Strontium Doped Hafnium Oxide Thin Films

– Wide Process Window for Ferroelectric Memories –

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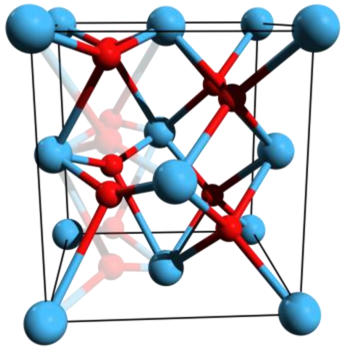
C. Adelmann, S. Van Elshocht and T. Mikolajick

ESSDERC 2013, Bucharest



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nanoelectronic materials laboratory

Outline

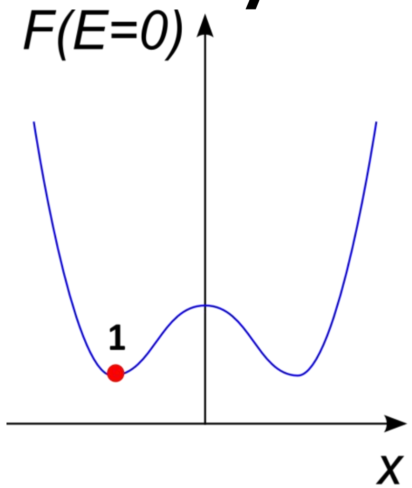
Outline

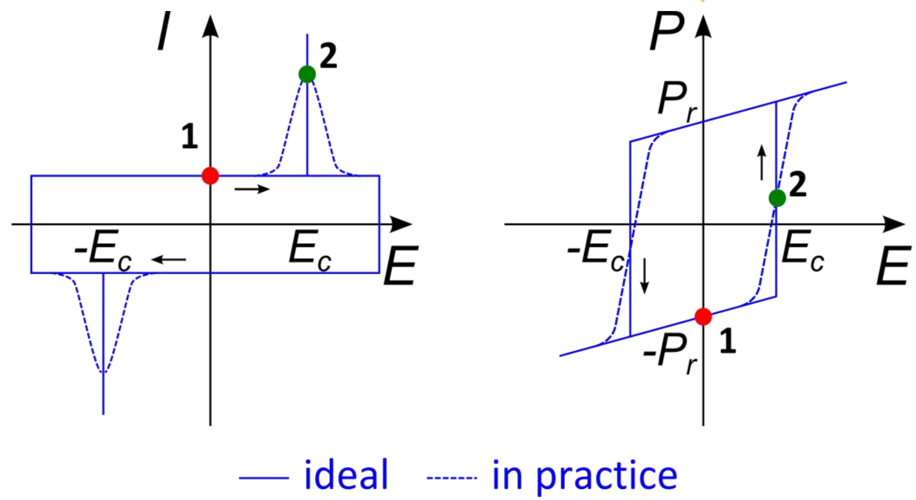
- Introduction
- Basic Characterization
- Simulations on Phase Stability
- Memory Characteristics
- Summary

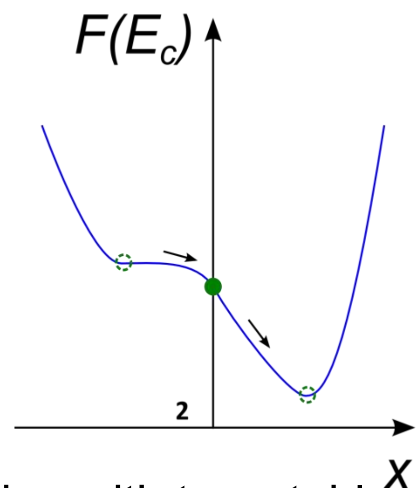
Introduction

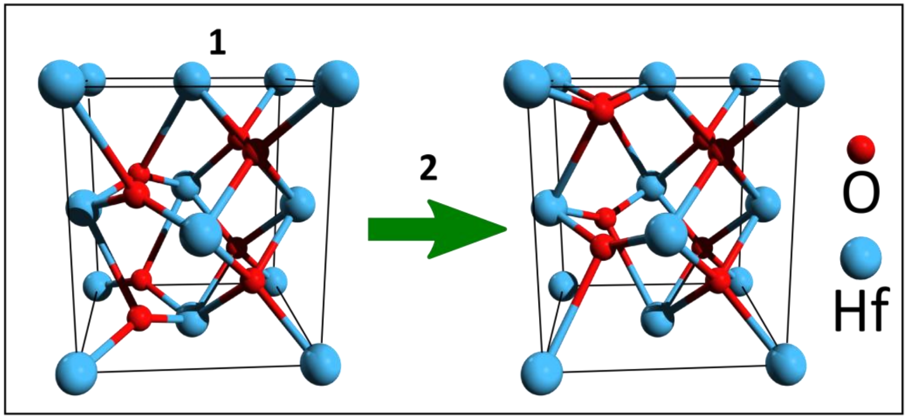
Ferroelectricity

$$P = \frac{1}{A}\int I\left(t\right)\,dt$$









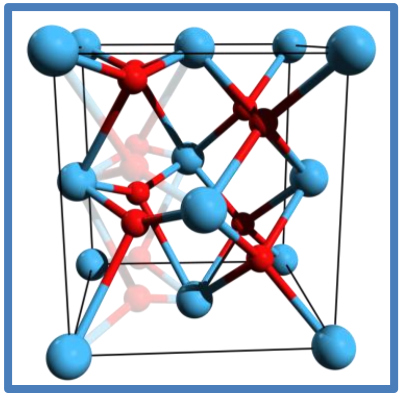
ion with two stable positions in crystal

"position change" of ion → current peak

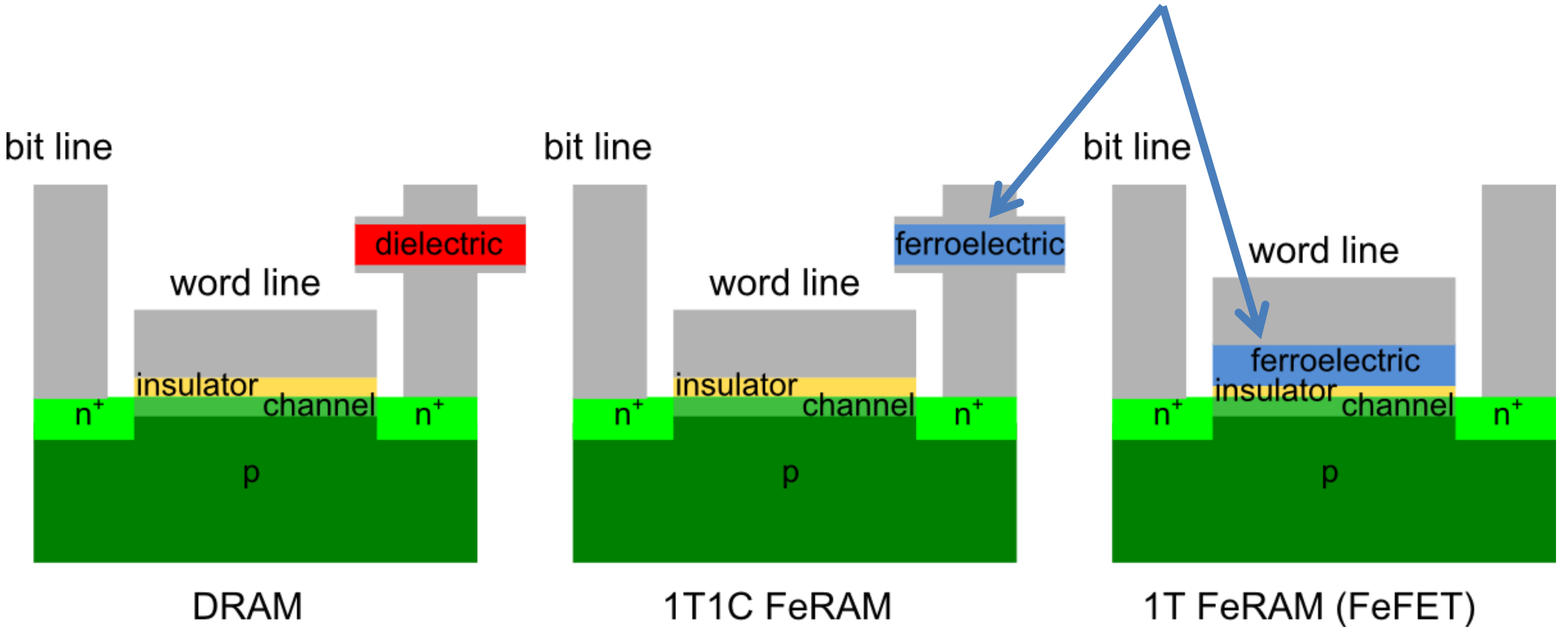
polarization hysteresis

Introduction

Ferroelectric Memories

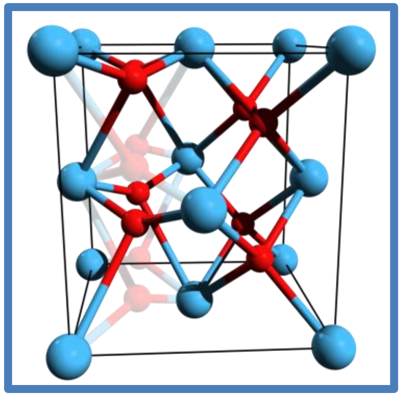


ferroelectric, orthorhombic HfO_2 phase



Introduction

Ferroelectric Memories



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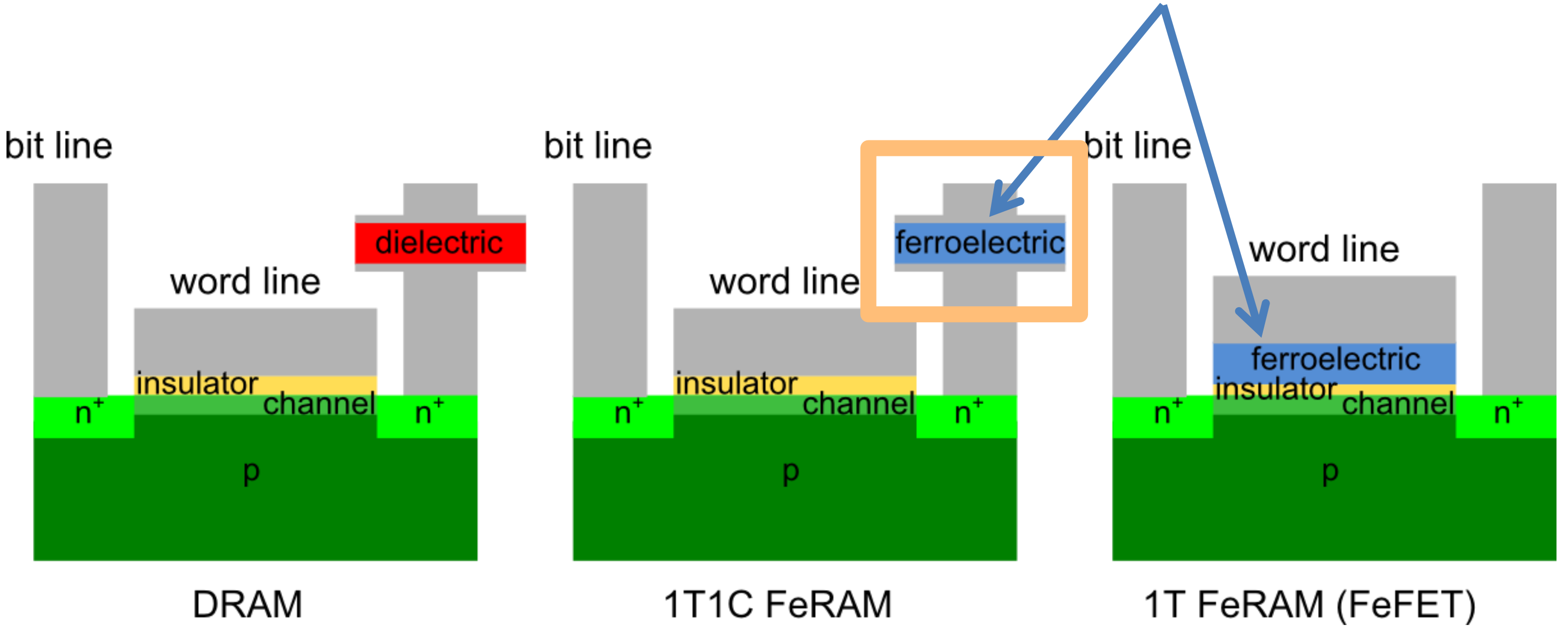
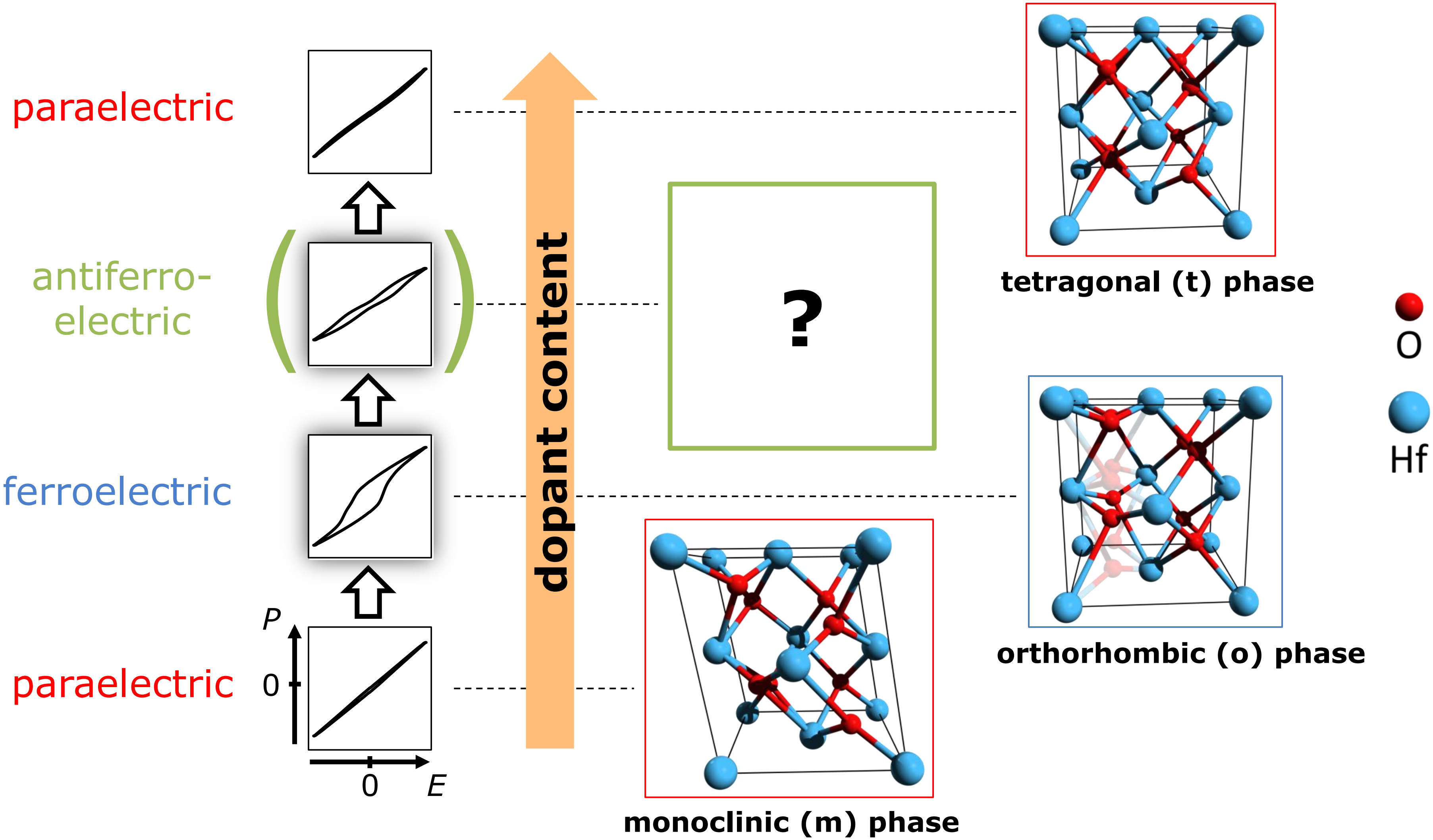


In this work: focus on simple capacitor structures

Introduction

Doping of HfO_2 Induces Ferroelectricity



Introduction

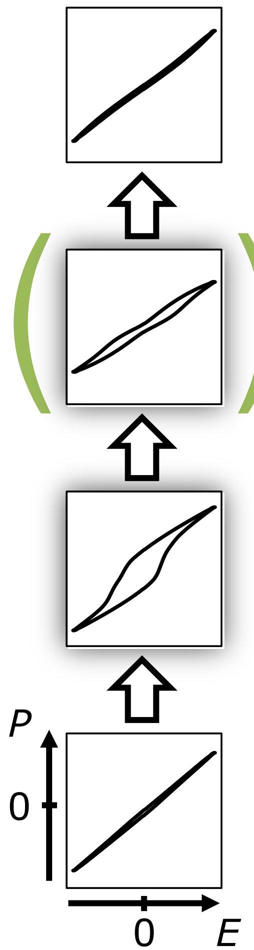
Doping of HfO_2 Induces Ferroelectricity

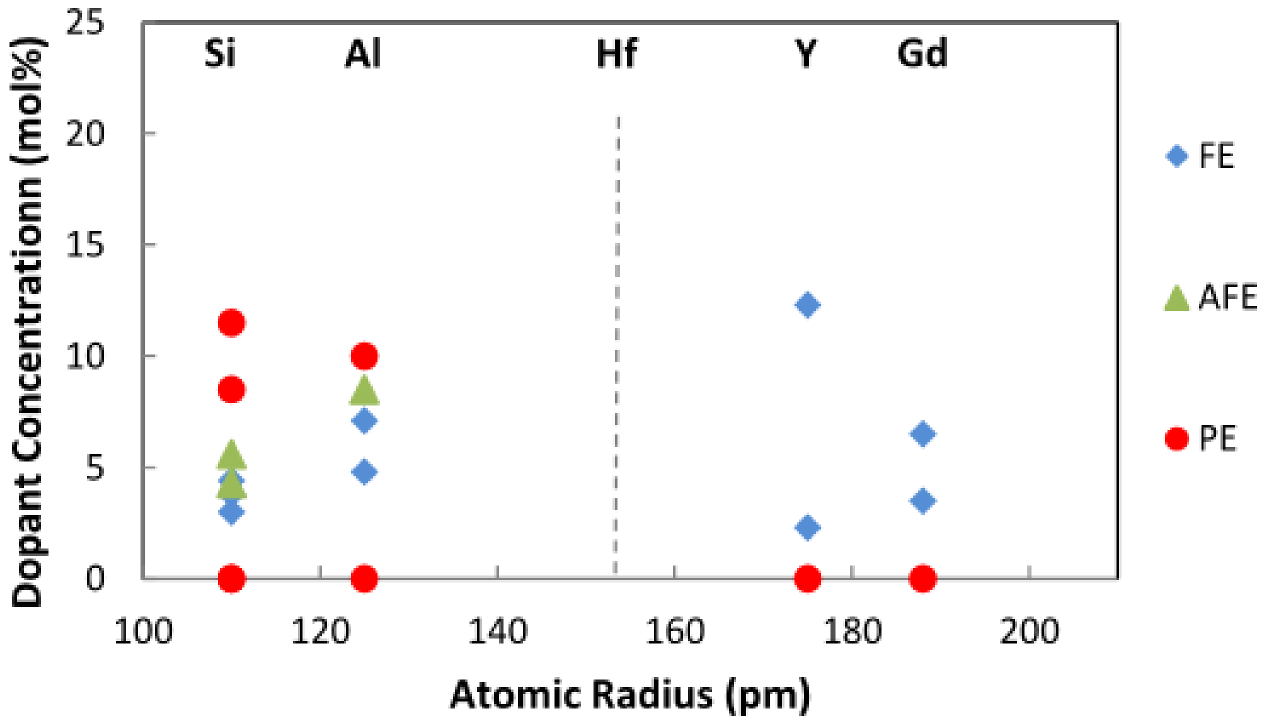
paraelectric

antiferro-
electric

ferroelectric

paraelectric



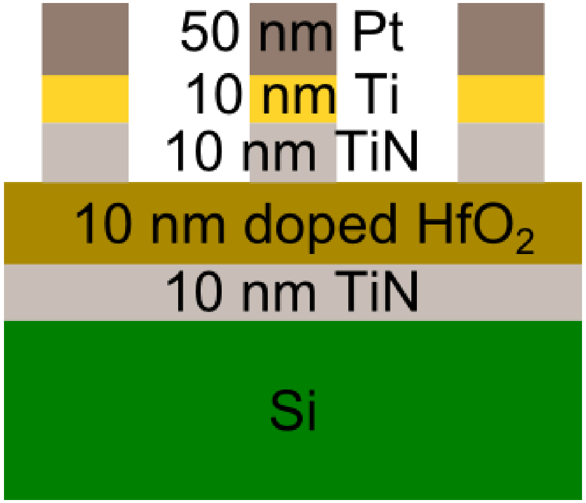


Ref.: U. Schroeder et al., ECS Journal of Solid State Science and Technology, 2 (4) N69-N72 (2013) (modified)

P_r = 10…24 µC/cm², E_c = 1…1.75 MV/cm

Outline

Basic Characterization



Structural

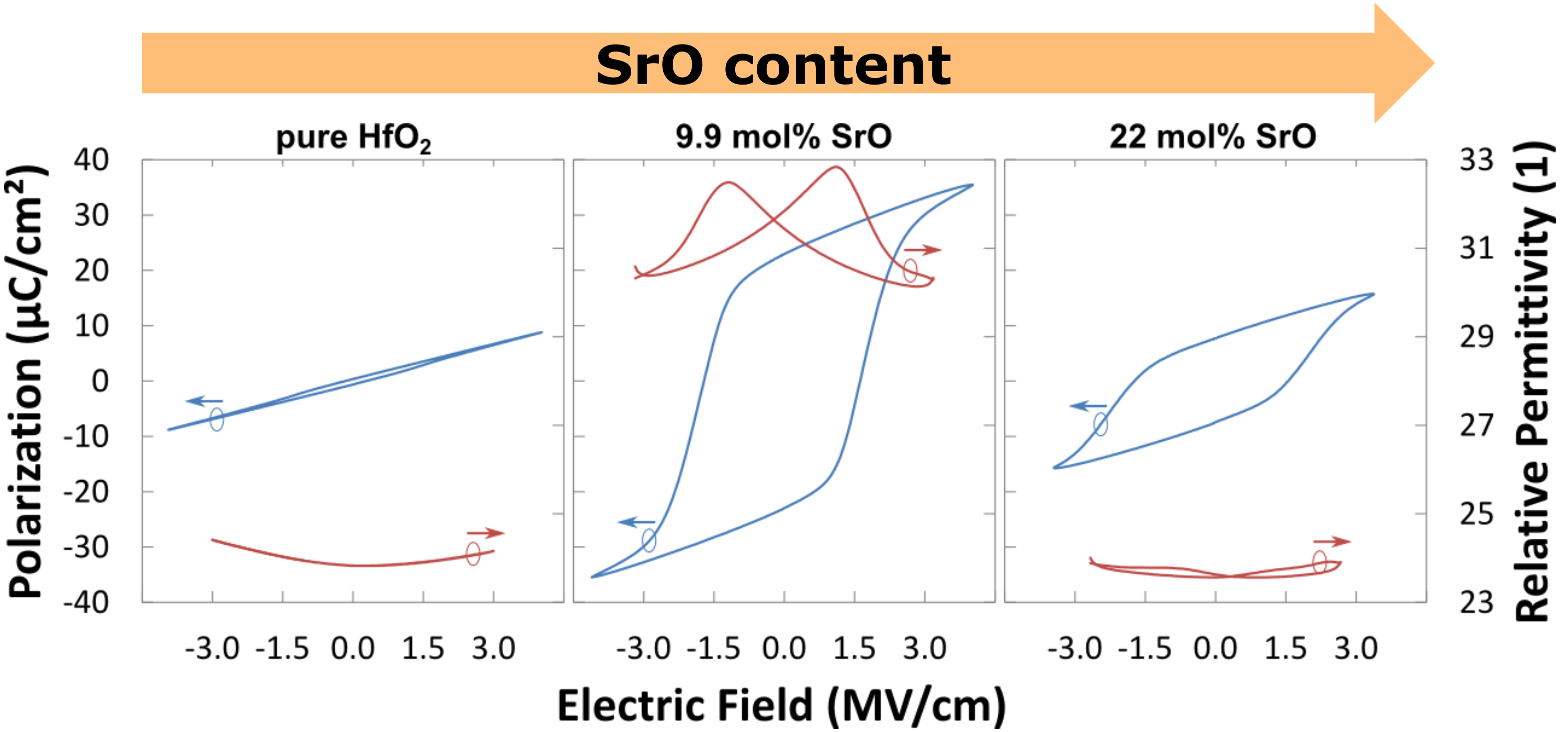
- GIXRD (phases)
- XRR (thickness, density, roughness)

Electrical

- *P*-*E* hysteresis
- small-signal *C*-*V* hysteresis

Basic Characterization

P-*E* and Small-Signal *C*-*V* Measurements (after preconditioning)



- as expected: pure HfO_2 with only barely visible *P*-*E* hysteresis
- clear hystereses for doped HfO_2
- no antiferro-electricity observed

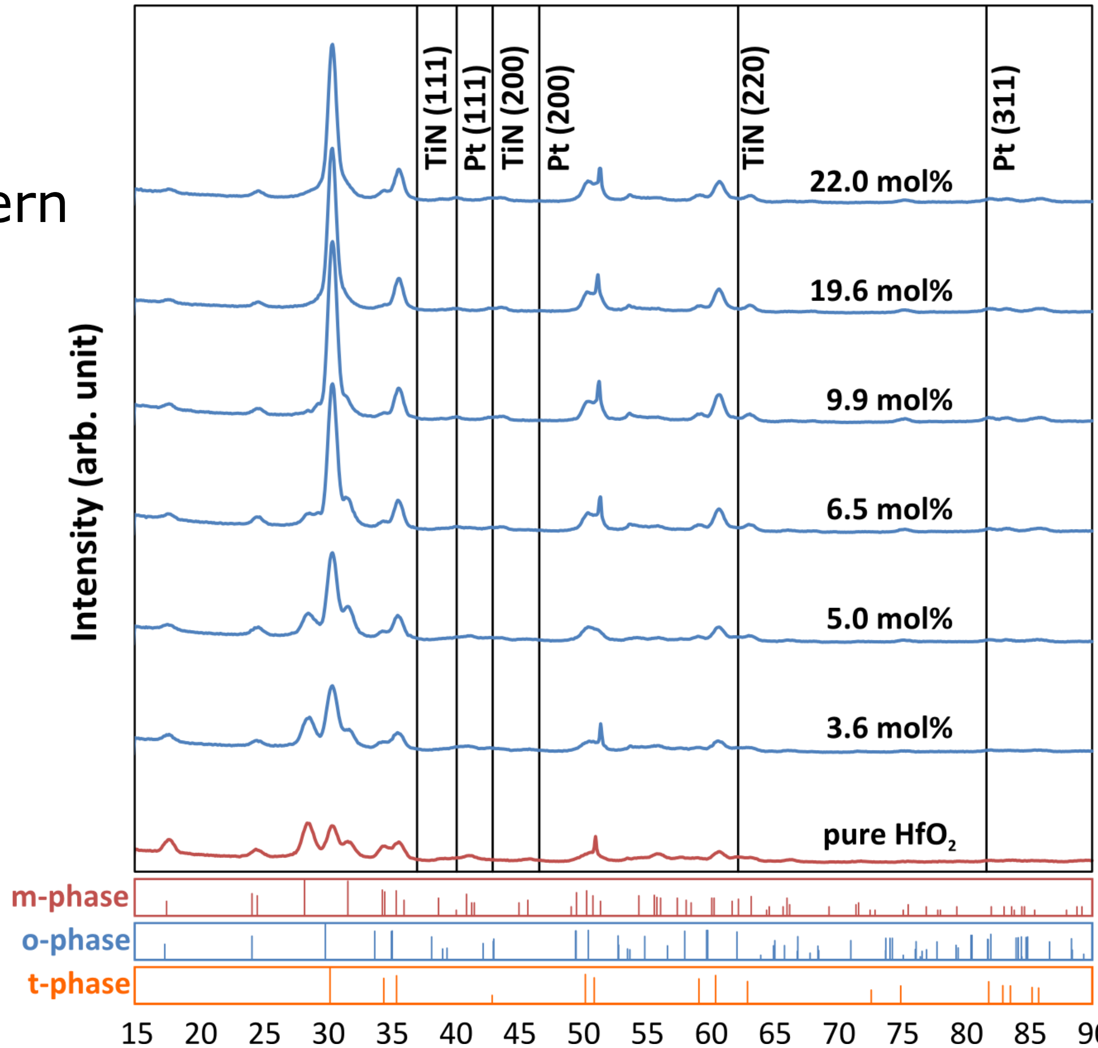
Basic Characterization

Grazing Incidence X-ray Diffraction

- pure HfO_2 with mainly monoclinic (m-phase) pattern

- all doped samples with presumably orthorhombic (o-phase) pattern

→ wide ferroelectric concentration window



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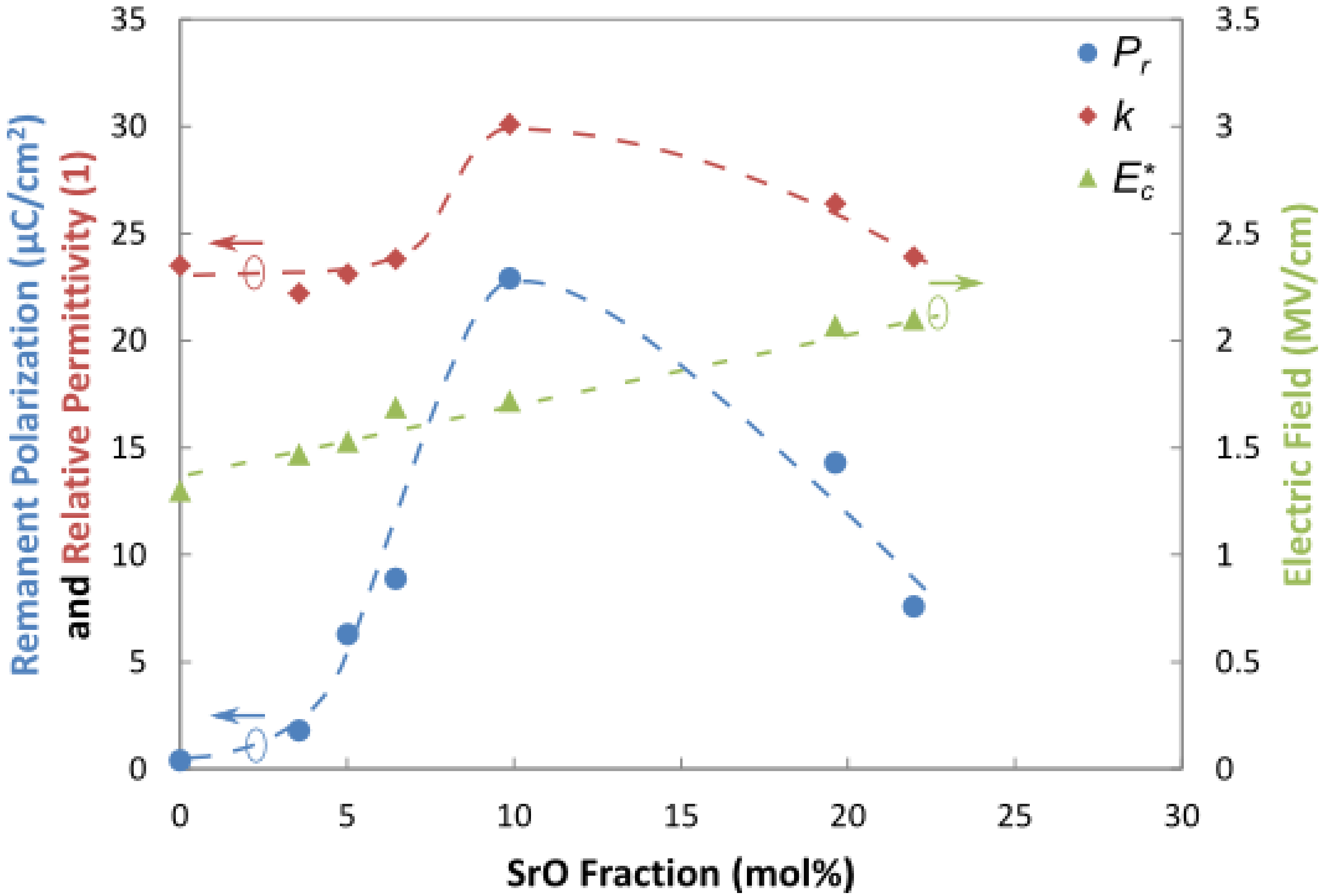
Basic Characterization



- k maximum around P_r maximum
- switching field E_c^* increases with dopant concentration

Outline

Simulations on Phase Stability

$$F = E_{tot} + F_{phon} + F_{surf}$$

free energy
min(F) = stable

total energy
m < o < t

phonon energy
f(T)
t < o < m
simulation: T = 0K

surface energy
t < m

Some Remarks

- at low T, E_{tot} with main effect → m favored
- high T always favors high symmetry phases → t favored
- due to F_{surf}, t-phase observable in thin films even at low T

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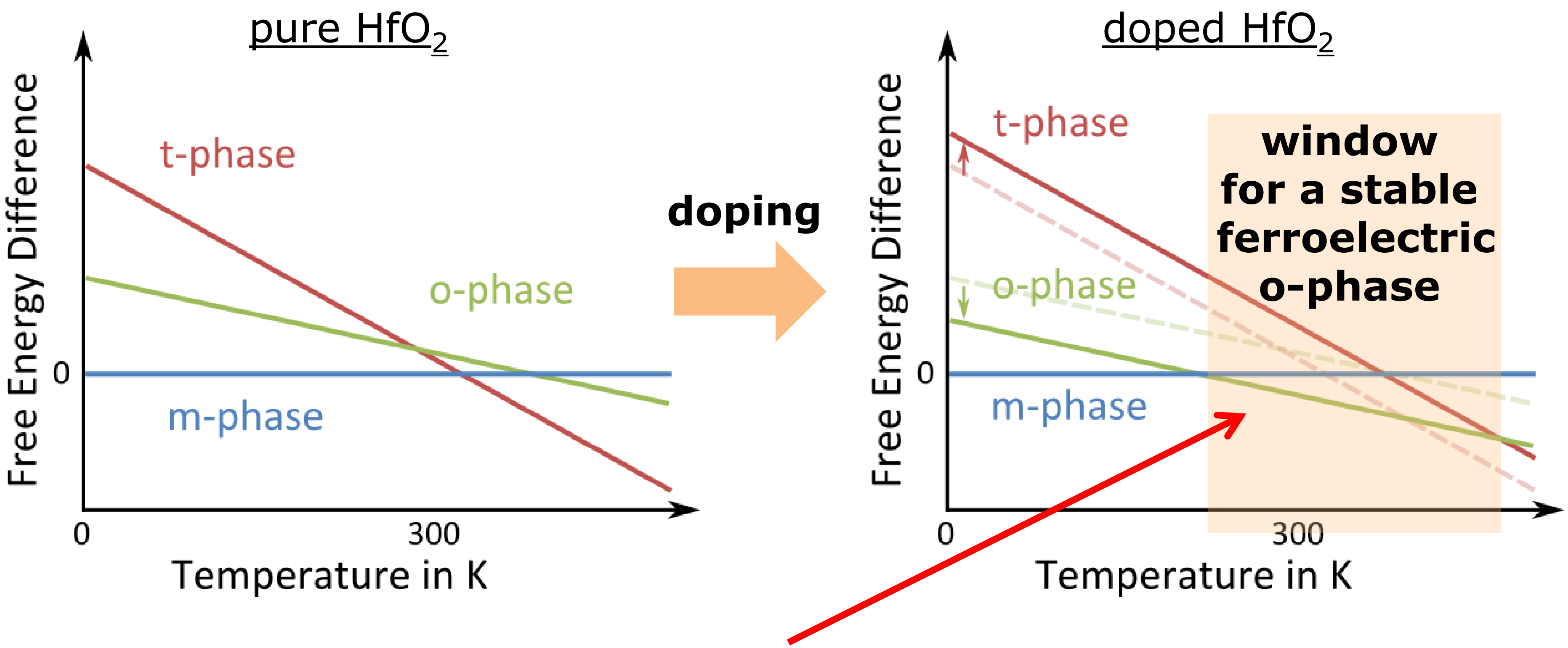
Idea Behind Doping

- change E_{tot}; F_{phon} and F_{surf} are left unaffected
- opening a T window between m and t for a stable o-phase

Simulations on Phase Stability

Sketch of the Idea

- phase with minimal $F(T)$ is stable at this temperature

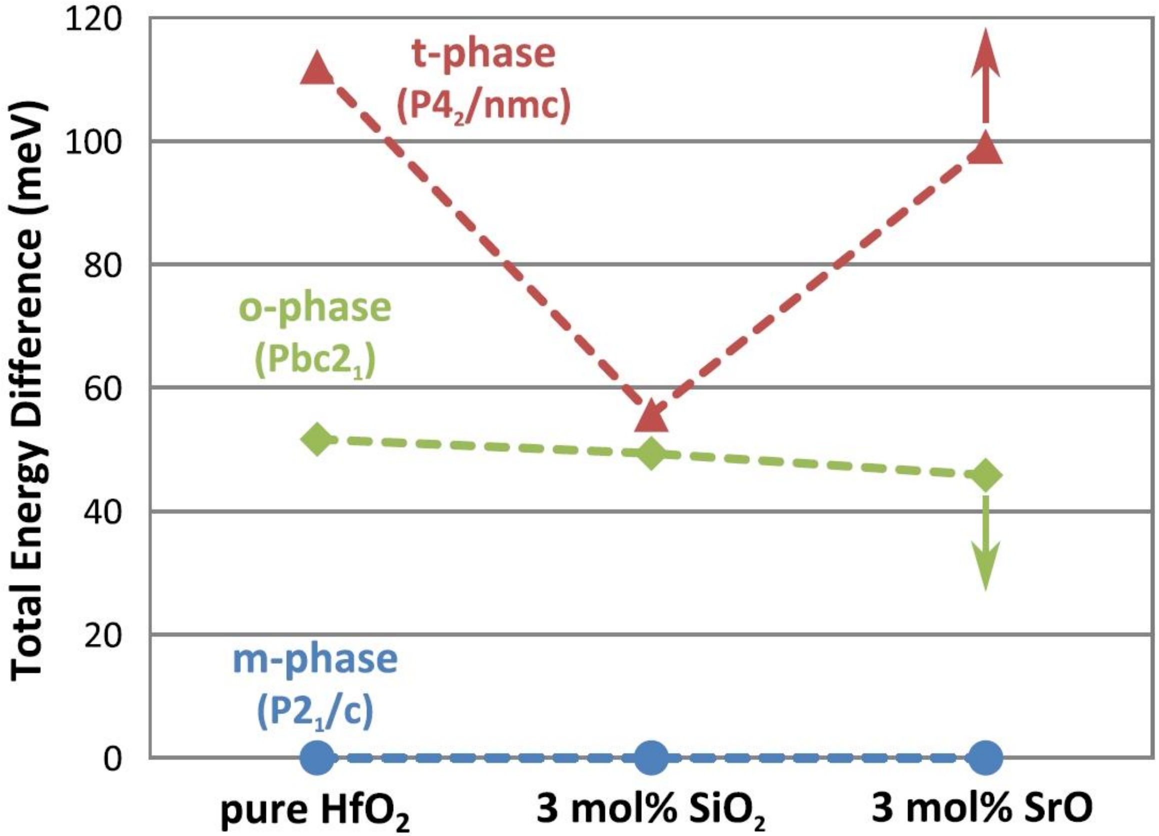


→ doping could open a *T* window for the o phase

Simulations on Phase Stability

Comparison with Si:HfO_2 as the Mostly Studied System

- Si:HfO_2 disadvantageous
  - o favored against m
  - t benefited to a tremendous extend
- Sr:HfO_2 preferable
  - o even more favored against m
  - t not that strongly benefited



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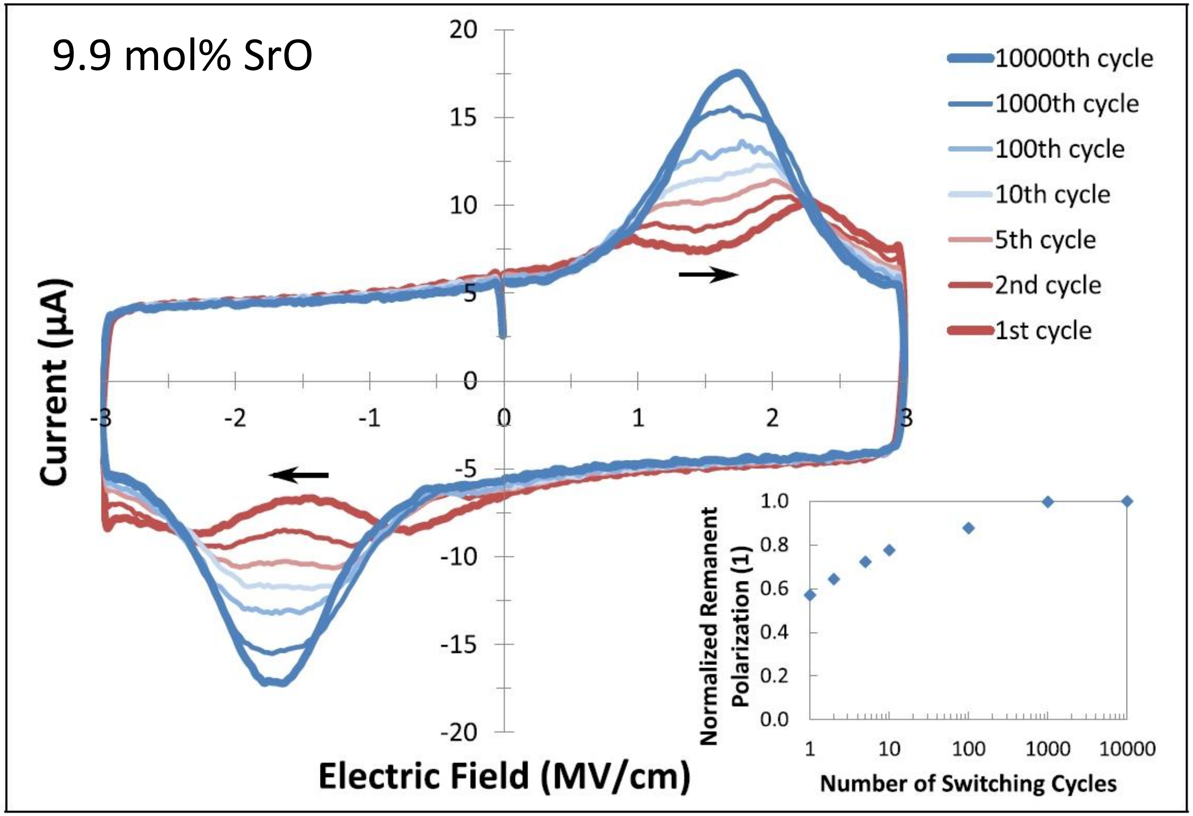
Memory Characteristics

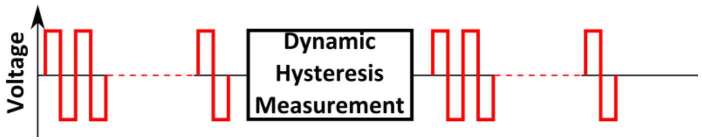
Conditioning Behavior

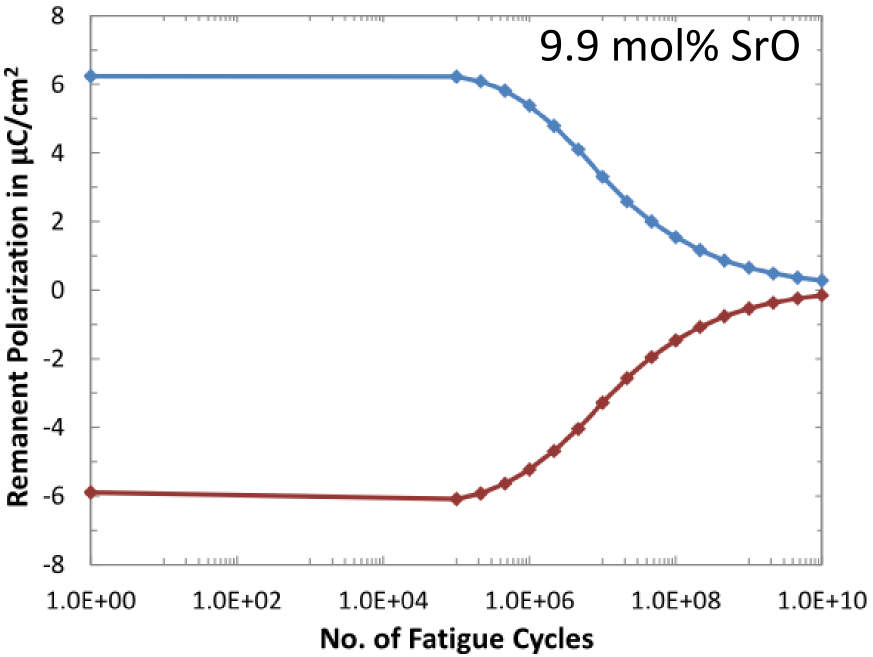


- two initial peaks merge into one single peak after cycling
- preconditioning necessary

Memory Characteristics

Endurance

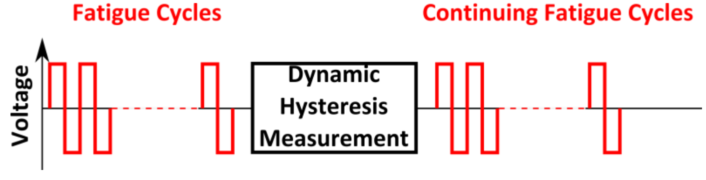


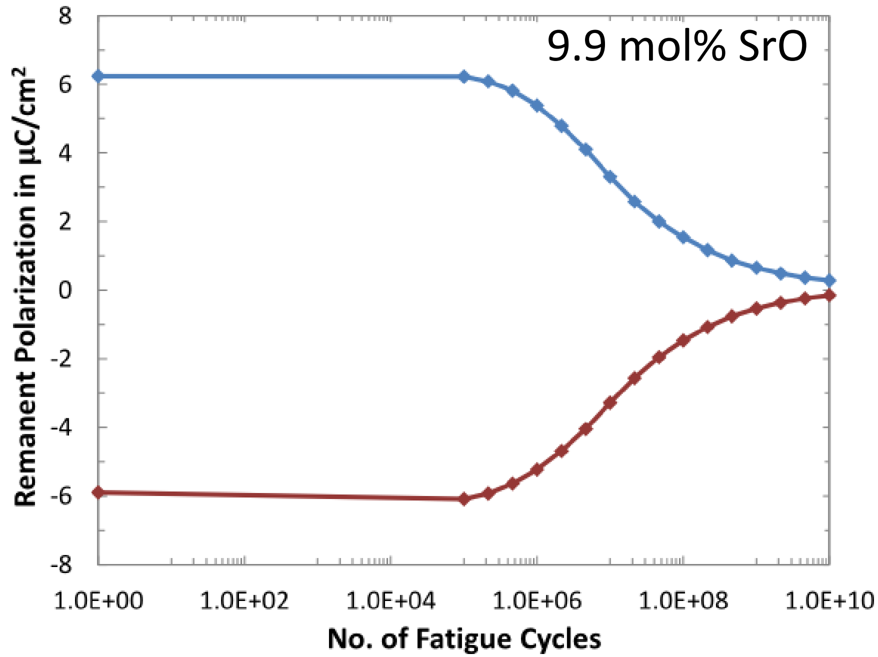


- 80 % of initial P_r after 10^6 cycles

Memory Characteristics

Endurance





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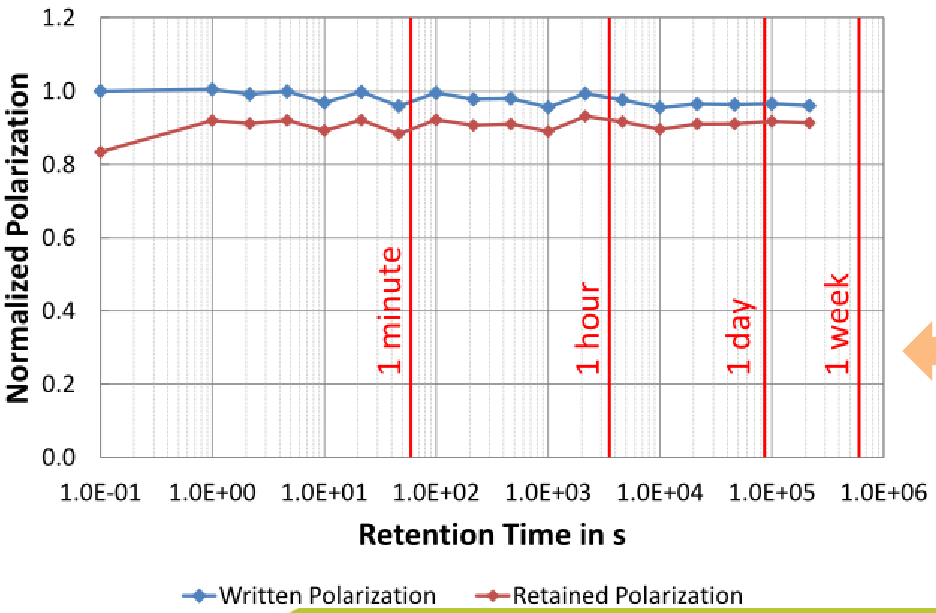
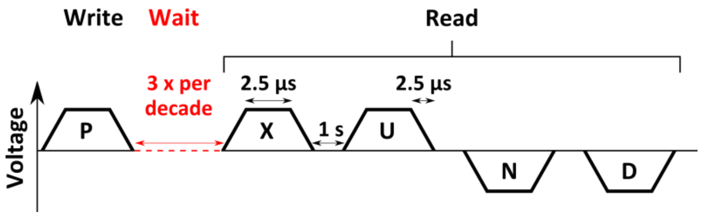


Retention



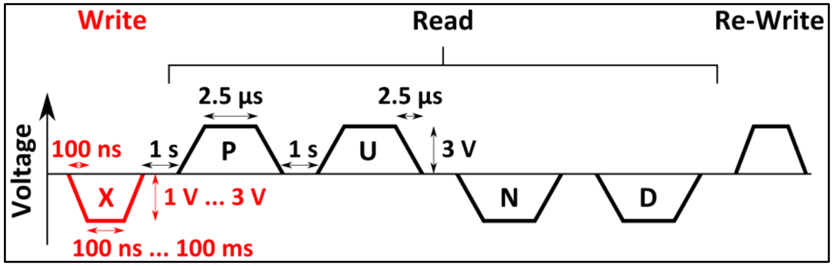
- > 90 % of P_r still retained after ~ 60 hours

Memory Characteristics

9.9 mol% SrO

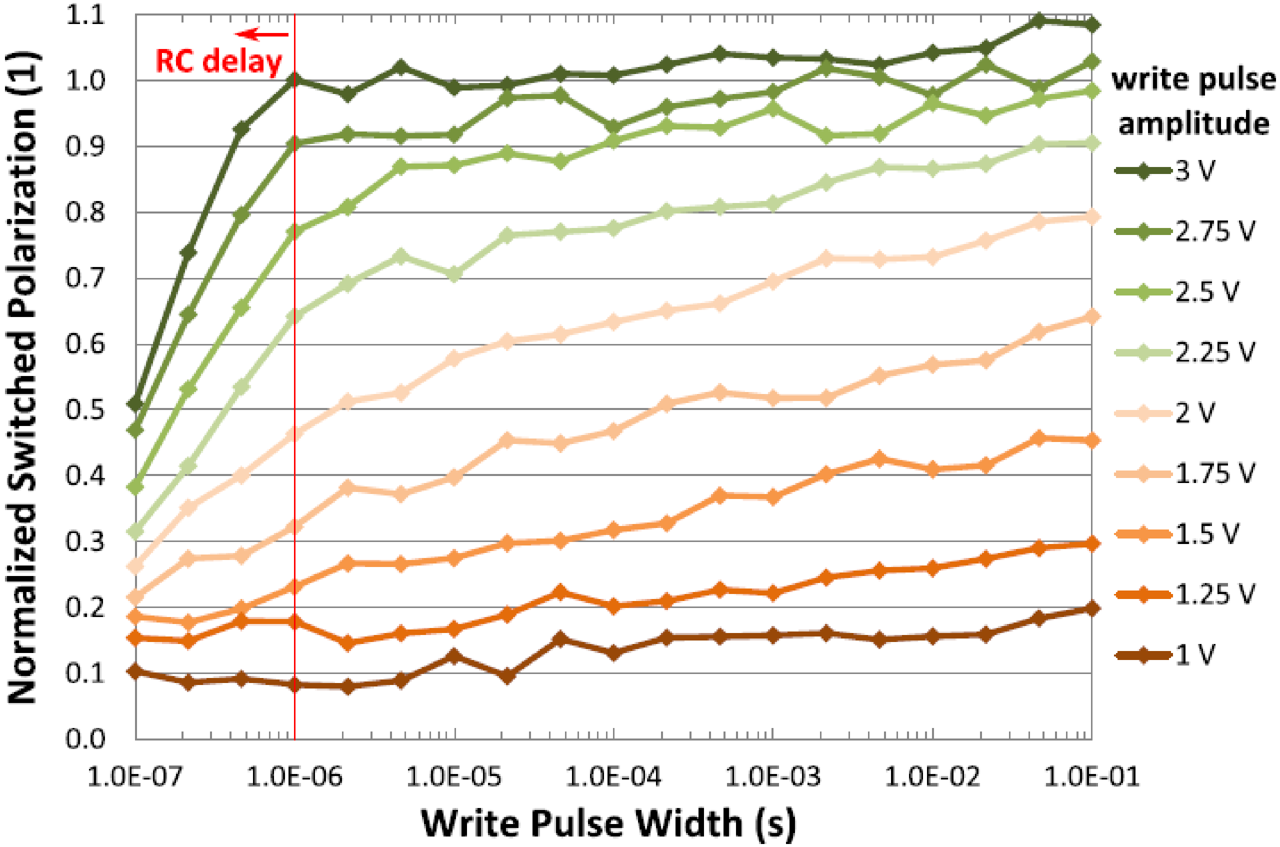
Switching Speed (PUND)

write pulse variation



- plateau widths: 100 ns … 100 ms
- pulse amplitudes: 1 V … 3 V

→ writing times below 1 µs possible



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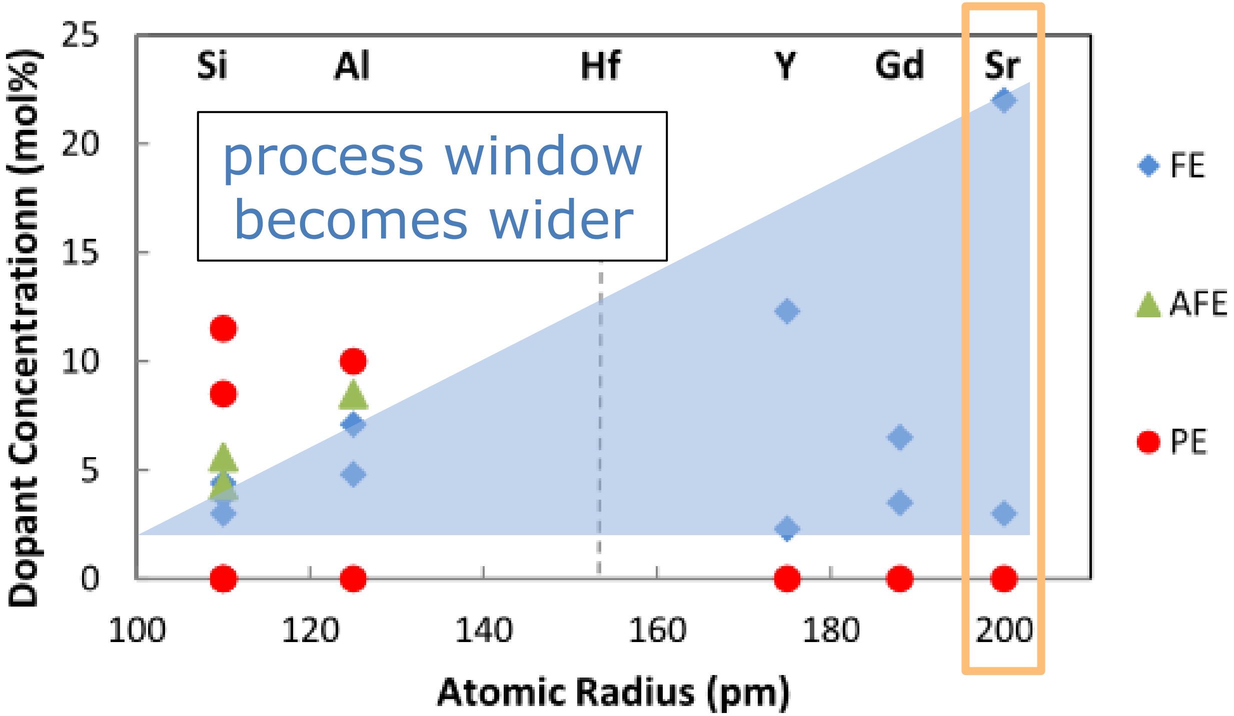
Summary and Outlook

Sr is up to Now…

- only bivalent dopant
- biggest dopant



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Benefits of Sr:HfO$_2$

- P_r up to 23 µC/cm^2
- $E_c \approx 2$ MV/cm
- wide FE mol% range
- switching in ns range
- retention proven up to ~ 60 hours
- endurance: 80% of P_r still retained after 10^6 cycles

Thanks for your attention!

ACKNOWLEDGMENTS

Many thanks to the NaMLab Ferro-Group and our cooperation partners at the Imec, Leuven and the Munich University of Applied Sciences for all the valuable discussions and their contributions to this work.

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Back up

Ferroelectricity

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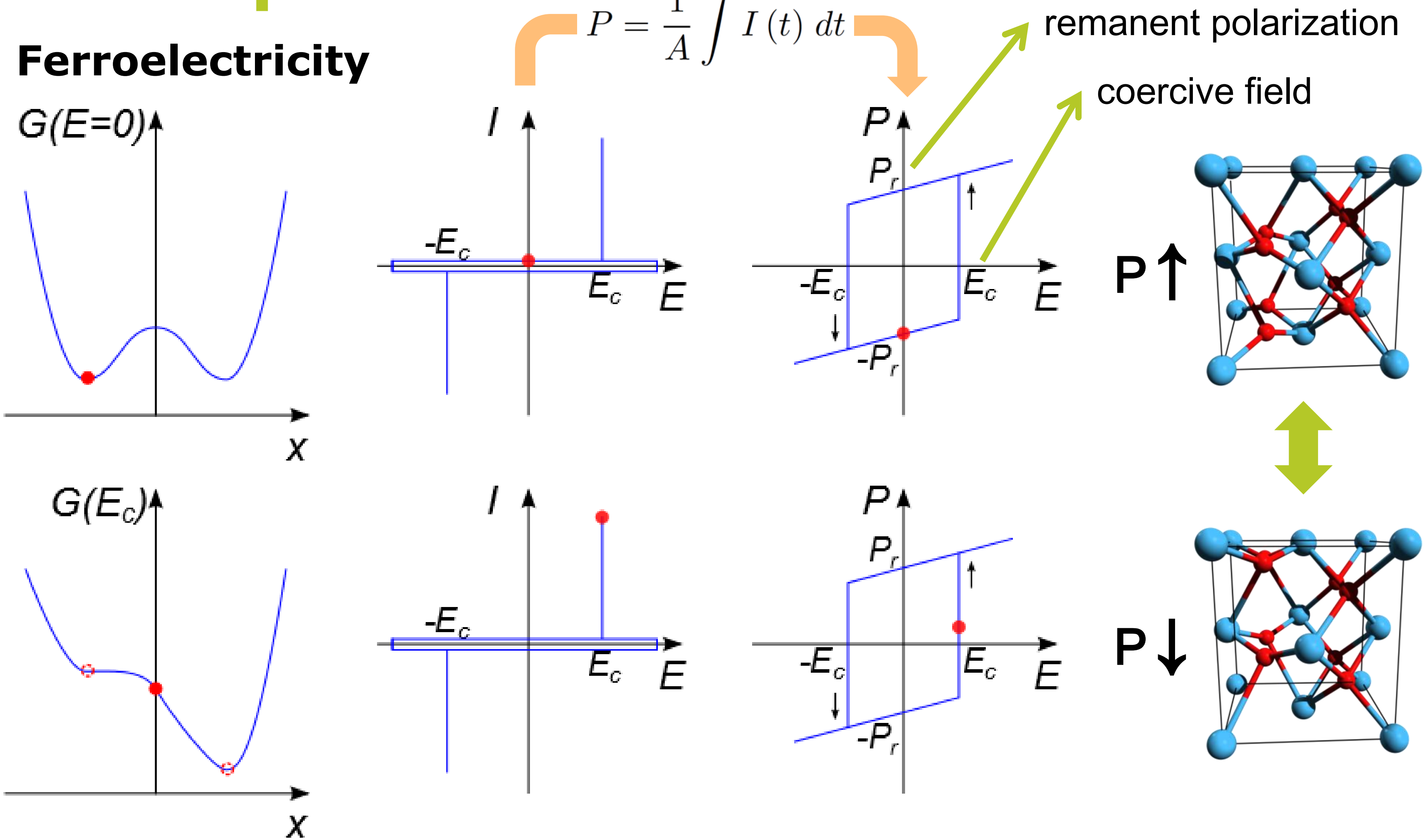


ion with two stable positions in crystal

“position change” of ion → current peak

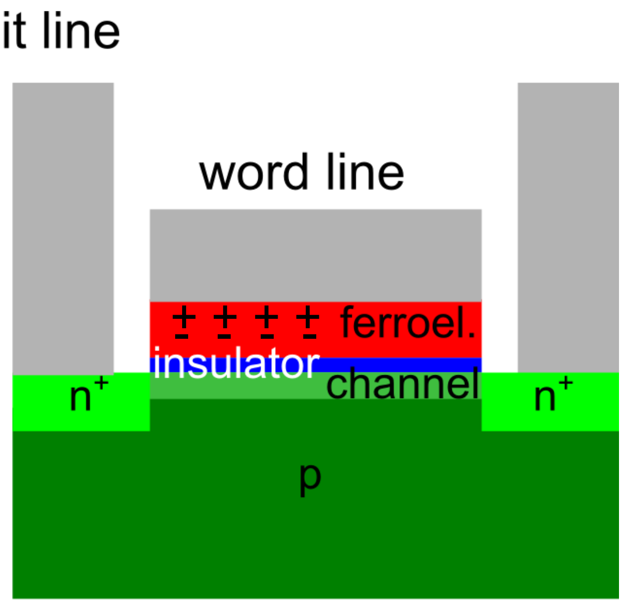
Polarization-hysteresis

orthorhombic HfO_2

Back up

Functional Principle of a FeFET

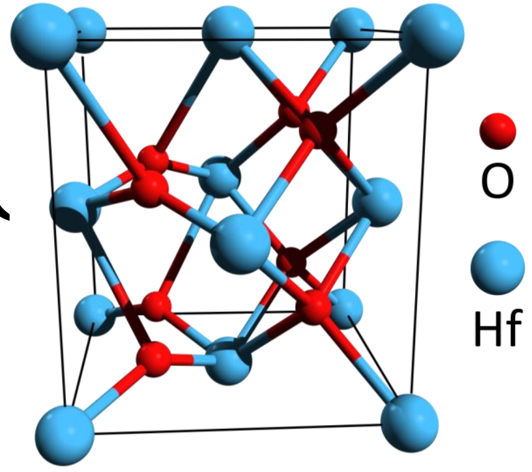
- gate voltage switches polarization of the ferroelectric
- remanent electric field shifts threshold voltage of the transistor

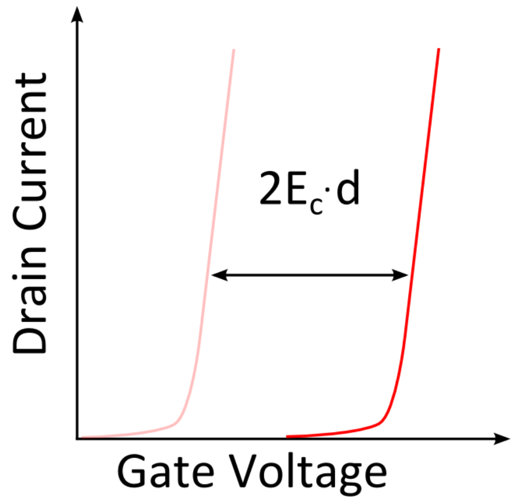


1T FeRAM (FeFET)

HfO_2 in Orthorhombic Phase

P↑





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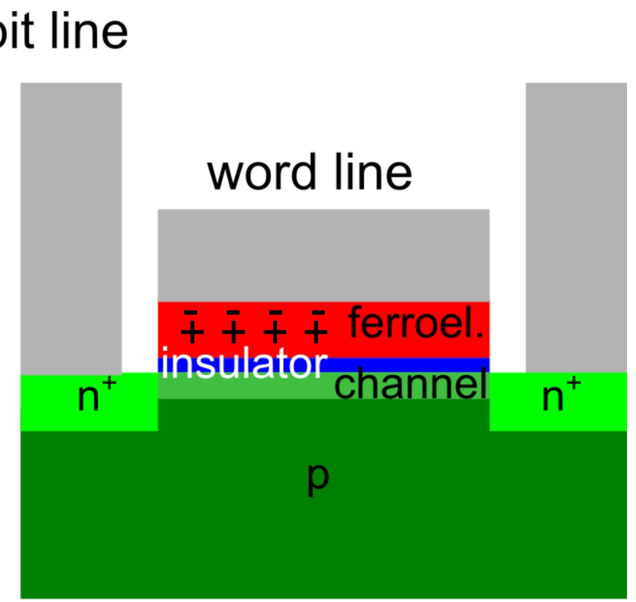
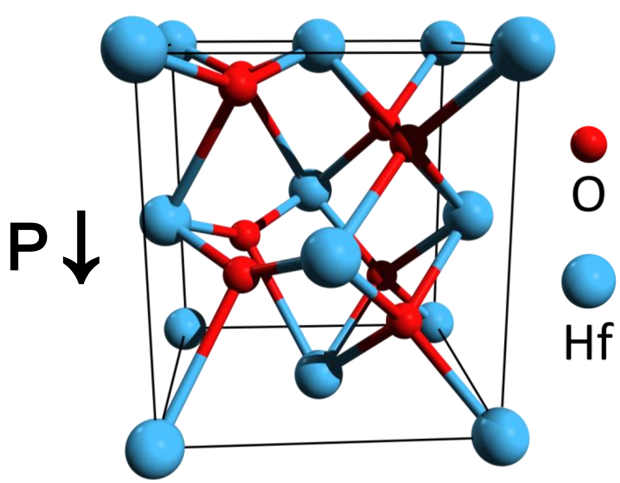


1T FeRAM (FeFET)

HfO_2 in Orthorhombic Phase



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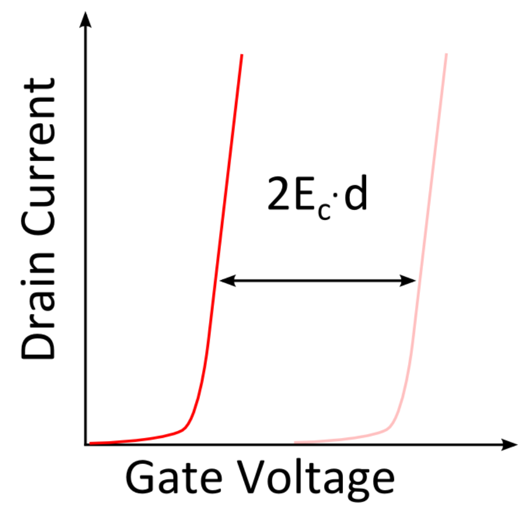

Back up

Reasons for the Claim of a Ferroelectric Phase

1. *P*-*E* hystereses exhibit concave areas
2. *k*-*V* hystereses with peaks and according to *P*-*E* hystereses
3. hystereses and maximum in *k* value at transition from monoclinic to tetragonal/cubic
4. films exhibit piezoelectricity
5. GIXRD: triplet between $2\theta = 82°$ and 87° → further phase(s)
6. FeFET → shift in of V_{th} not to be explained by trapping
7. remarkable retention for a film stack that was not designed like a flash stack
8. typical wake up and fatigue behavior