with less orthorhombic phasae



ICMAB
INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA
EXCELENCIA SEVERO OCHOA
CSIC