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EMD ELECTRONICS

Tuning coercive field and polarization in inherently ferroelectric HZO film deposited using HfD-04 and ZrD-04

Raisul Islam, San Jose, CA, 06/29/2021

Martin McBriarty, Mario Laudato, Ryan Clarke, Son Hoang,
Charlene Chen, Ganesh Panaman and Karl Littau

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ALD 2021
21st International Conference on Atomic Layer Deposition
JUNE 27-30, 2021 • VIRTUAL MEETING

EMD ELECTRONICS

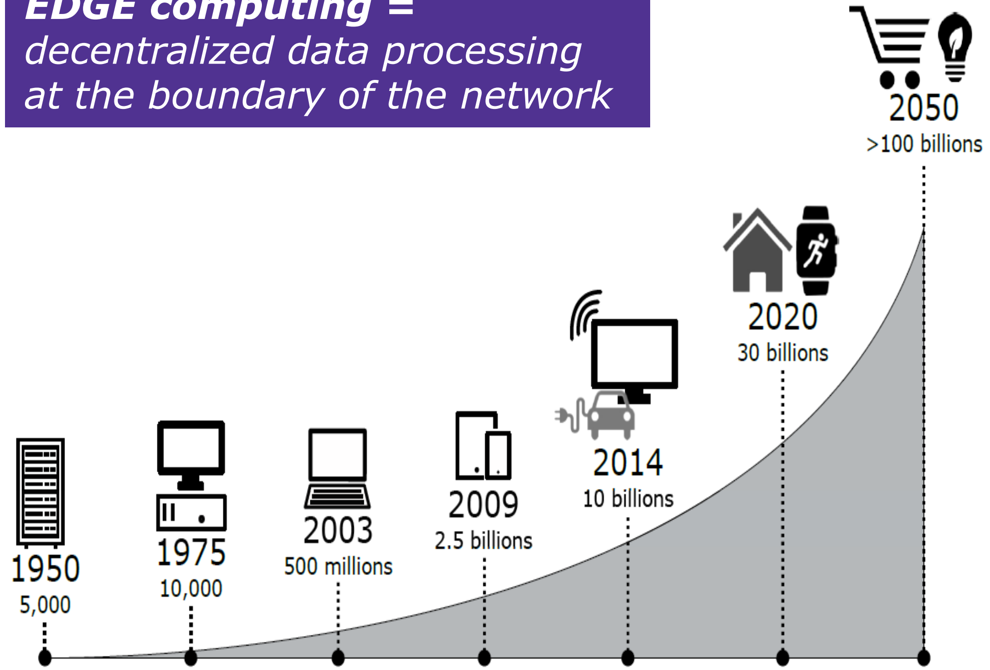
Agenda

From the cloud to the edge
AI will be needed away from servers

Why do we need Edge AI?

30bn IoT devices fueling the edge 2020

EDGE computing =
decentralized data processing
at the boundary of the network



Source: Maurizio Capra, Future Internet 2019, 11, 100

"Fundamentally because that's where all the data is!"

Airbus A-350 jet has over 6,000 sensors and generates **2.5 terabytes** of data each day it flies

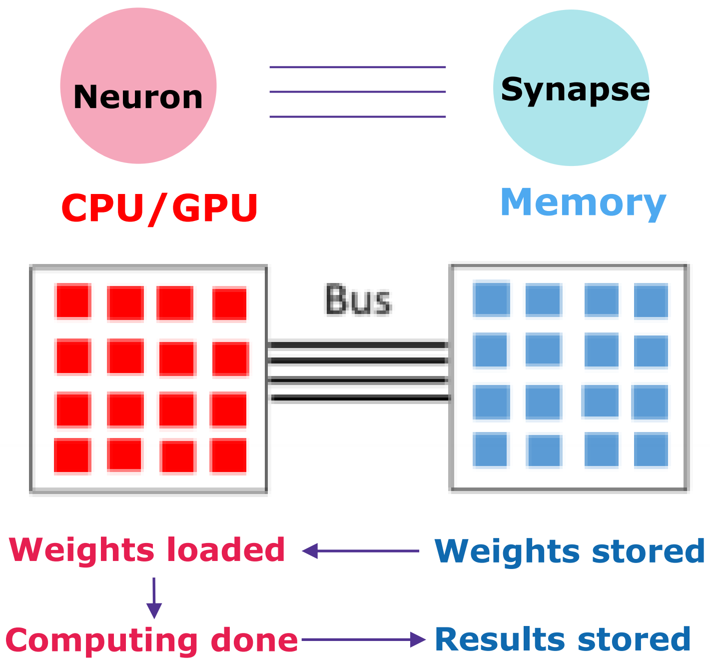
Globally security cameras create about **2,500 petabytes** of data per day

If everybody used their Android Voice Assistant for **3 min per day** they would have **to double** the number of data centers they owned.

Source: Deloitte, TMT Predictions 2020 ; Pete Warden, Google

Challenge in today's hardware
Memory Wall Bottleneck

- In traditional computers, the synaptic weights are stored in memory, and the computation happens in a logic core on a CPU or GPU. **The weights must be transferred back and forth from memory**.
  - Traditional CPUs **have off-chip memory**.
  - GPUs have large on-chip memory, but it is **mostly SRAM** which is expensive and inadequate.



The impact of compute element and memory element separated by a slow bus:

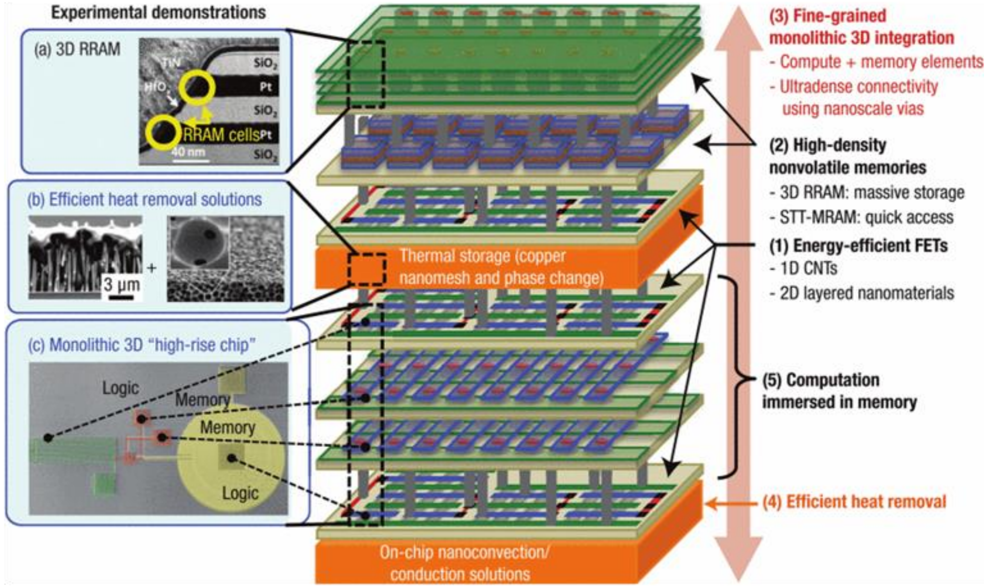
1) **Energy inefficiency**
2) **Bandwidth bottleneck**
3) **Inadequate size of cache memory**

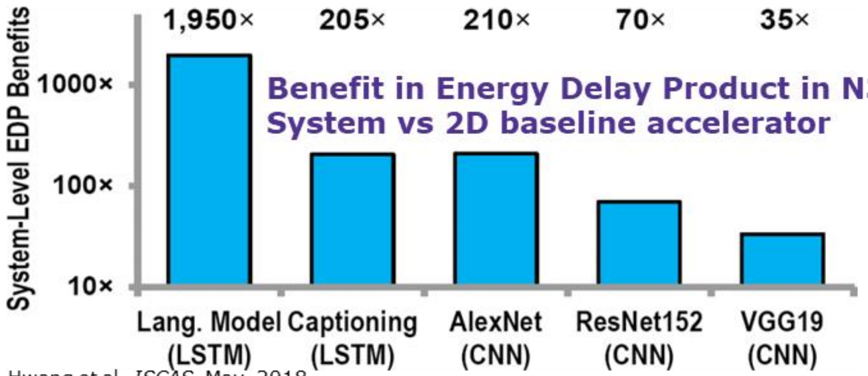
Near-memory Computing Solution
Fine Grained Connectivity of Logic with Large On-chip Memory

Bringing memory and logic close to each other is the Key

Technology Enablers	Potential Solution
Energy Efficient Digital Logic	2D TMD Materials, BEOL Transistors
On-Chip Memory	BEOL Compatible, Low Energy, Fast Access Scalable Non-Volatile Memory
Ultra-Dense Fine-Grained 3D Integration	New Metals, Selective ALD for via filling

Proposed monolithic 3D integrated N3XT system by Stanford University



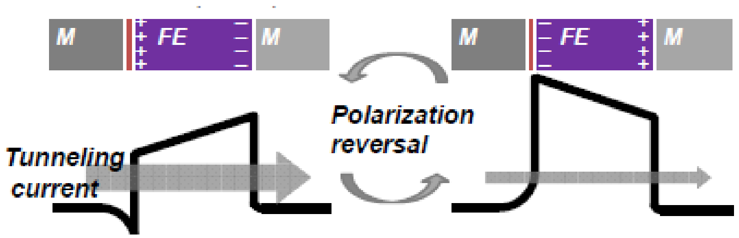


W. Hwang et al. *ISCAS*, May. 2018

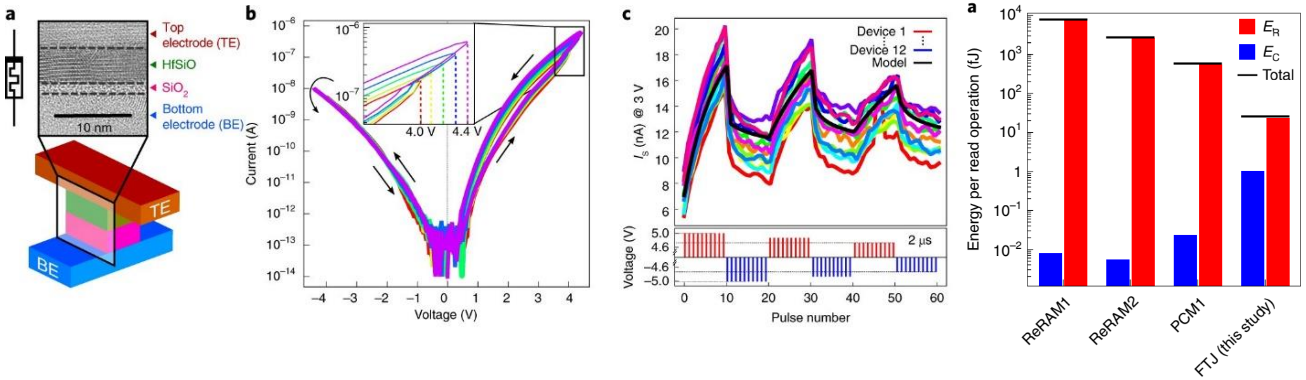
Low Power On-Chip Memory Solution
Ferroelectric Memory: FTJ and FeFET

Ferroelectric Tunnel Junction (FTJ)

Barrier height is modulated by a change in polarization, inducing a resistance switch



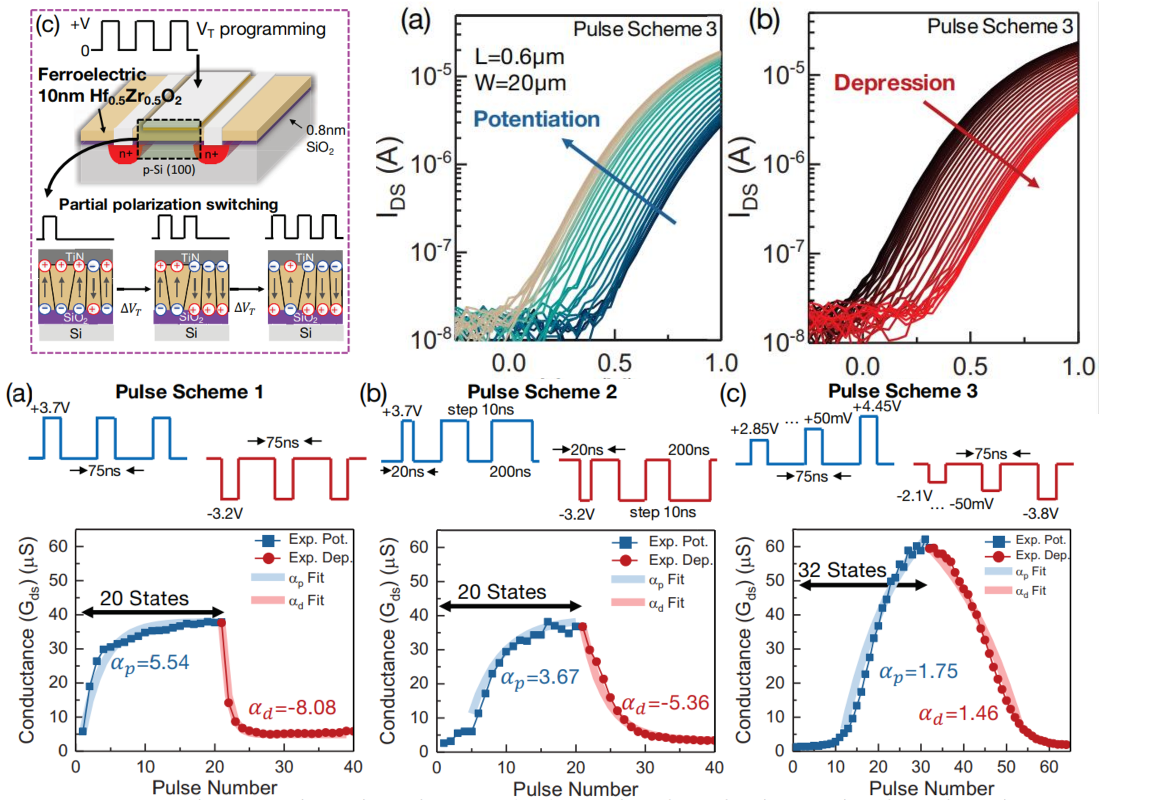
Fujii et. al., Toshiba, 2016 Symposium on VLSI Technology Digest of Technical Papers



Berdan, R. et al. (Kioxia) Nat. Electron. (2020) https://doi.org/10.1038/s41928- 020-0405-0

Ferroelectric FET(FeFET)

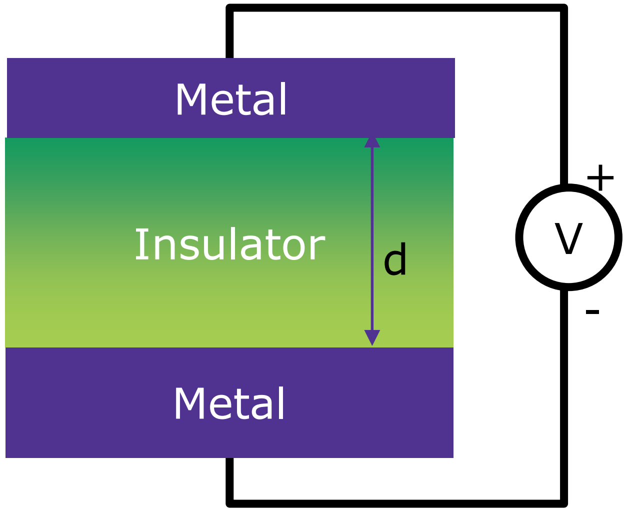
Channel conductance is modulated by switching the threshold voltage of the transistor by switching FE gate polarization

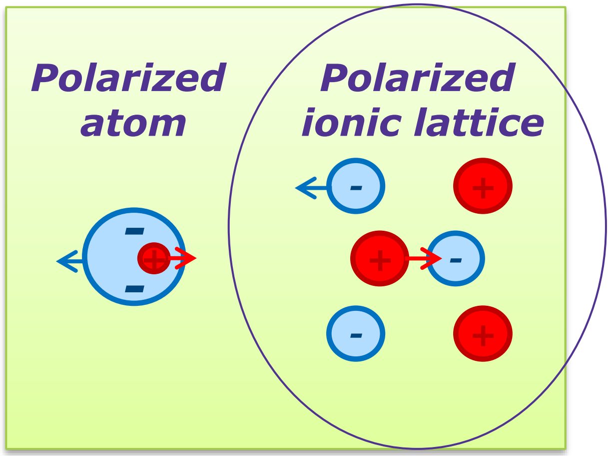


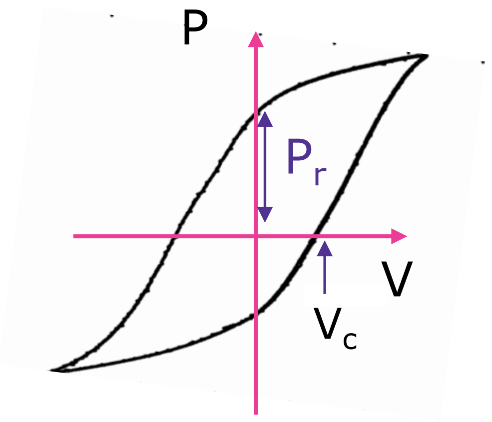
M. Jerry et al. (Univ. Notre Dame) IEDM (2017) https://doi.org/10.1109/IEDM.2017.8268338

Ferroelectric Materials
Basic Physics

Ferroelectric materials are non-linear capacitors.







Ferroelectrics have an apparent “stored charge” called the “remnant polarization,” P_r
The electric field that is required to flip the electric dipole is called the coercive field $E_c=V_c/d$

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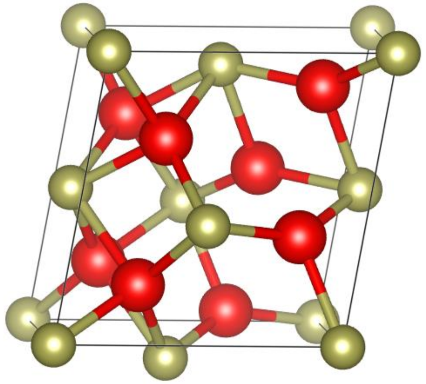
Ref: V. K. Narasimhan, ALD/ALE 2020

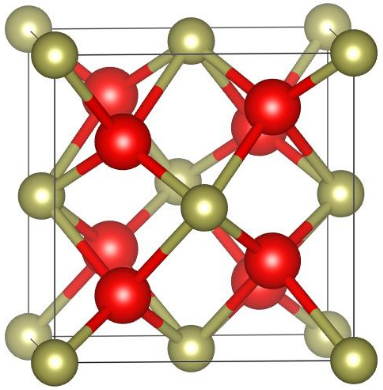
HfO_2 as Ferroelectric Materials
Basic Crystallography

Monoclinic phase ($P2_1/c$)



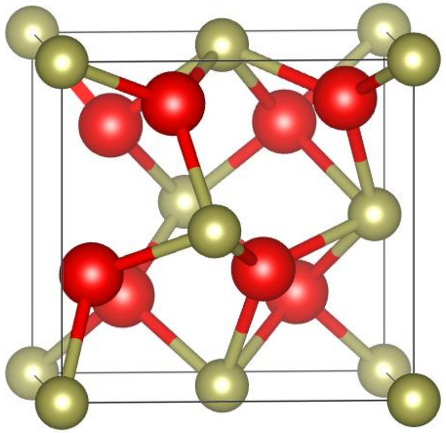
- The *most stable phase* at room temperature and standard pressure
- Not Ferroelectric

Tetragonal phase ($P4_2/nmc$)



- Has a very high dielectric constant
- Anti-ferroelectric-like behavior

Orthorhombic phase ($Pca2_1$)



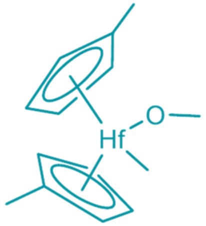
- Metastable Structure
- Non-centrosymmetric
- Ferroelectric phase

Dopants such as Zr, La, Y, Gd, Si are important to stabilize the orthorhombic phase

Overview of HfD-04 and ZrD-04 precursors

ALD of $Hf_{0.5}Zr_{0.5}O_2$

Alternate cycles of HfD-04 and ZrD-04 precursors are used with ozone reactant pulsing in between



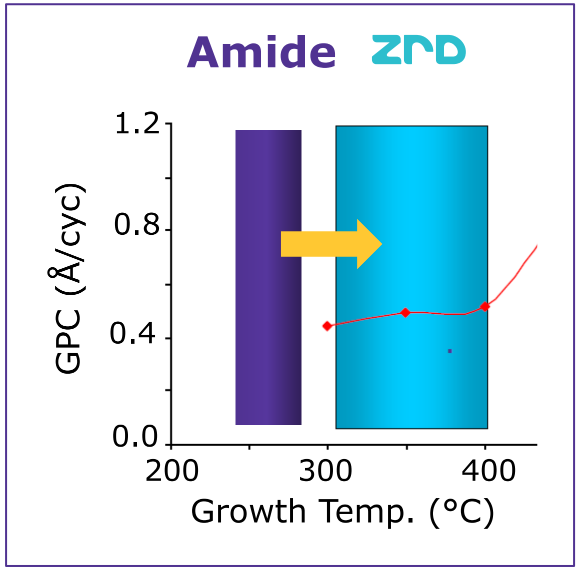
HfD-04: bis(methylcyclopentadienyl)methoxymethylhafnium

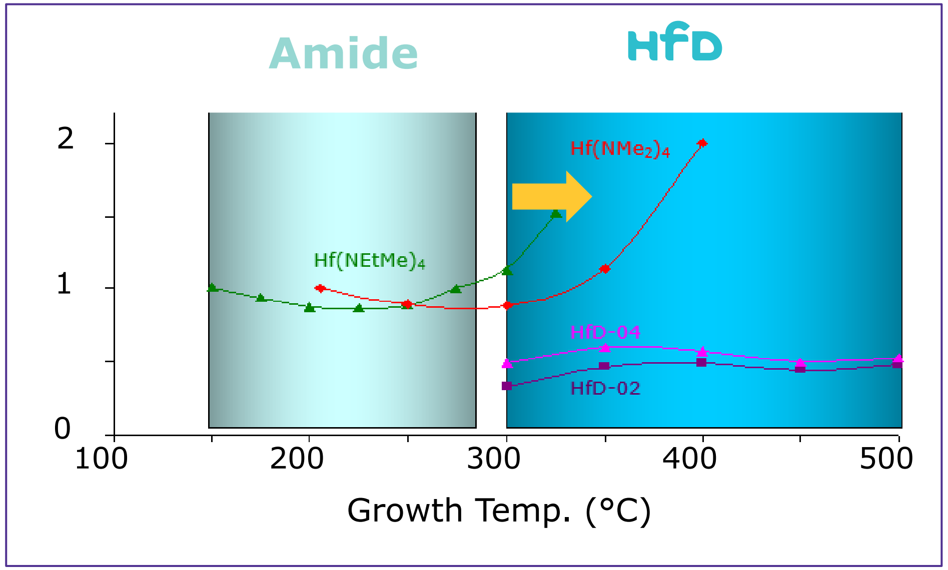
ZrD-04 : bis(methylcyclopentadienyl)methoxymethylzirconium

The goal of this work is

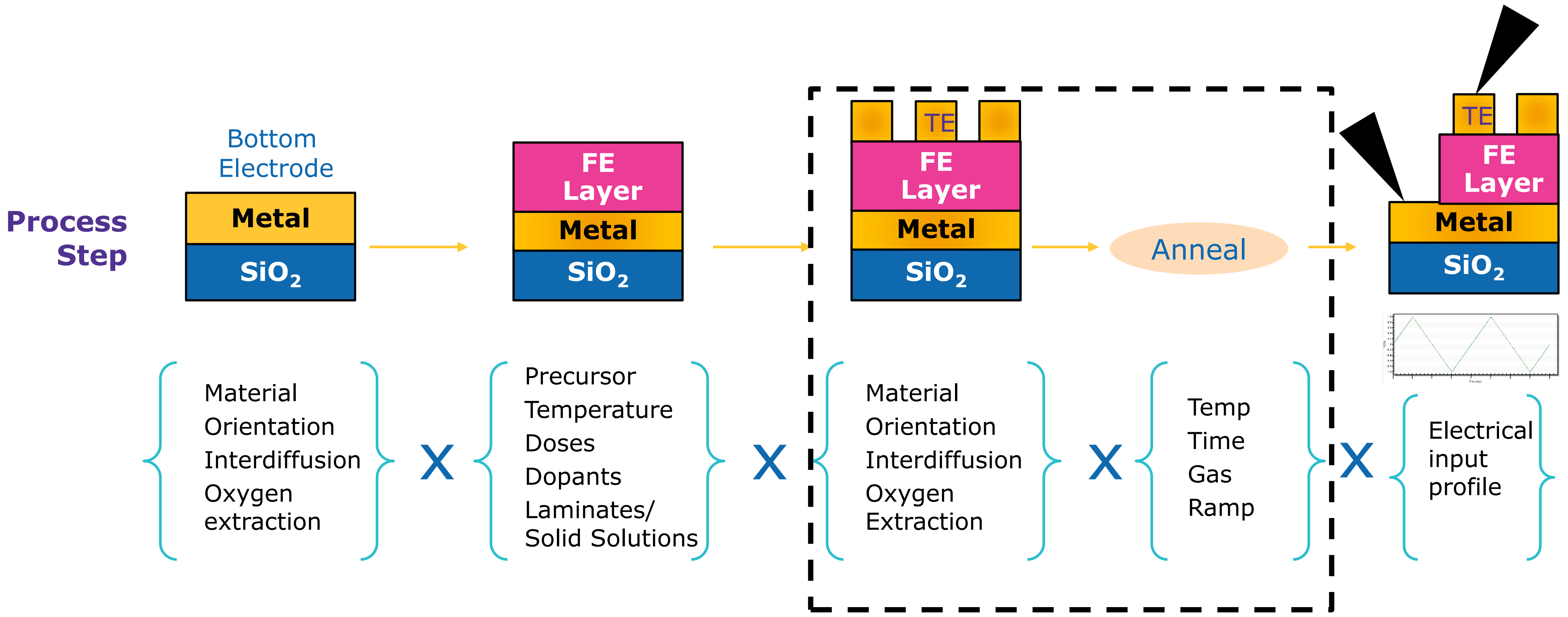
(i) To tune the as-deposited film polarization with ozone concentration

(ii) To study the FE behavior of the film after post-metallization annealing



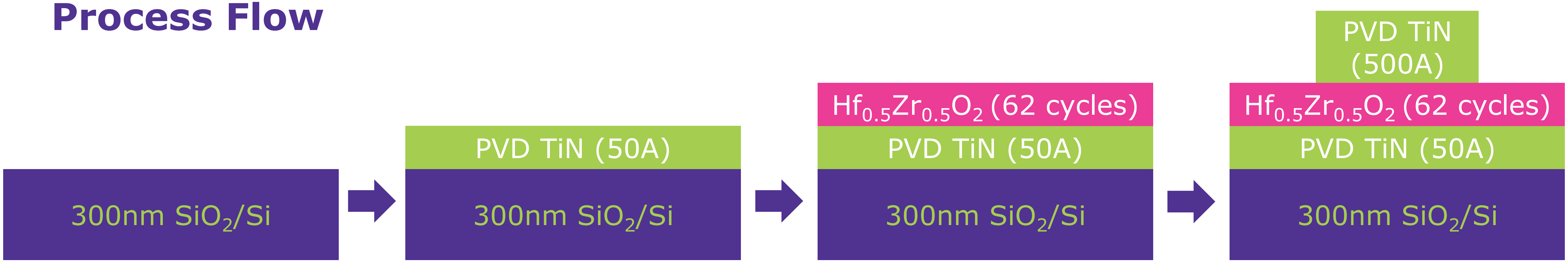


Different process conditions and electrodes
Controlling Ferroelectric Properties in ALD HZO Films



Ref: V. K. Narasimhan, ALD/ALE 2020

Process Flow



Process Conditions:

TiN Deposition Temperature: 250C

Hf Sub-cycle pressure: 1000mT

Zr Sub-cycle pressure: 500mT

HfD-04 dose: 20s

ZrD-04 dose: 60s

Ozone dose: 10s

HfD-04 temperature: 125C

ZrD-04 temperature: 70C

Deposition temperature: 300C

Process Variables:

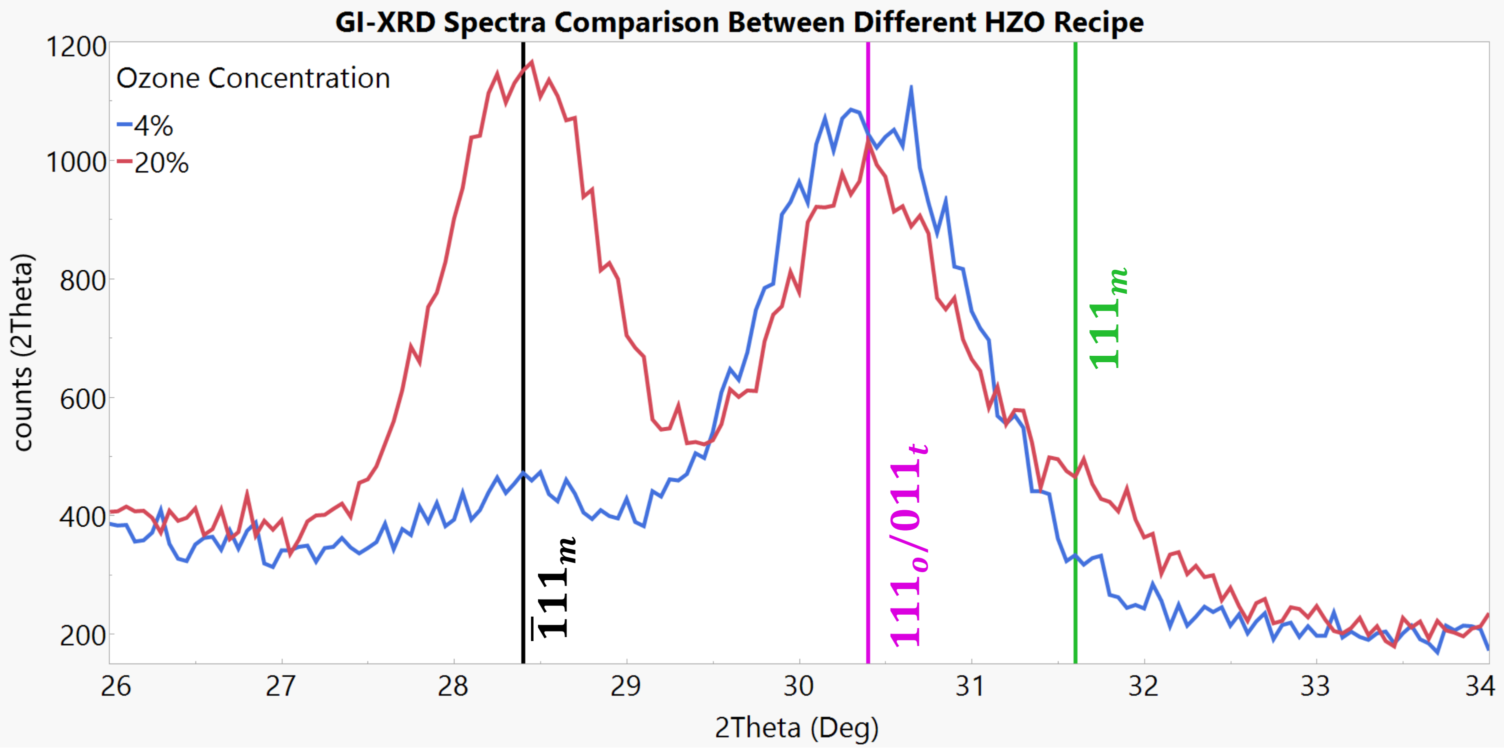
Ozone concentration: 4% vs 20% (flow rate 800 sccm)

Post-metal anneal temperature: 400C vs 525C 5min in N_2

Growth per cycle comparison:

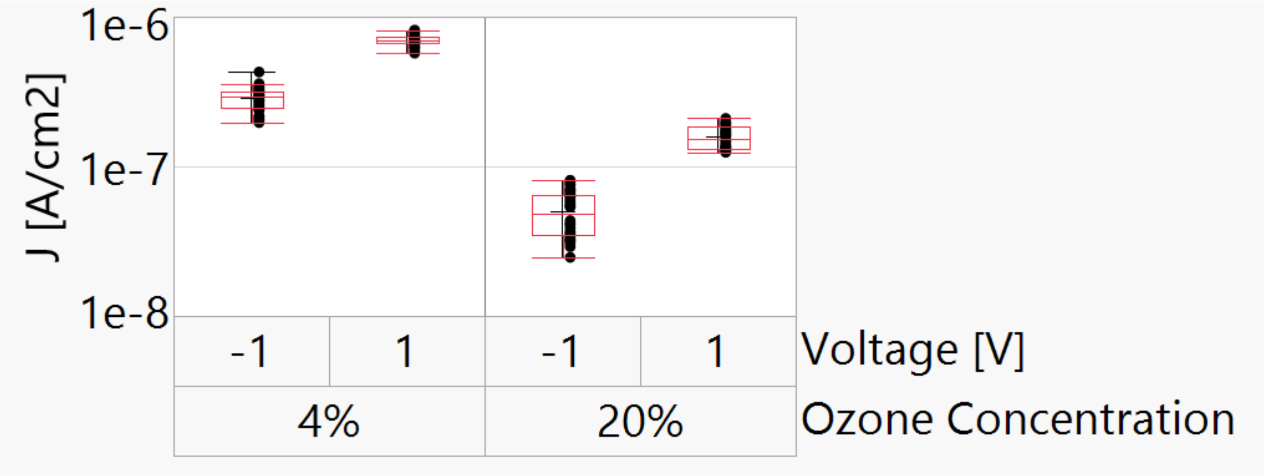
Ozone concentration	GPC
4%	1.05A/cycle
20%	1.37A/cycle

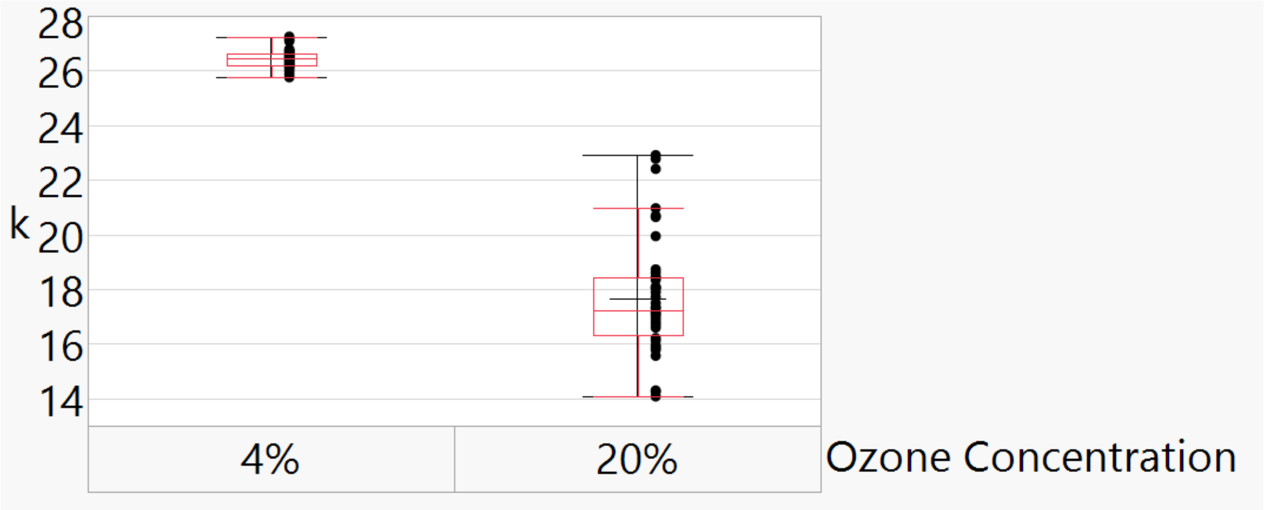
Ozone Concentration Variation
Comparison of Film Crystallinity



	4% Ozone	20% Ozone
Non-monoclinic	83.2%	41.4%
Monoclinic	16.8%	58.6%

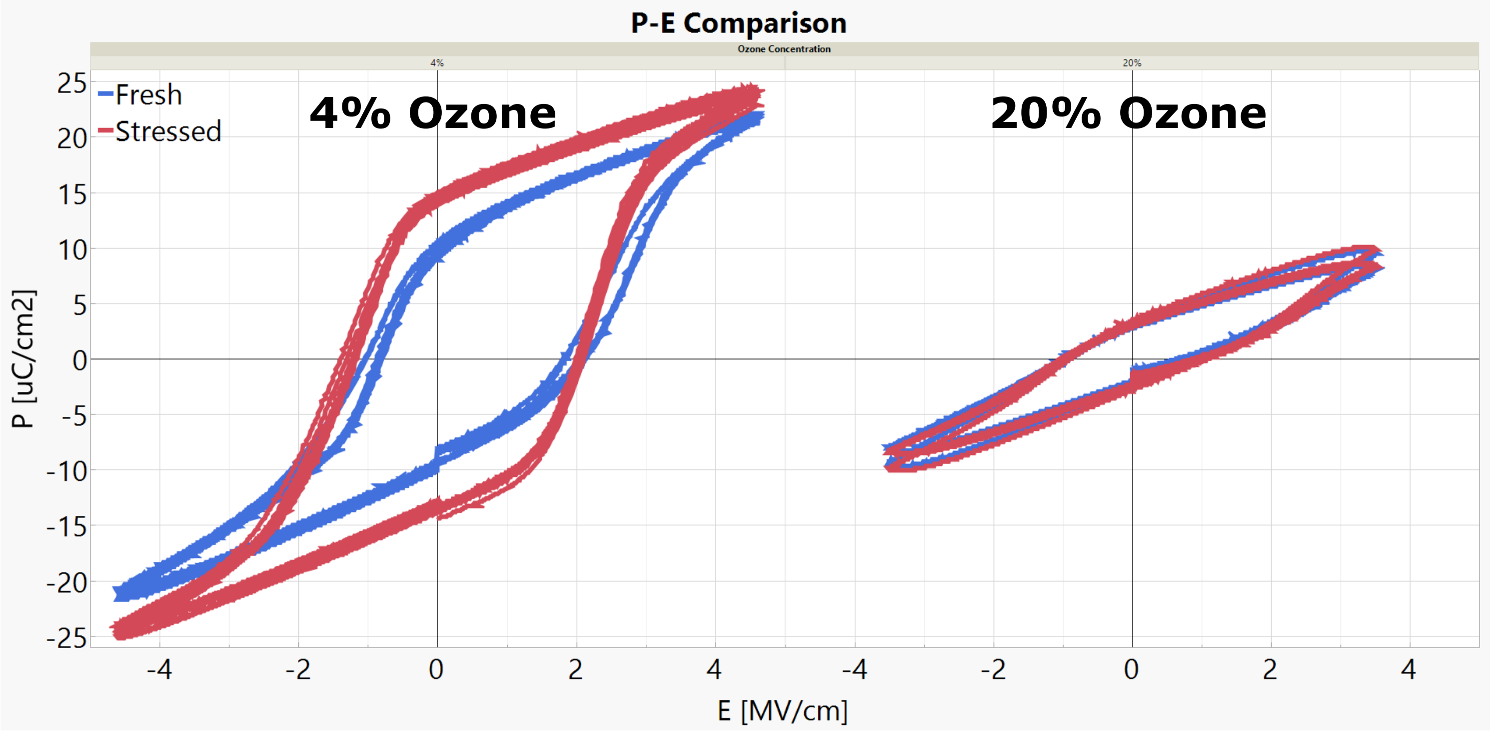
Ozone Concentration Variation
Leakage and Dielectric Constant of the Film





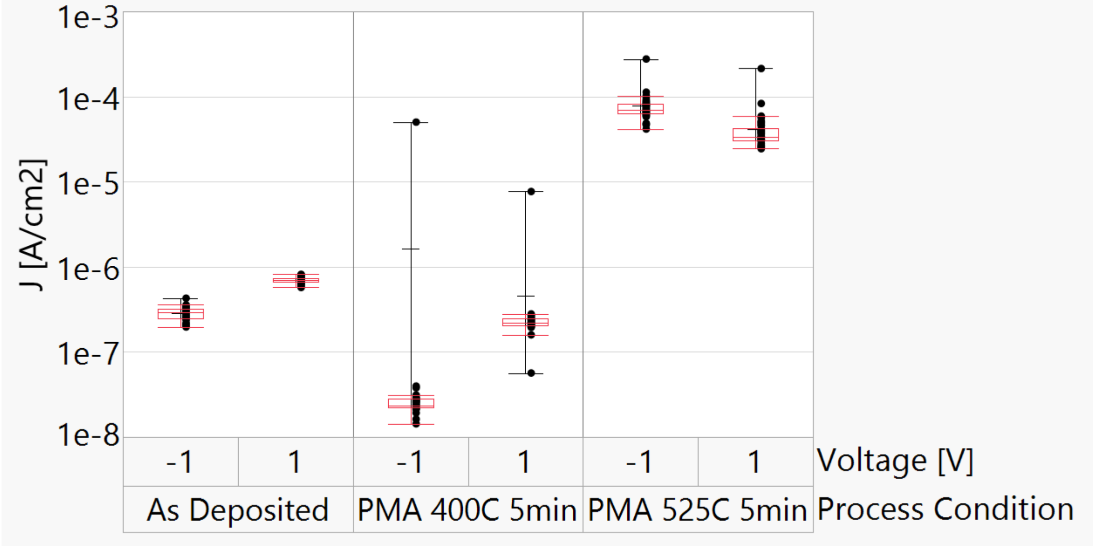
- Higher leakage in 4% ozone film possibly because of larger point defect density and grain boundary conduction in the film
- Asymmetry in leakage indicates partial oxidation of the bottom electrode
- Ozone concentration significantly impacts the dielectric constant and leakage of the film

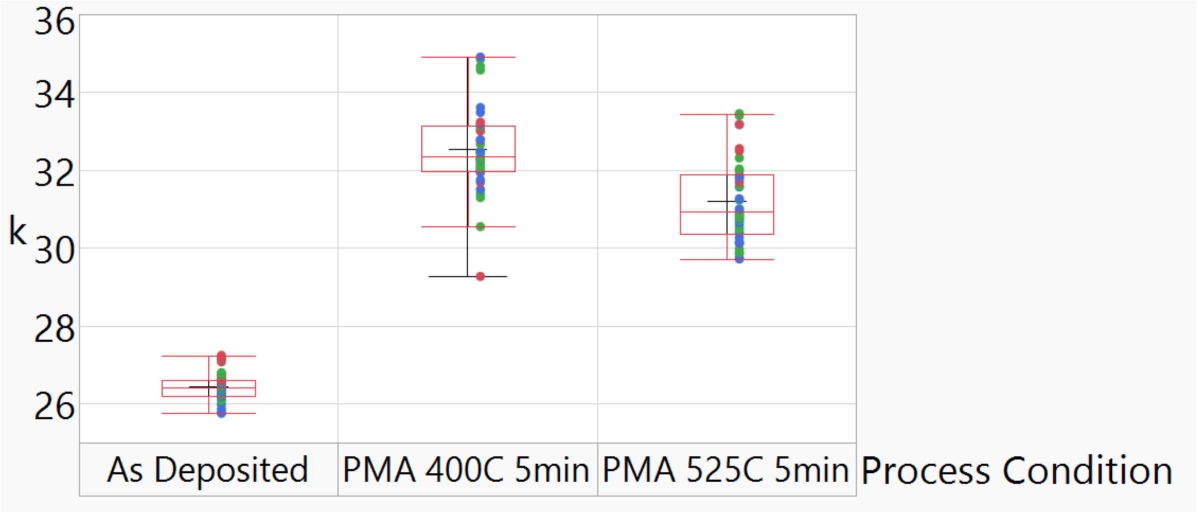
Ozone Concentration Variation
Ferroelectric Polarization Comparison



Ozone Concentration	Hysteresis, P_r (uC/cm²)		Coercive Field, E_c (MV/cm)	
	Fresh	Stressed	Fresh	Stressed
4%	+10,-10	+15,-14.37	-1,+2	-1.15,+2.1
20%	-2.4,+2.76	+3.15,-2.76	-0.93,+0.875	-1,+1

Post-Metal Anneal
Leakage and Dielectric Constant of the Film





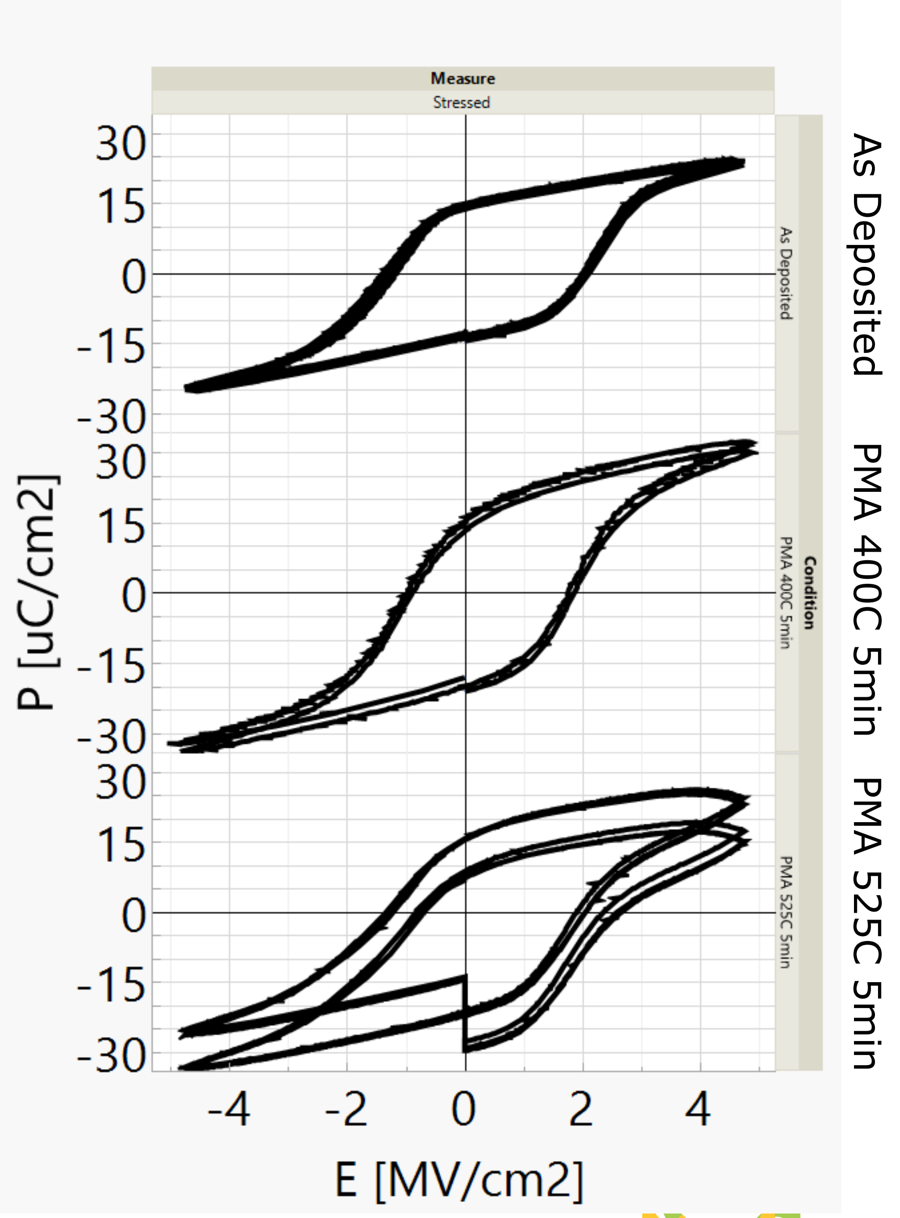
Film having 4% ozone concentration

- 400C post-metal anneal shows the lowest leakage with the highest k value indicating it might be optimized for FE response

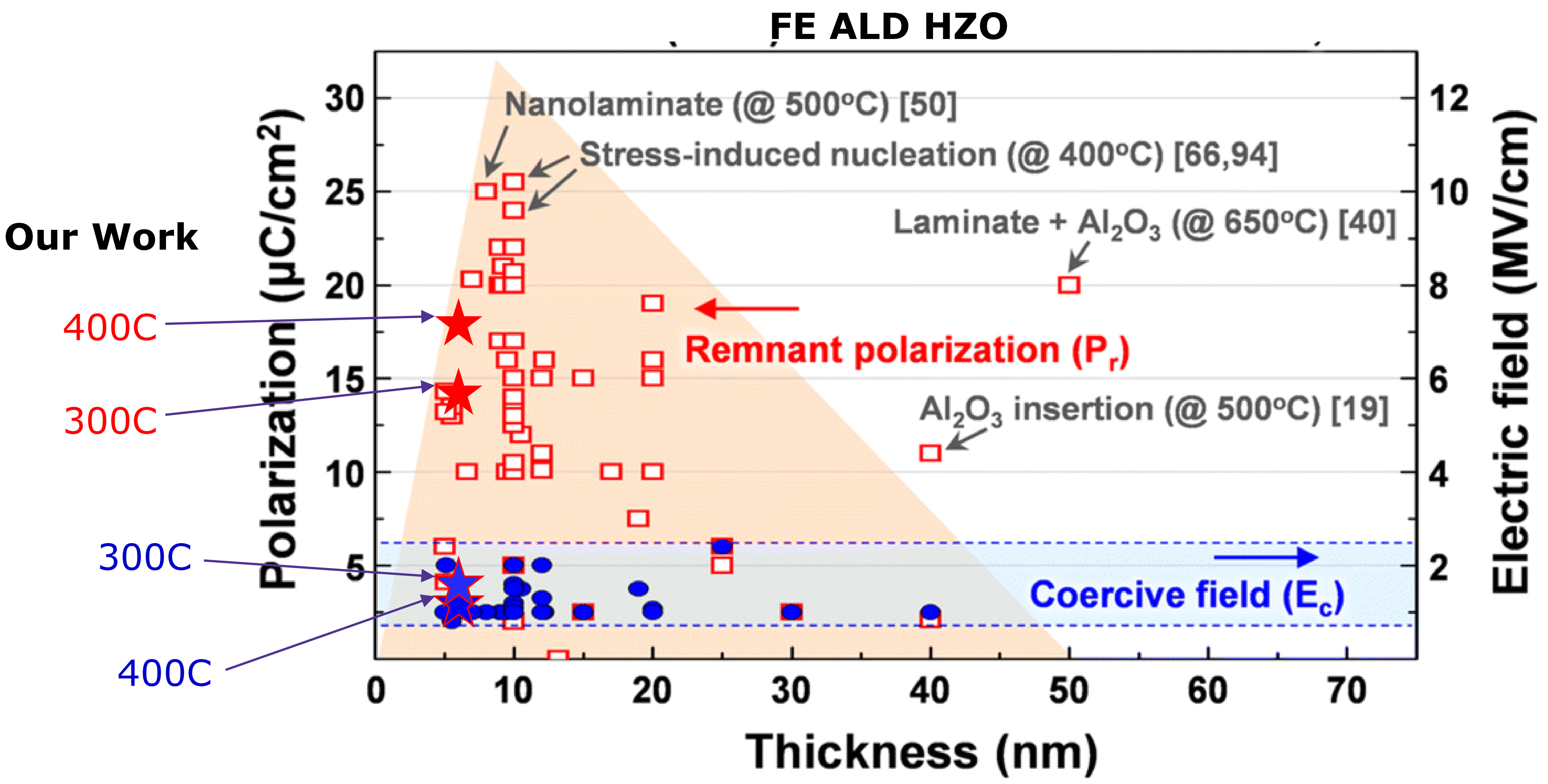
Post-Metal Annealing
Ferroelectric Polarization Comparison

Process Condition	Hysteresis, P_r (uC/cm^2)	Coercive Field, E_c (MV/cm)
As Deposited	**+15,-14.37**	**-1.15,+2.1**
PMA 400C 5min	**+15.6,-20**	**-0.9,+1.7**

- 2Pr window increases from 29.37 uC/cm^2 for as deposited sample to 35.6 uC/cm^2 for 400°C annealing -> **a 21% increase**
- Average coercive field decreases from 1.6 MV/cm to 1.3 MV/cm -> **a 18.75% decrease**
- 525°C annealing introduces significant leakage.



Benchmarking Results



Ref: S. J. Kim et al., JOM volume 71, pages 246–255 (2019)

Summary and Conclusions

Ozone concentration during the ALD deposition

- Lower ozone concentration increases non-monoclinic phase fraction

4% Ozone

- Demonstrated $2P_r$ window of 29.37 uC/cm^2 in 65A film at 300C deposition

Ferroelectric HZO from the ALD of HfD-04 and ZrD-04 precursors

Post-metal anneal

- Post-metal anneal increases the dielectric constant of the film and hence reduces the coercive field besides also increasing remnant polarization

400C Anneal

- Demonstrated ~20% reduction in coercive field and 34 uC/cm^2 $2P_r$ window in 65A film.

Thank You

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