ADVANCING DIGITAL LIVING

EMD ELECTRONICS

Inherently Ferroelectric ALD Films

Using ZrD-04 and HfD-04

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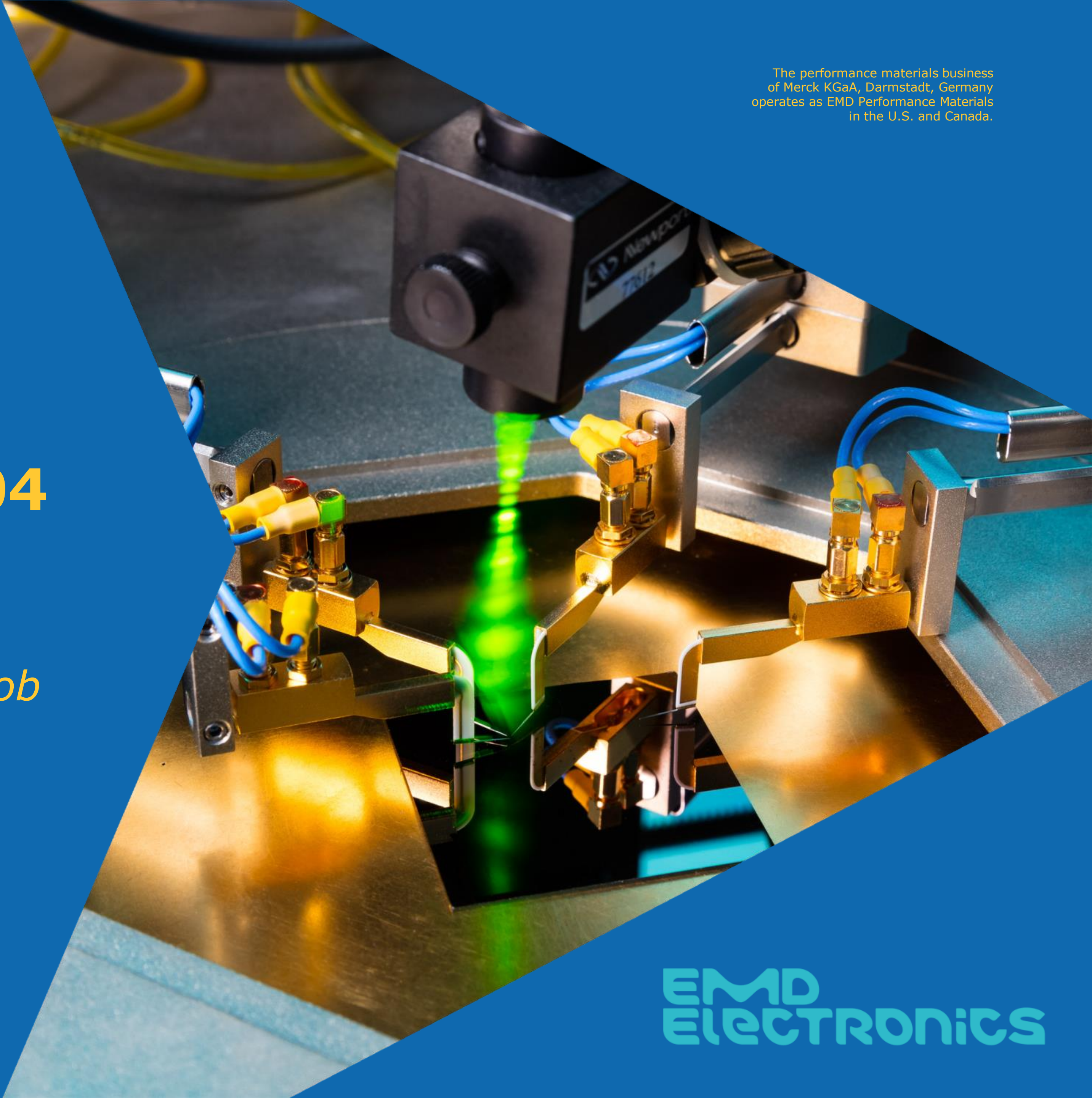

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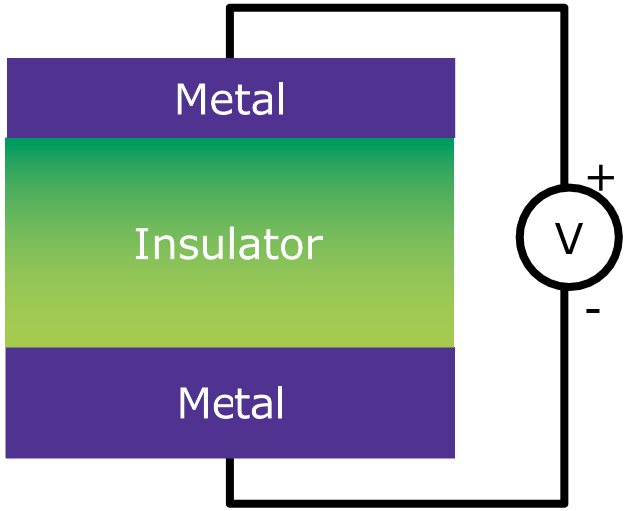
Agenda

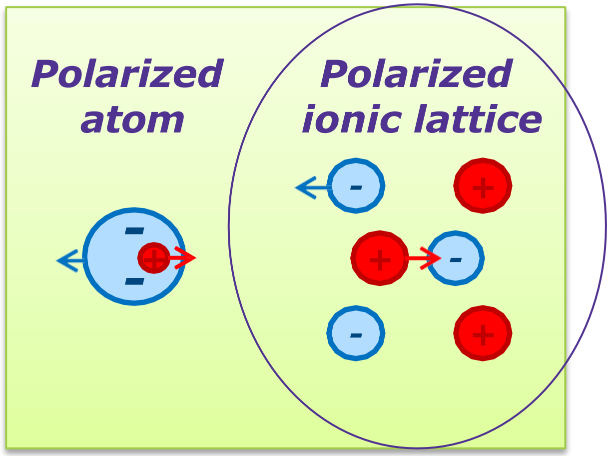
01

Background and Motivation

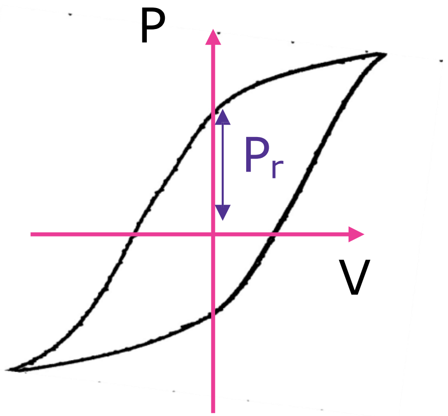
Ferroelectric principles

Ferroelectric materials are non-linear capacitors.





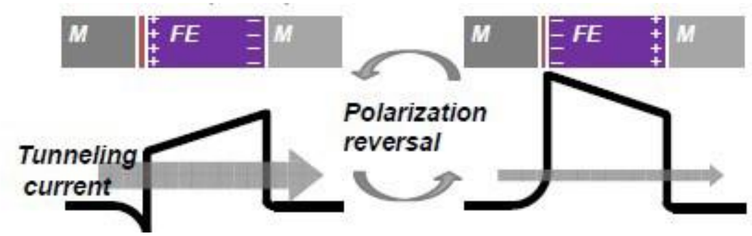
Ferroelectrics have an apparent “stored charge” called the “remanent polarization,” P_r



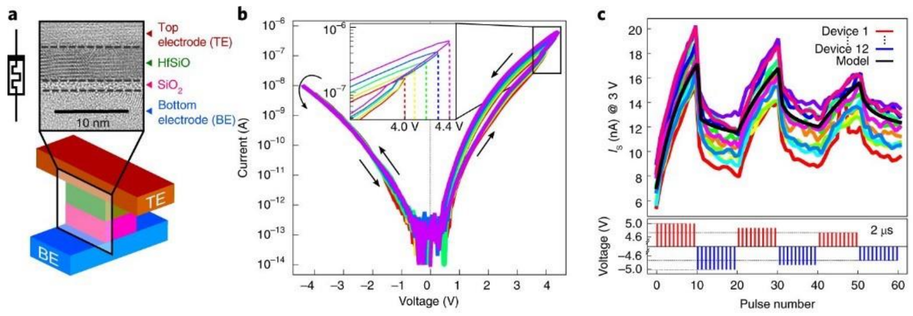
Potential uses of ferroelectric materials for computing

Tunnel Junction

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



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

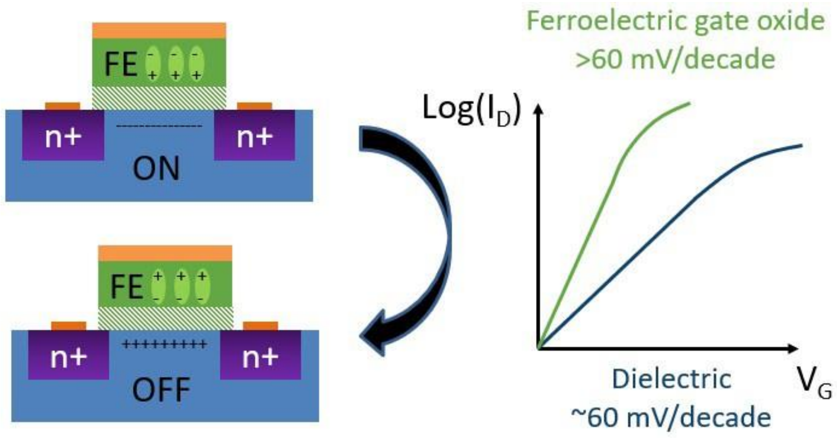


Berdan *et al.*, Kioxia, *Nature Electronics* (2020).

DOI: 10.1038/s41928-020-0405-0

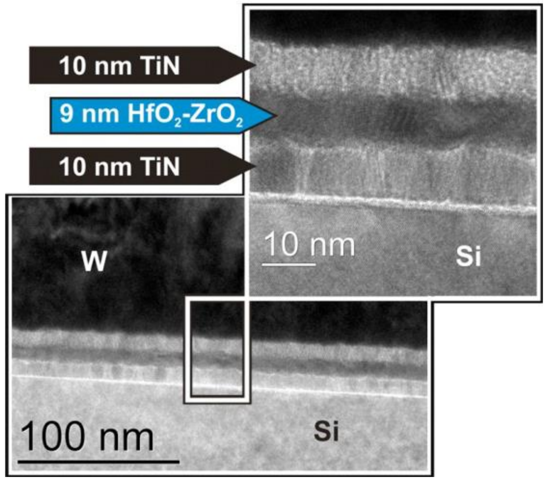
Negative Capacitance Transistor

Ferroelectric layer in a transistor gate enables negative capacitance resulting in higher subthreshold slope for low power logic operation

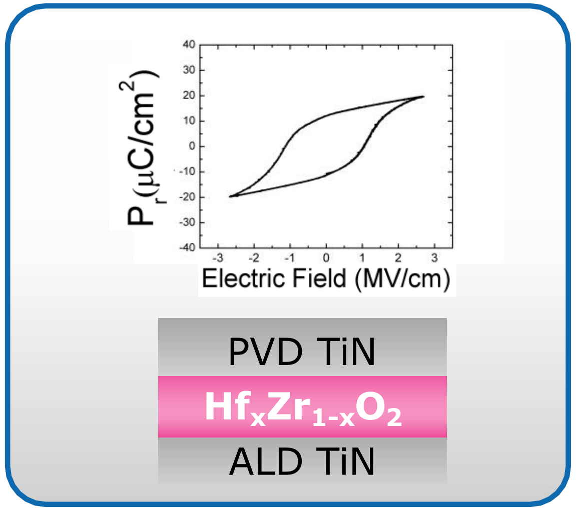


HfO_2-based ferroelectrics

- Discovered in 2011 [Boscke, Muller, et al, *APL* ***99*** *(2011)*]
- Can be deposited by atomic layer deposition
  - e.g. Hf precursor like TDMA-Hf or HfD-04, oxidant like water or ozone
- Offer better CMOS integration than the more traditional FE (e.g. PZT)



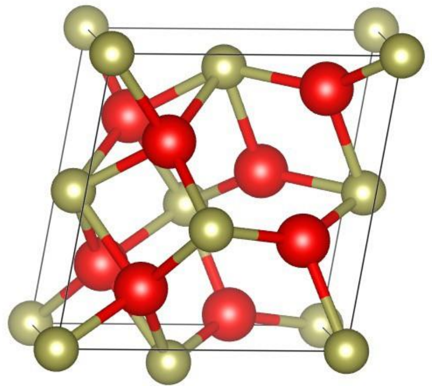
Muller et al, Nano Lett.
2012



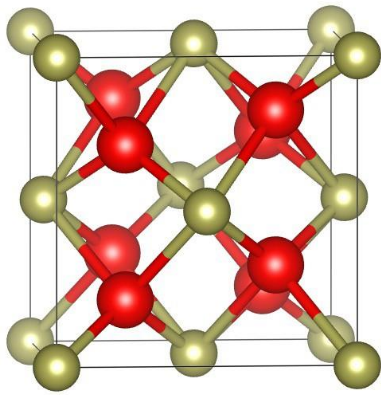
Polarization hysteresis in one of the stacks studied at Intermolecular

Having the right atomic structure of HfO_2 is crucial

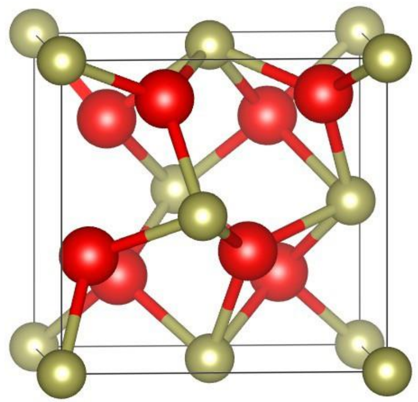
The crystallographic phase of HfO_2 has a direct effect on the electrical characteristics of the film



A **monoclinic phase** ($P2_1/c$) is the *most stable phase* at room temperature and standard pressure, but is not ferroelectric.

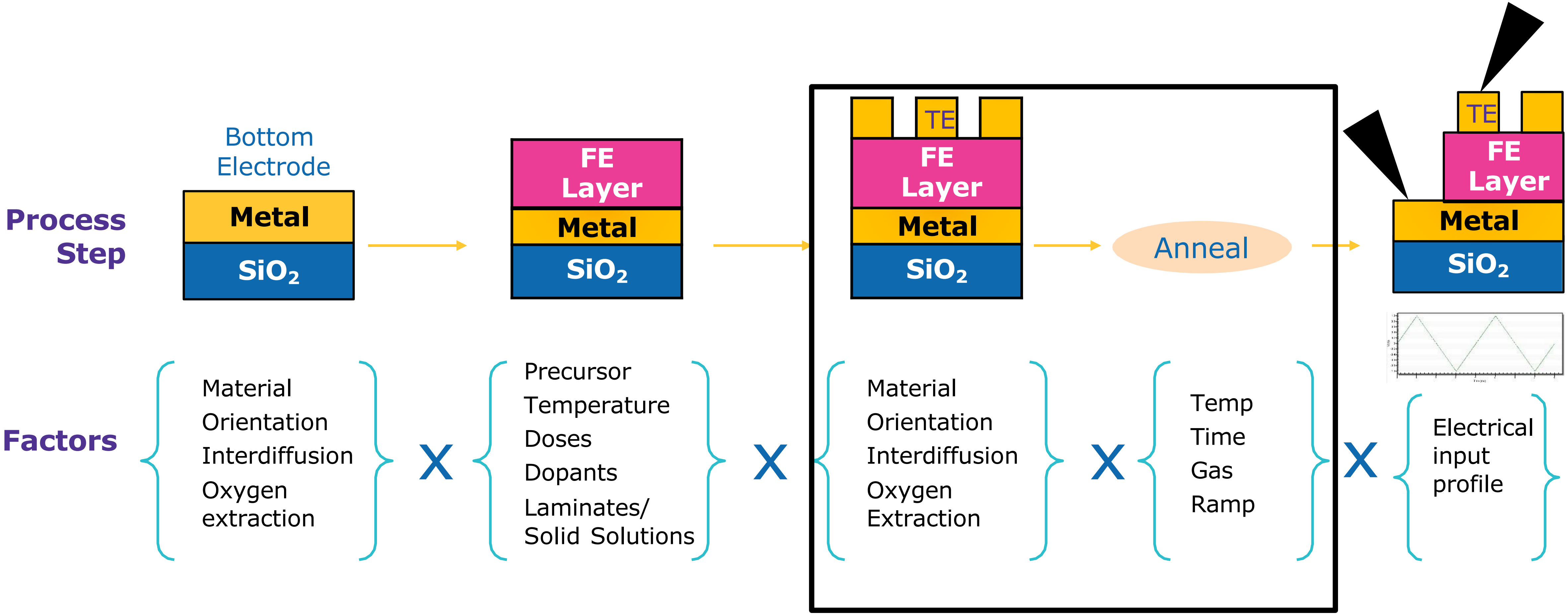


A **tetragonal phase** ($P4_2/nmc$) has a very high theoretical dielectric constant (κ=75) and a large bandgap (E_g = 6 eV). It can also produce anti-ferroelectric-like behavior.



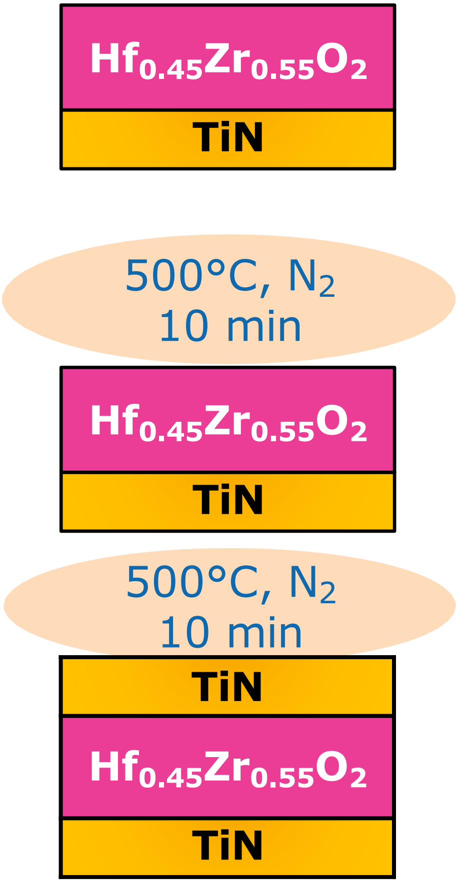
An **orthorhombic phase** ($Pca2_1$), a metastable structure, is not centrosymmetric, and can therefore demonstrate *ferroelectric behavior*

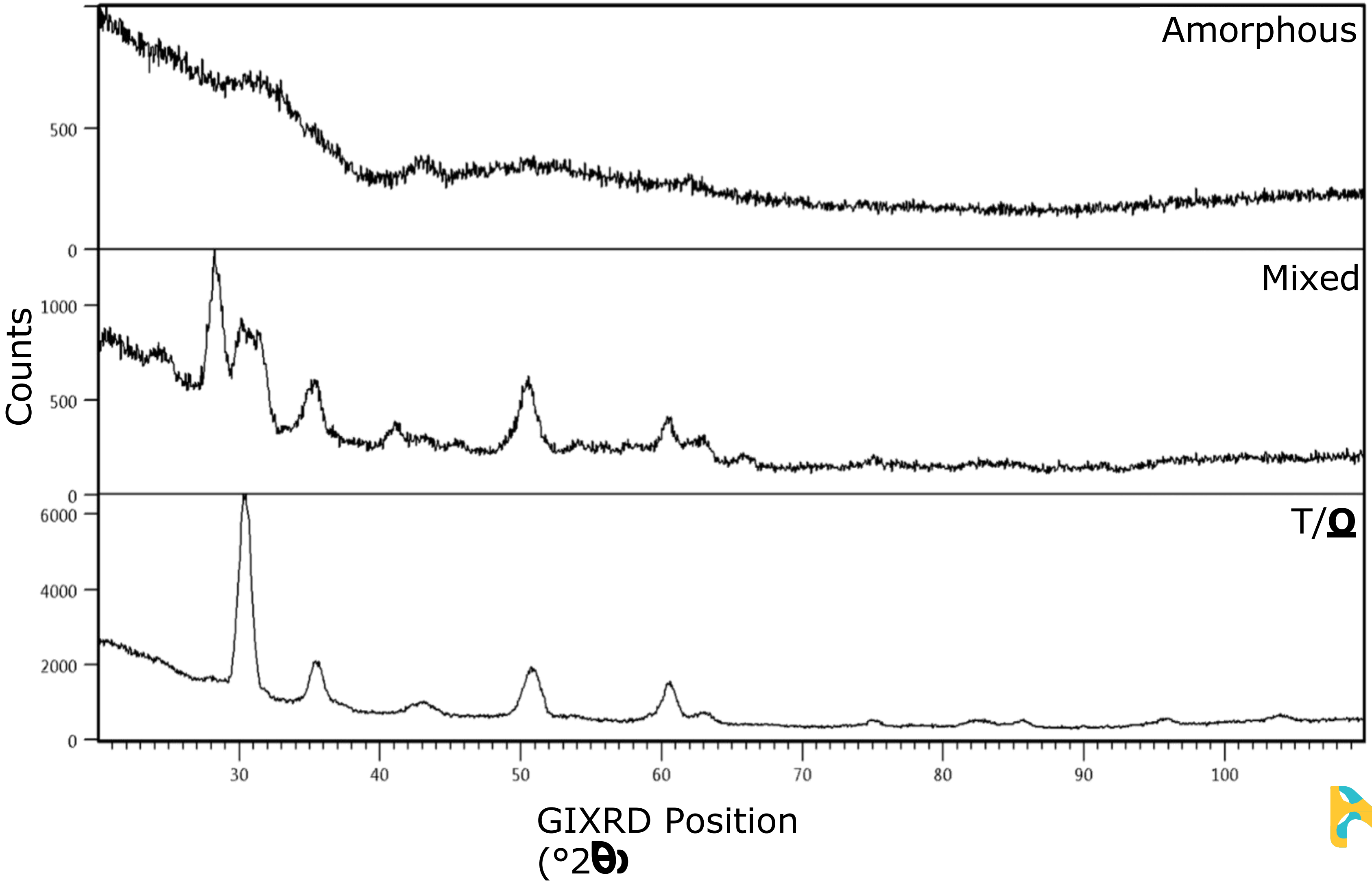
A wide parameter space influences the ferroelectricity of HfO_2



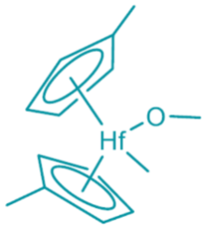
Typically, top electrode and annealing strongly influence phase

Example: 7nm oxide materials deposited by ALD with amide-type precursors at 285°C



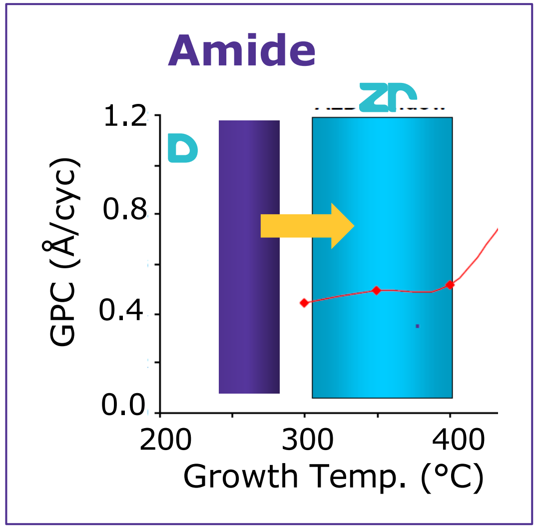


High temperature metallocene precursors



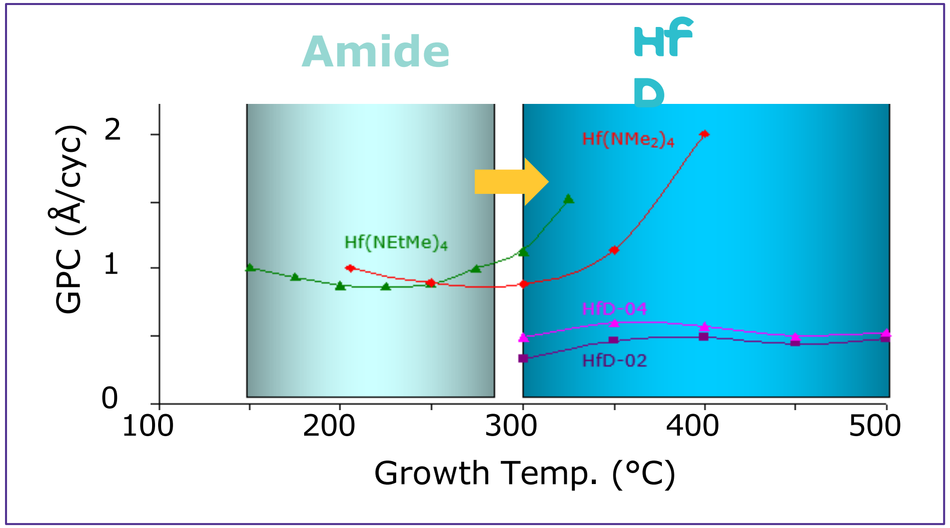
HfD-04:
bis(methylcyclopentadienyl)methoxymethylhafnium

ZrD-04 :
bis(methylcyclopentadienyl)methoxymethylzirconium



For these precursors, the growth temperature can be near or above the crystallization temperature of the oxide film that is produced.

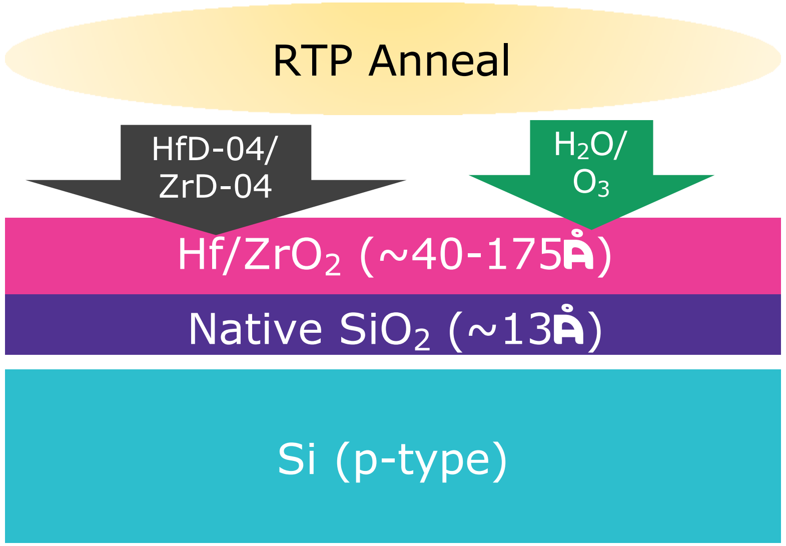
The goal of this study was to **examine the crystallization and ferroelectric properties** of films deposited from these high-temperature precursors.



02

ZrD-04 and HfD-04 films

Process Flow



Fixed conditions

Reactor: Cambridge Nanotech Savannah (200 mm cross-flow)

Precursors: ZrD-04, HfD-04

Bubbler temperature: 125°C

Precursor dose: 3s

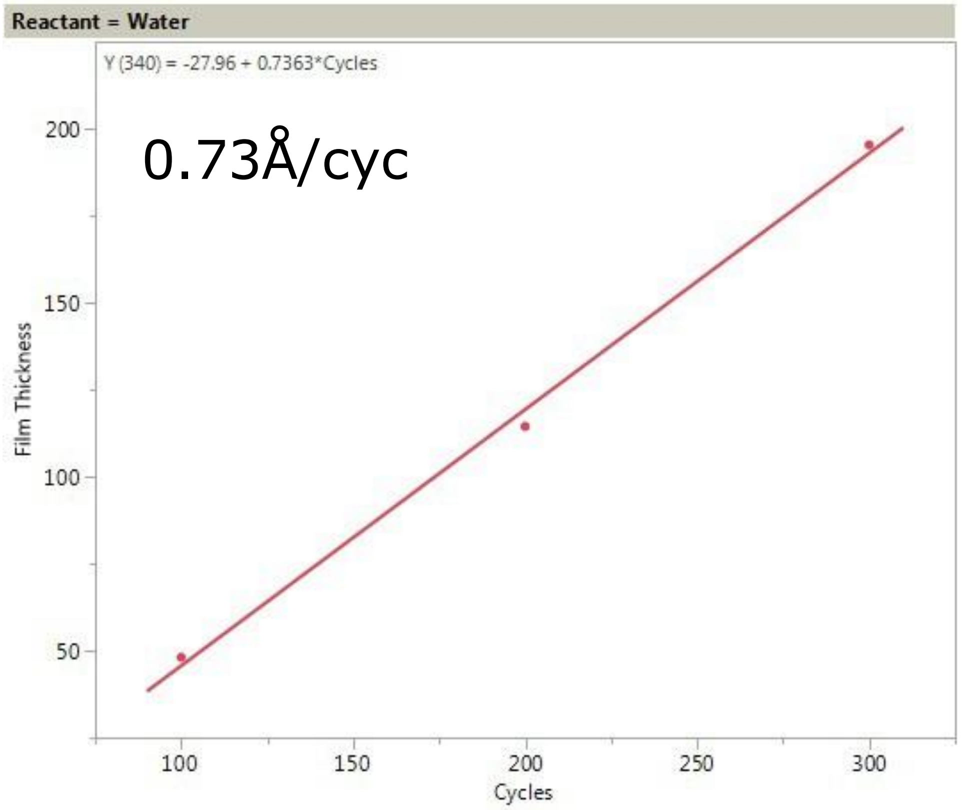
Reactant dose: 2s

Purges: 10s

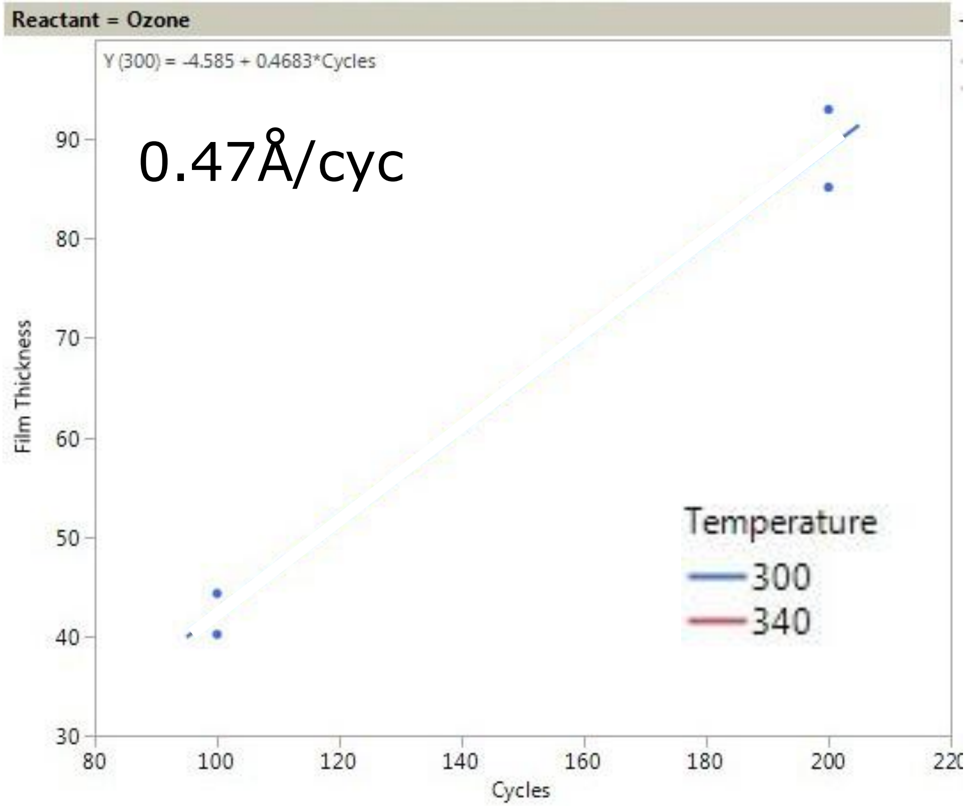
Reactants	Temperatures	Anneal
H_2O	300°C	None
O_3	340°C	500°C

HfD-04 Growth Curves

Water @ 340°C

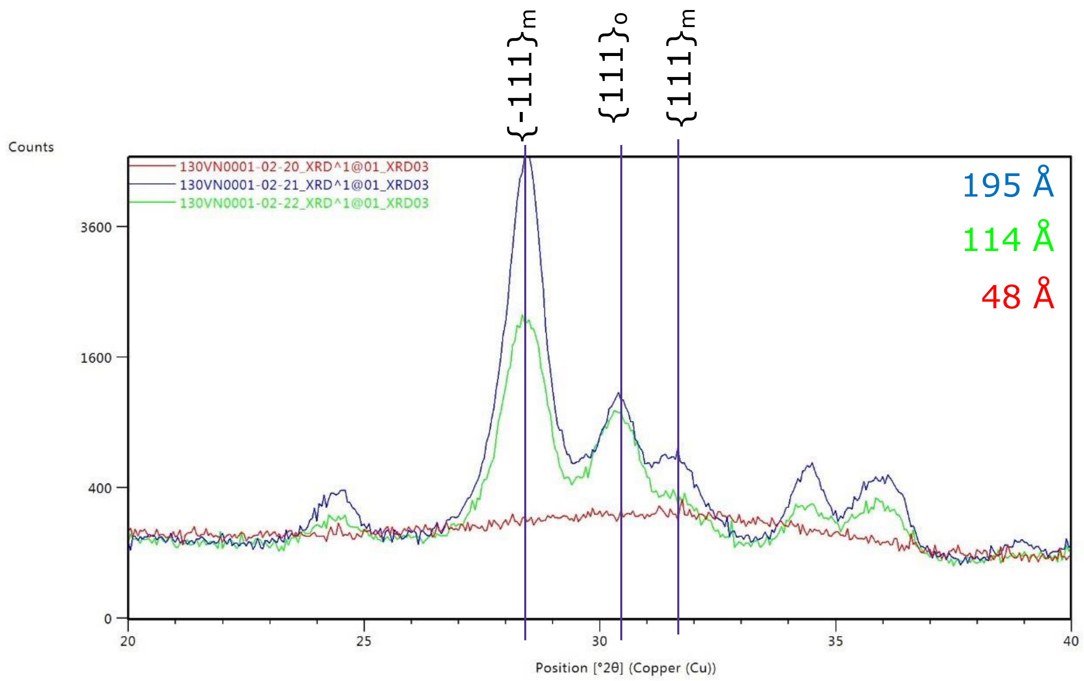


Ozone @ 300°C

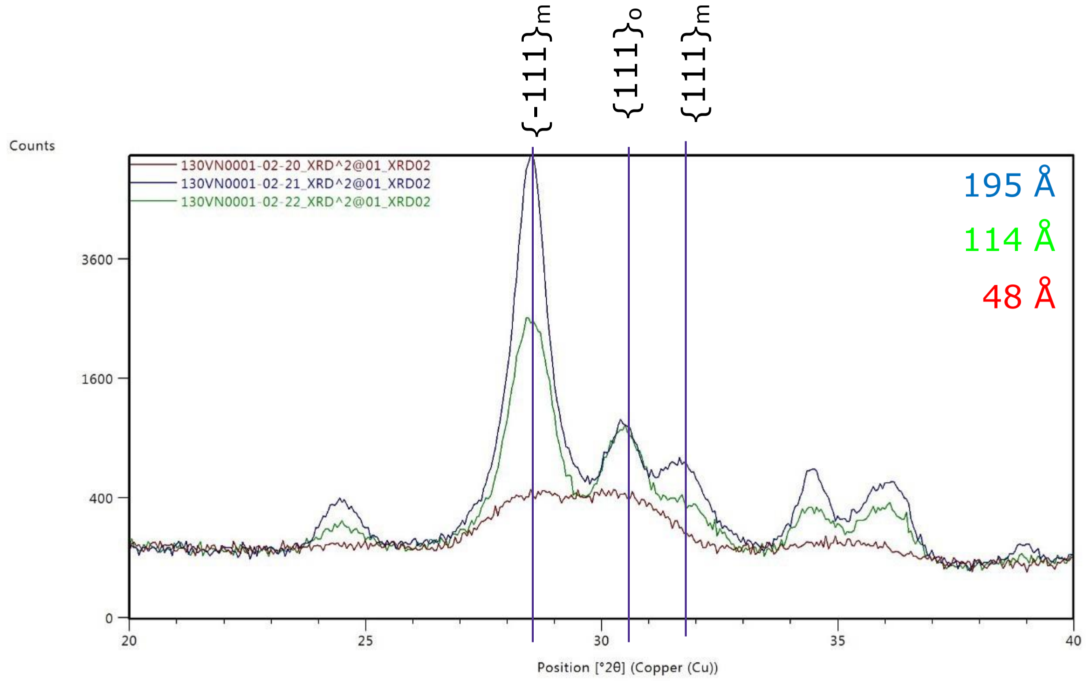


GIXRD for Water-based HfO_2 film
Crystallinity

Water, T_{dep} = 340°C, No anneal



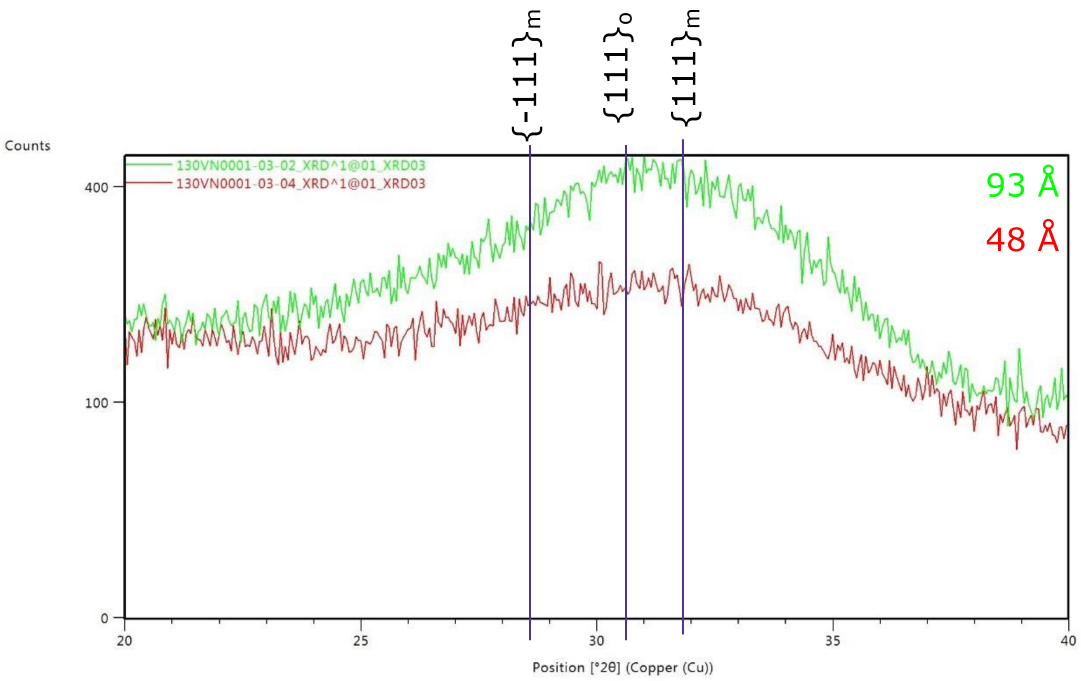
Water, T_{dep} = 340°C, After anneal



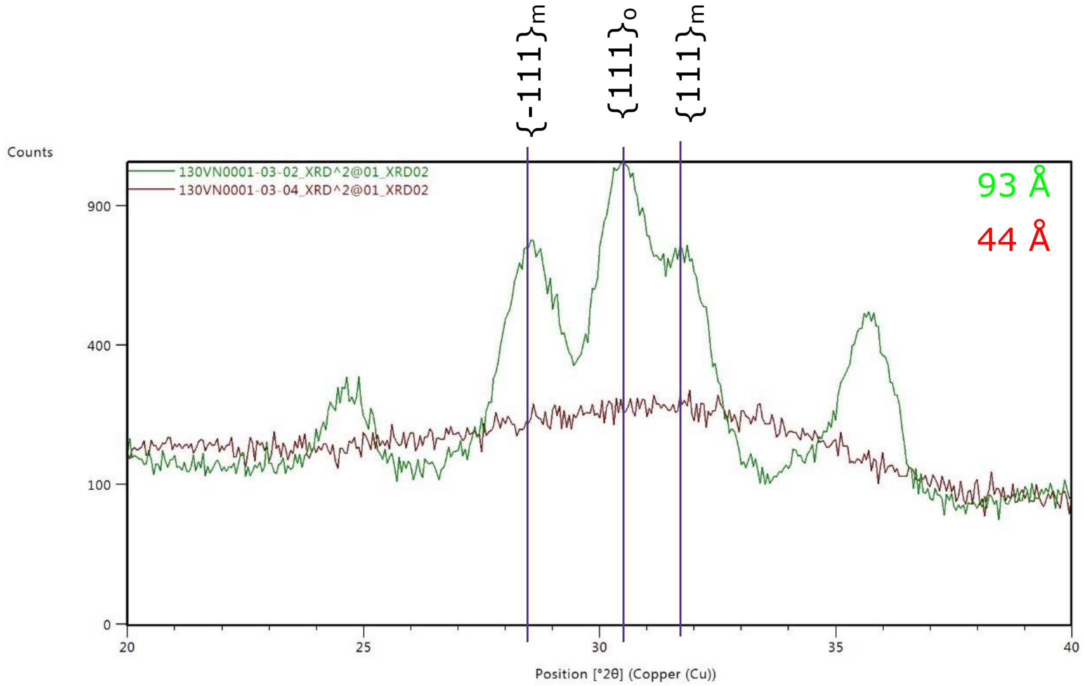
- HfO_2 films at all thicknesses are mixed phase with a dominant monoclinic fraction.
- Thick films are crystalline as deposited, whereas the thinnest film only shows broad crystalline features after 450°C annealing.

GIXRD for Ozone-based HfO_2 film
Crystallinity

Ozone, T_{dep} = 300°C, No anneal



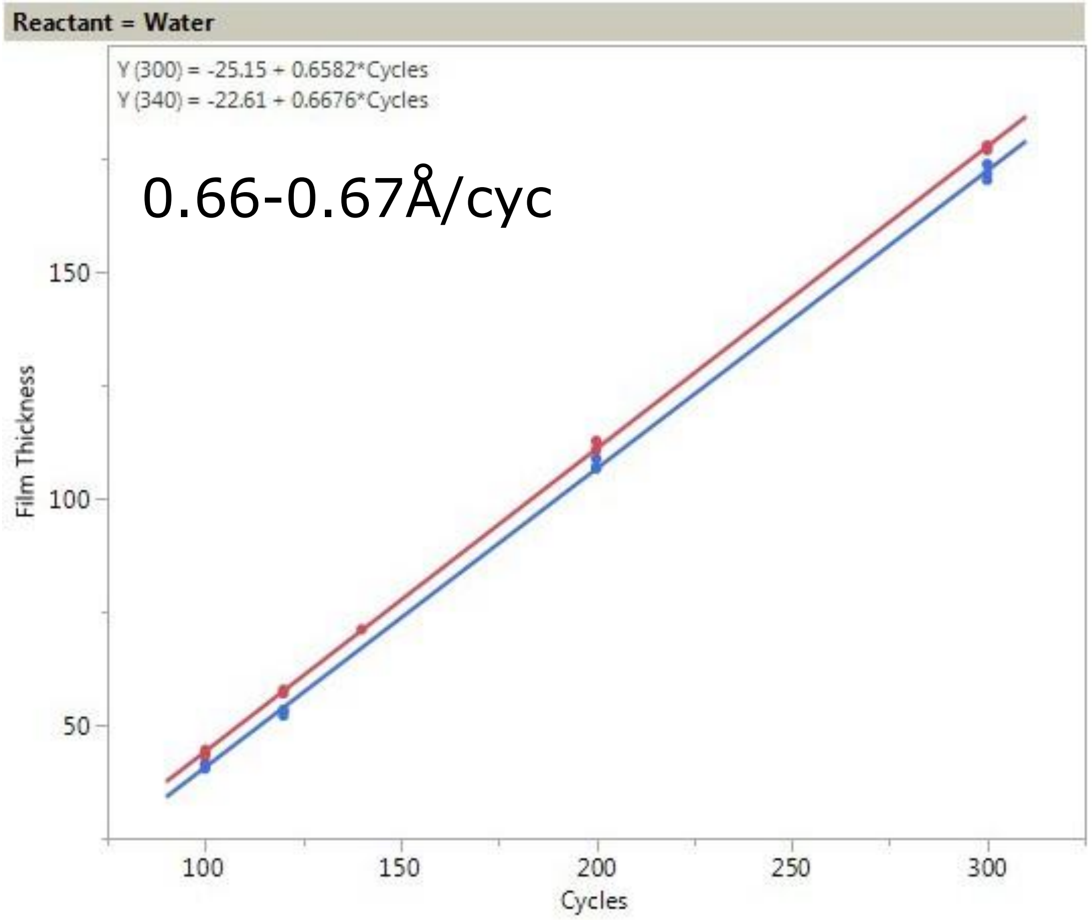
Ozone, T_{dep} = 300°C, After 500°C anneal



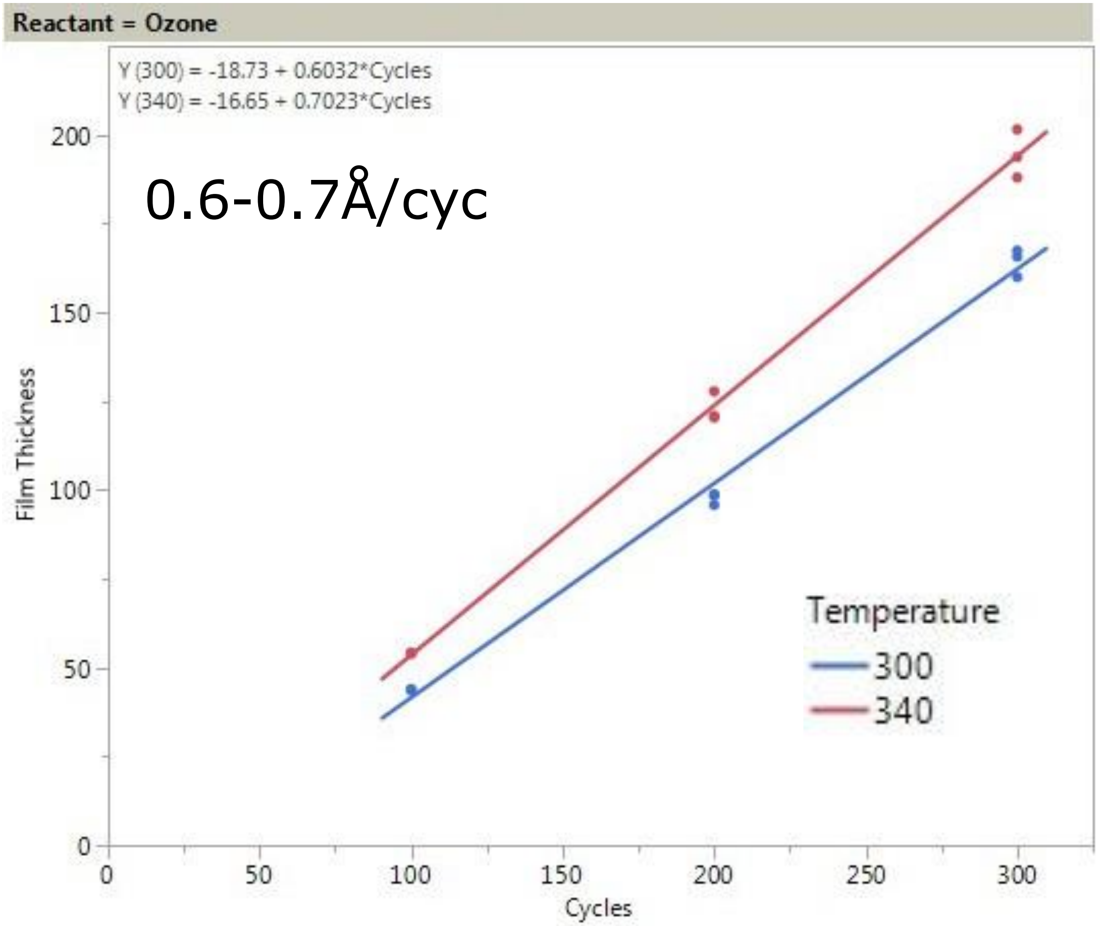
- Films are amorphous as deposited, and thinnest film remains amorphous even after annealing.
- Thicker film is mixed phase with a dominant monoclinic fraction, but orthorhombic (tetragonal) fraction is larger than the film deposited at 340°C with water

ZrD-04 Growth Curves

Water

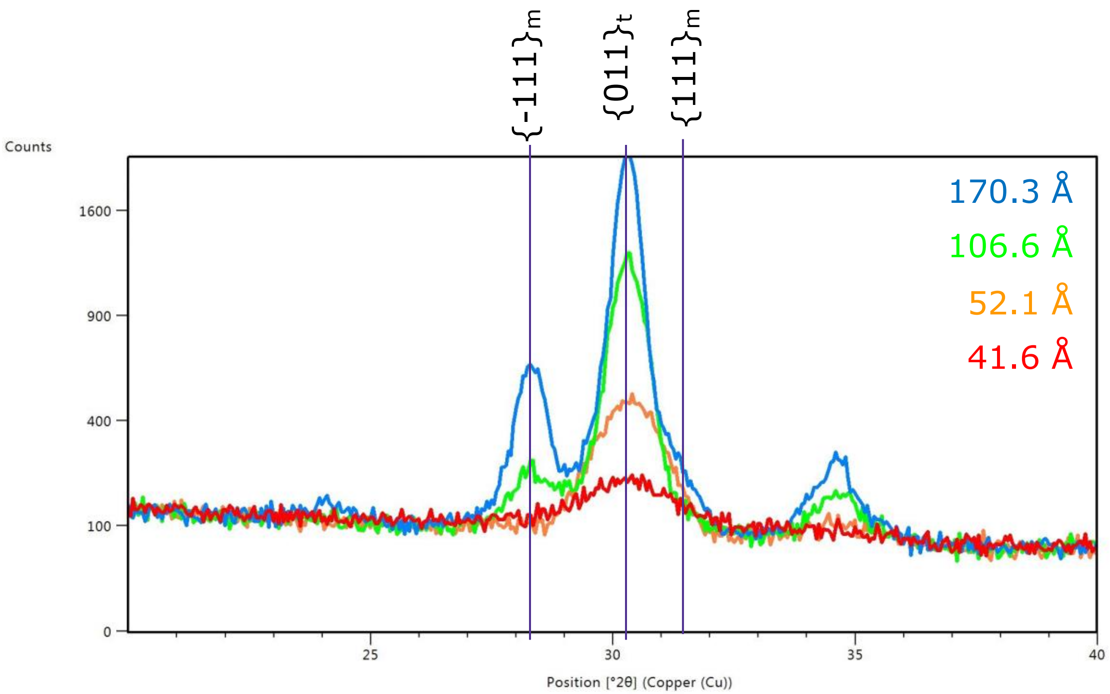


Ozone



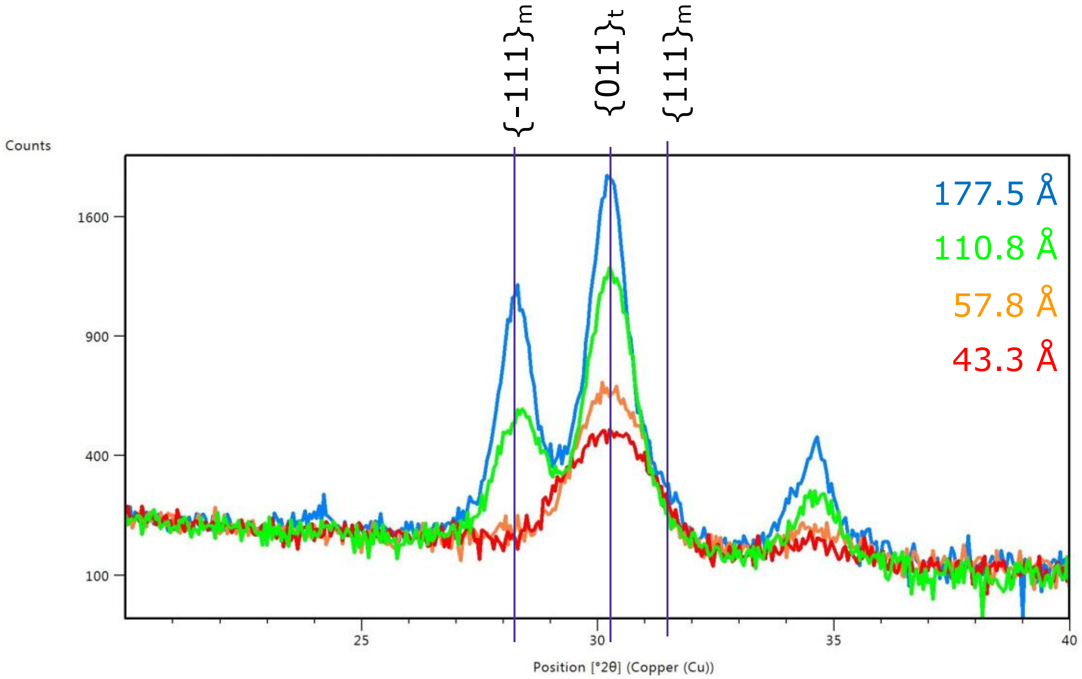
GIXRD for Water-based ZrO_2 Films
Crystallinity, as deposited

Water, T_{dep} = 300°C



Thickness	41.6 Å	52.1 Å	106.6 Å	170.3 Å
Tetragonal	100%	100%	73%	64%
Monoclinic	0%	0%	27%	36%

Water, T_{dep} = 340°C

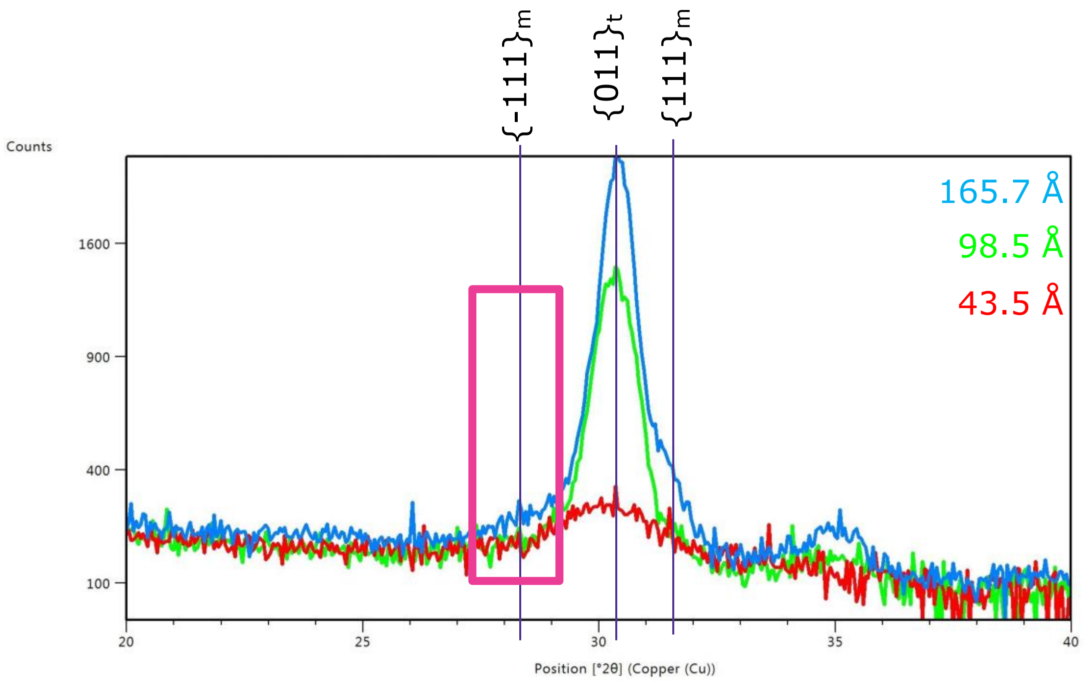


Thickness	43.3 Å	57.8 Å	110.8 Å	177.5 Å
Tetragonal	100%	100%	57%	50%
Monoclinic	0%	0%	43%	50%

- Overall, films below ~ 60Å show no significant monoclinic fraction, whereas thicker films are mixed-phase (tetragonal-monoclinic). The thicker films at 340°C have a larger monoclinic fraction than films of similar thickness grown at 300°C.

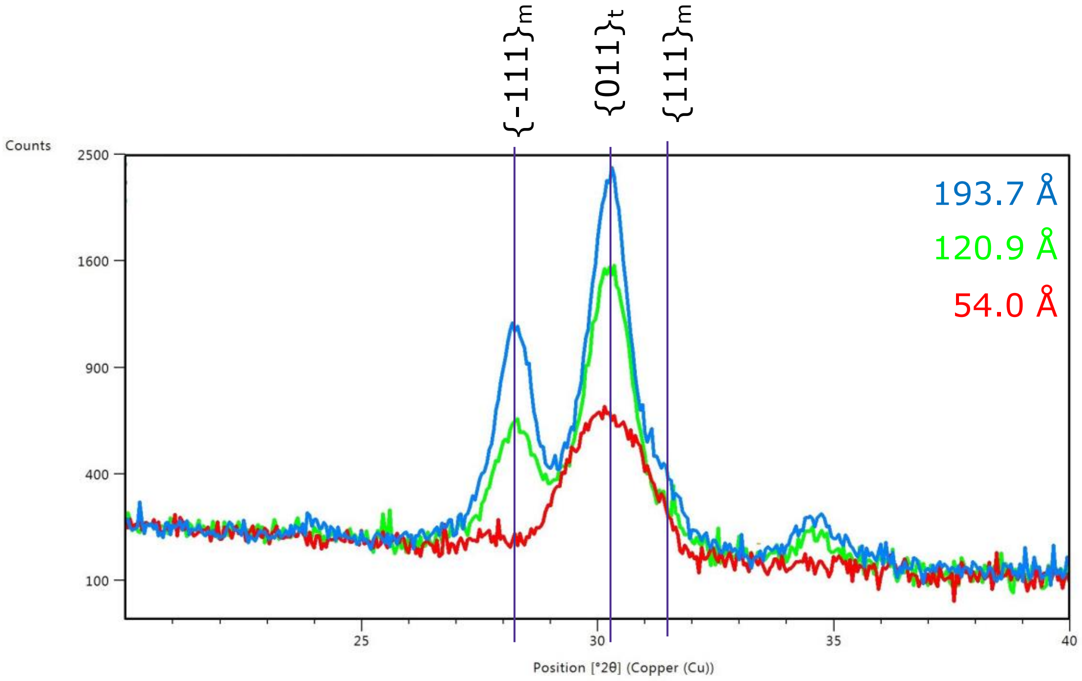
GIXRD for Ozone-based ZrO_2 Films
Crystallinity, as deposited

Ozone, T_{dep} = 300°C



Thickness	43.5 Å	98.5 Å	165.7 Å
Tetragonal	100%	100%	94%
Monoclinic	0%	0%	6%

Ozone, T_{dep} = 340°C

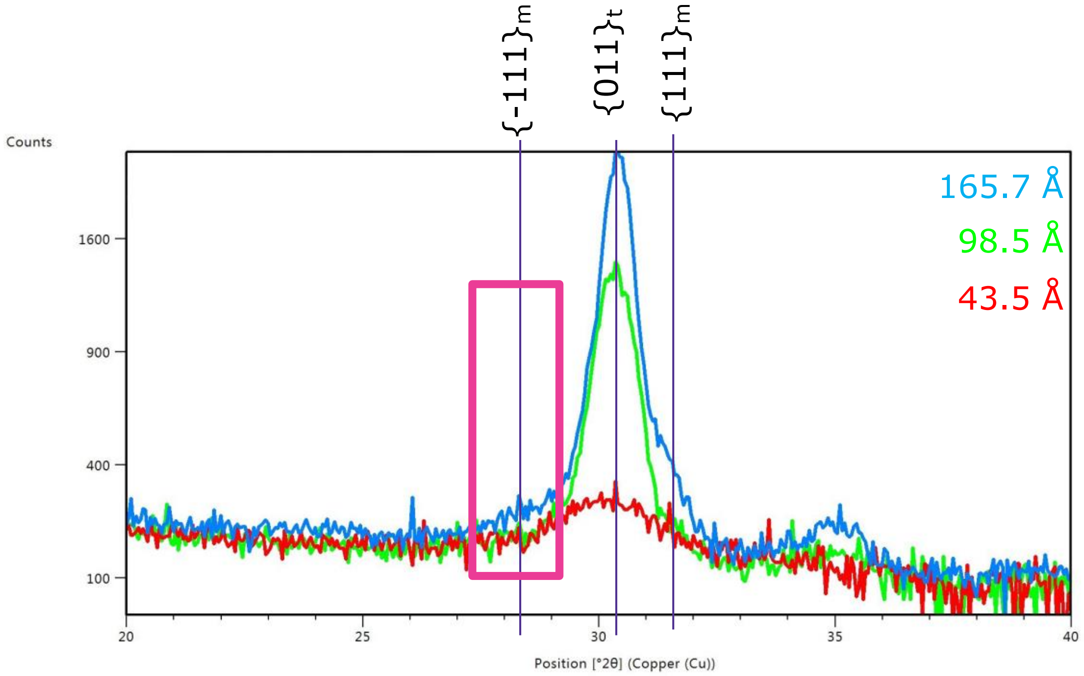


Thickness	54.0 Å	120.9 Å	193.7 Å
Tetragonal	100%	61%	55%
Monoclinic	0%	39%	45%

- All films deposited with **ozone at 300°C** show **suppression of the monoclinic phase**
- Thicker films deposited with ozone at 340°C show a strong monoclinic signal

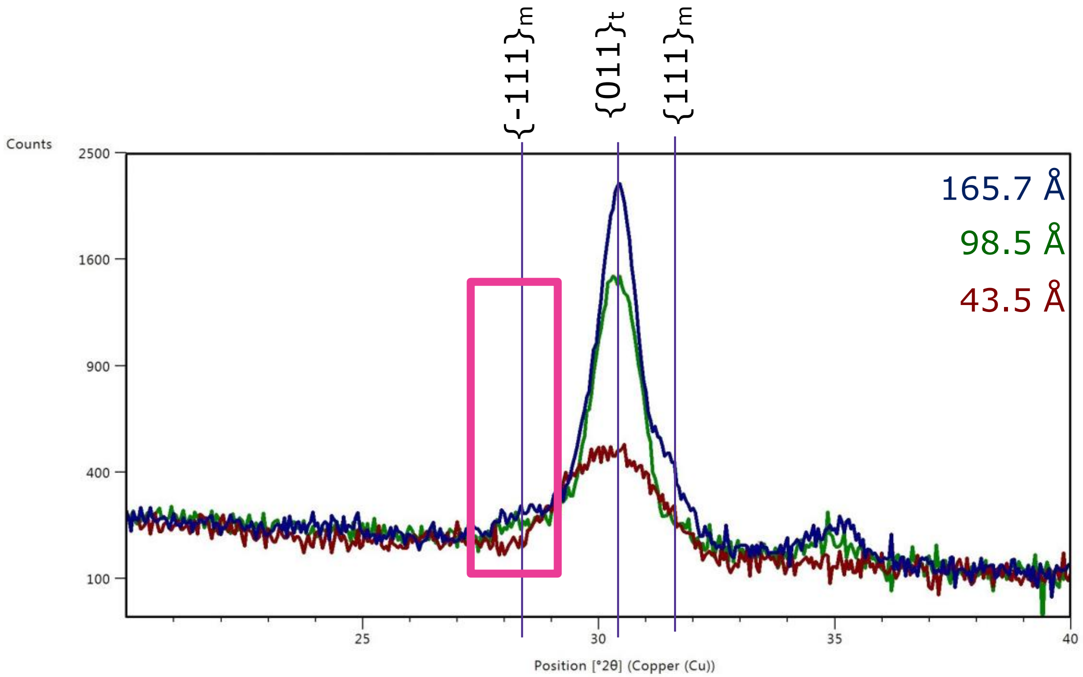
GIXRD for Ozone-based ZrO_2 Films
Crystallinity, before and after annealing (RTA 500°C, 5 min, N_2)

Ozone, T_{dep} = 300°C



Thickness	43.5 Å	98.5 Å	165.7 Å
Tetragonal	100%	100%	94%
Monoclinic	0%	0%	6%

Ozone, T_{dep} = 300°C



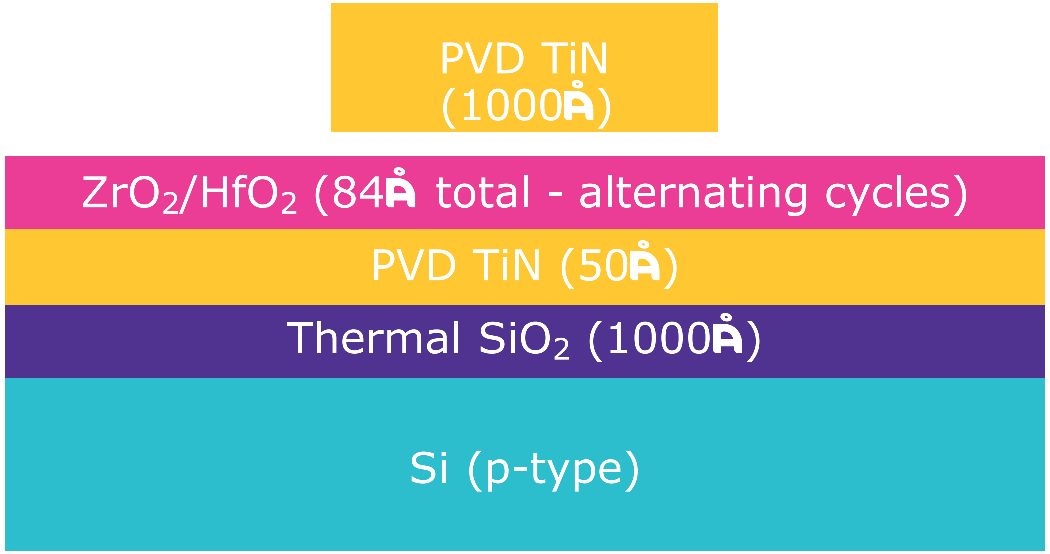
Thickness	43.5 Å	98.5 Å	165.7 Å
Tetragonal	100%	92%	96%
Monoclinic	0%	8%	4%

- Films deposited with ozone at 300°C maintain their tetragonal character after annealing

03

ferroelectric testing

Experimental Conditions



<u>Conditions</u>

TiN deposition temp: 250°C

Precursors: ZrD-04 and HfD-04

Reactant: Ozone

Bubbler temperature: 125°C

Precursor dose: 3s

Reactant dose: 2s

Purges: 10s

ALD Deposition temp: 300°C

PV Hysteresis-Stress Measurement

PV Hysteresis Waveform

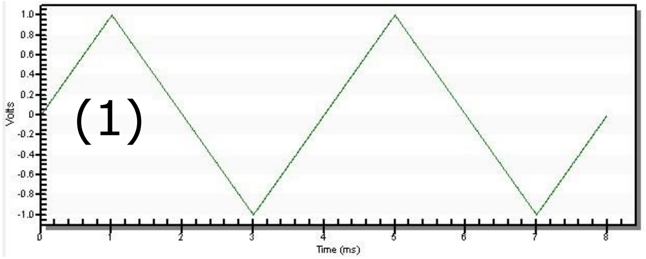
- Bipolar / Triangular Waveform
- Period = 8 ms (double sweep)
- Frequency = 250 Hz
- Voltage: ±1V➔3V, 0.25 V step

Stress / Wake-Up Waveform

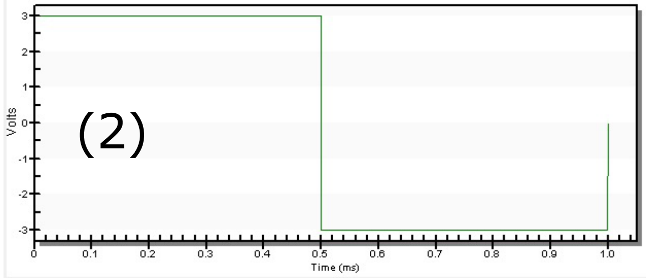
- Bipolar / Square Wave
- Period = 1 ms
- Frequency = 1 kHz
- Duration: 1 sec / 1k cycles
- Voltage: ±3 V

Measurement Sequence

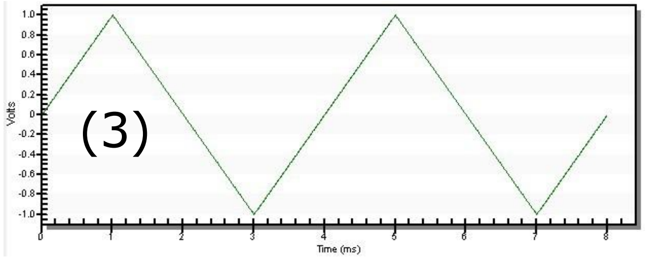
1) PV Hysteresis (±1V➔3V) [pre-stress]
2) Stress / Wake-Up (± 3V)
3) PV Hysteresis (± 1V➔3V) [post-stress]



Hysteresis [pre-stress]
Bipolar / Triangle (250 Hz)

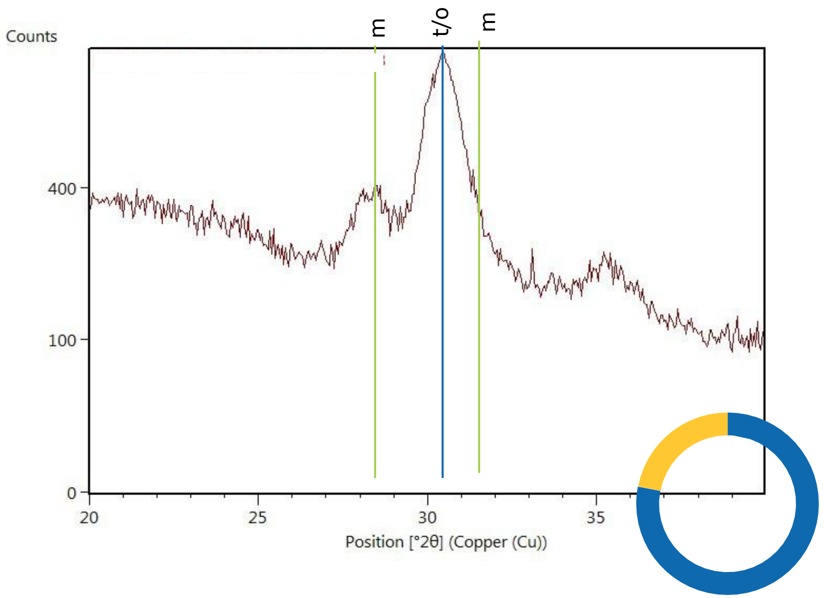


Stress / Wake-Up
Bipolar / Square (1 kHz)

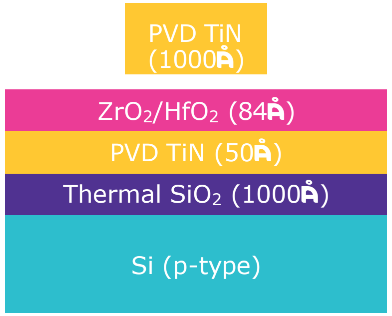


Hysteresis [post-stress]
Bipolar / Triangle (250 Hz)

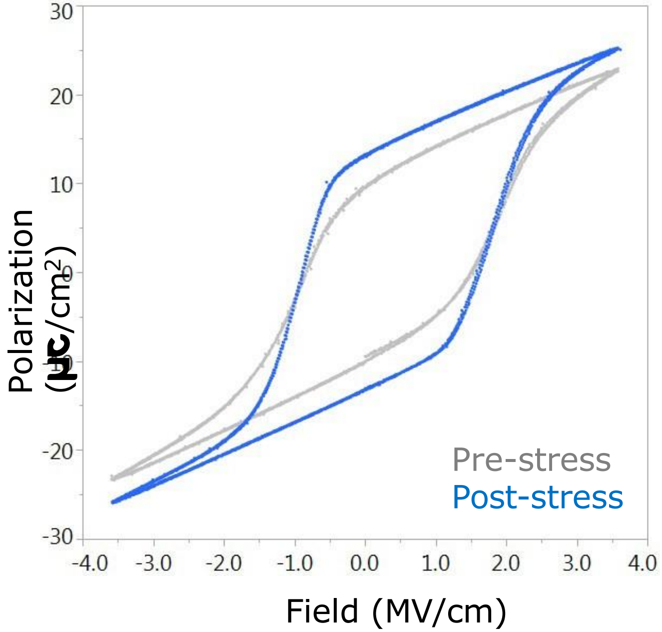
The monoclinic phase was effectively suppressed in the blended film, and the film is strongly ferroelectric as deposited.



~20% monoclinic



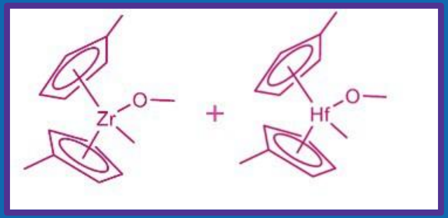
Inherent Ferroelectricity

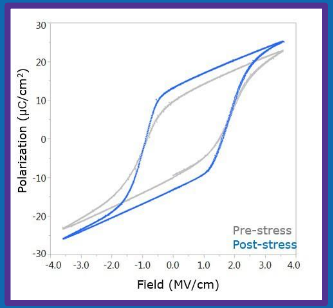


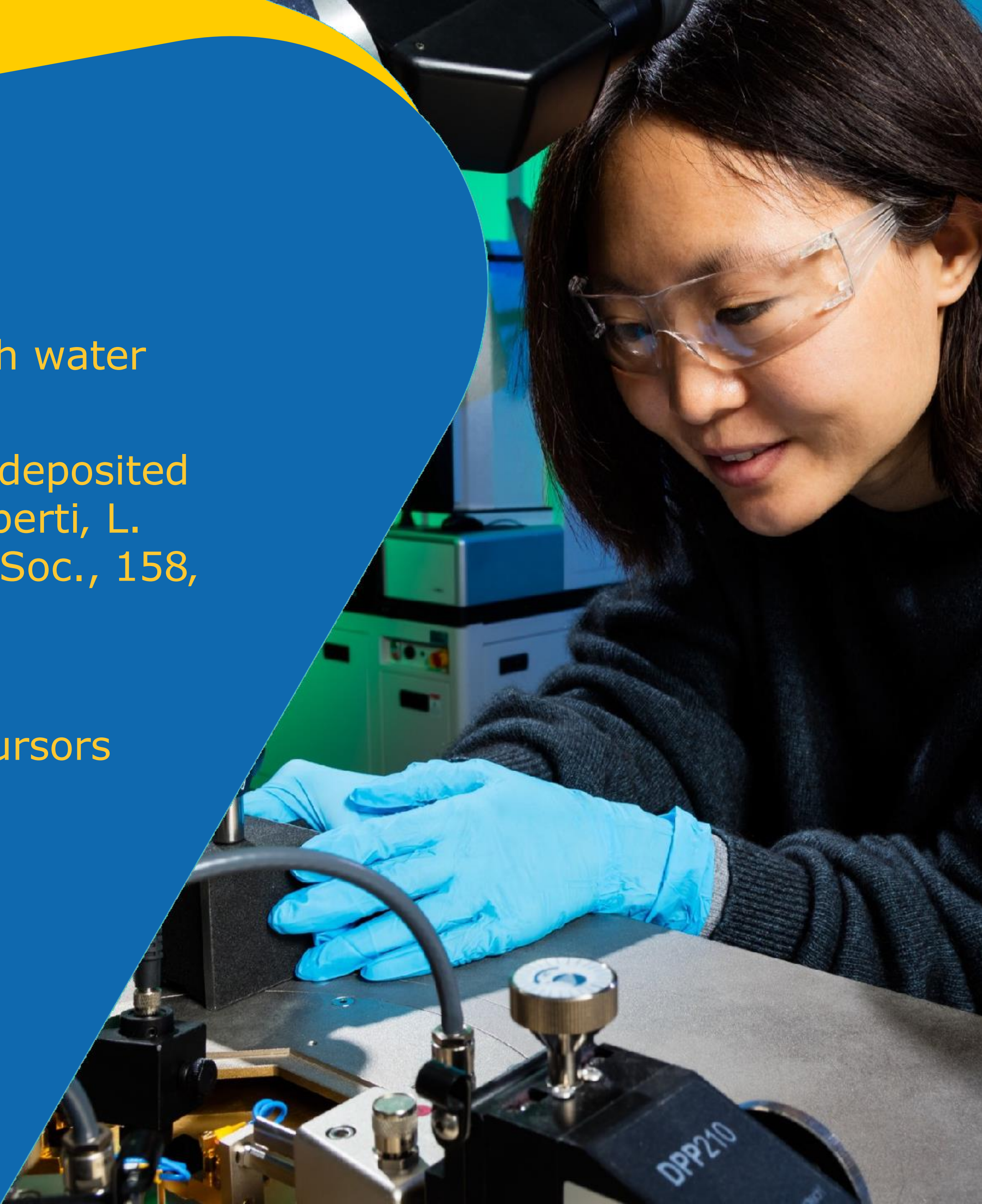
$2P_R = 27 \mu C/cm^2$

SUMMARY

- HfD-04 and ZrD-04 show linear ALD growth with both water and ozone.
- There is strong monoclinic suppression in ZrO_2 films deposited with ozone at 300°C (extending results from A. Lamperti, L. Lamagna, G. Congedo, and S. Spiga, J. Electrochem. Soc., 158, G221, 2011).
- HfO_2 films are amorphous as deposited at 300°C.
- Alternating cycles of ZrO_2 and HfO_2 using these precursors produce a crystalline film with strong ferroelectricity.







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