Anti-ferroelectrics: A unique phase transition material system

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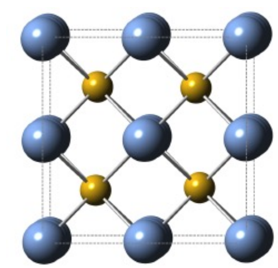
Phase transition in Antiferroelectrics

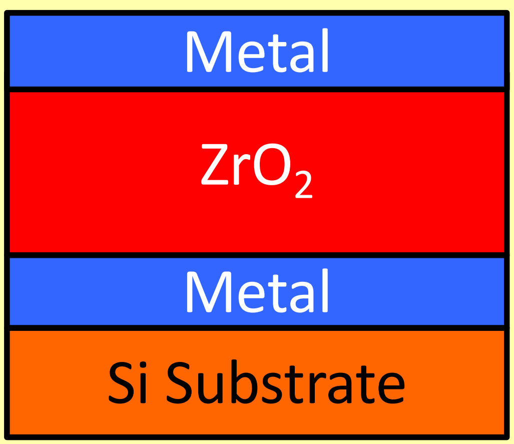
Electric field induced **1st order phase transition** from a non-polar ground state into a polar phase

Cubic (non-polar)

High Temperature Reference Phase



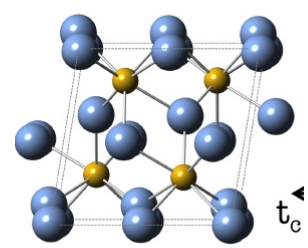
Zirconia (ZrO_2)
In semiconductor manufacturing for 50 years



Standard processing conditions

Non-polar Monoclinic

Ground State



Muller et al. Nano Lett. 2012

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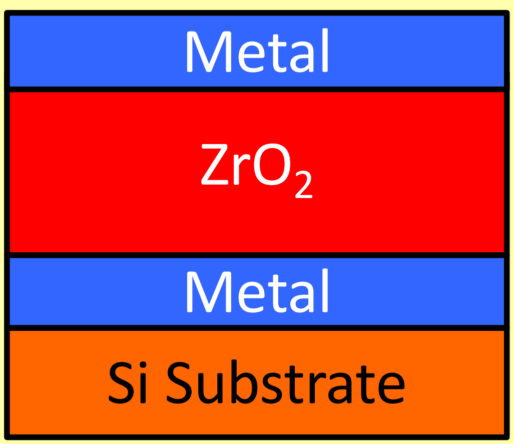

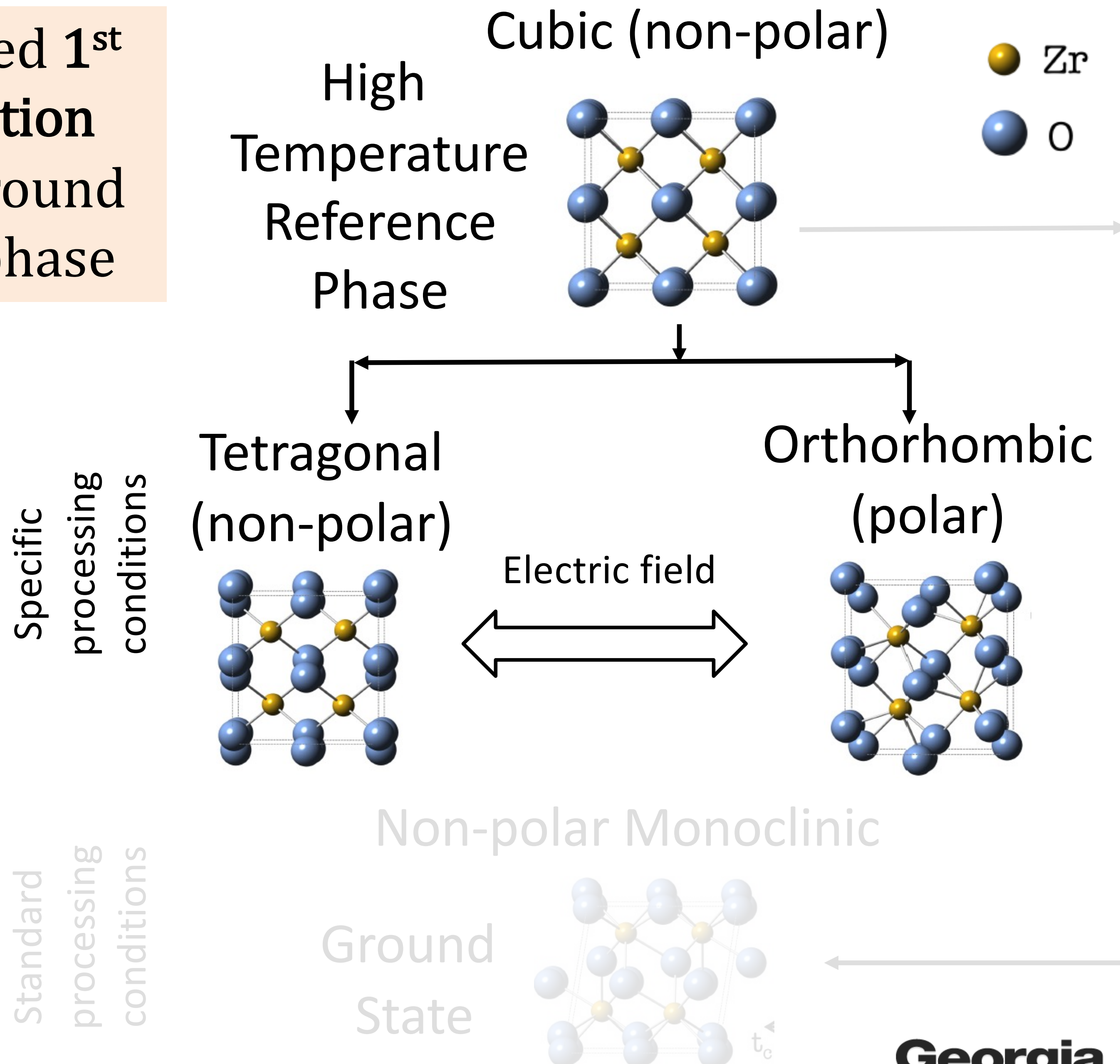

Georgia Tech

Phase transition in Antiferroelectrics

Electric field induced **1st order phase transition** from a non-polar ground state into a polar phase

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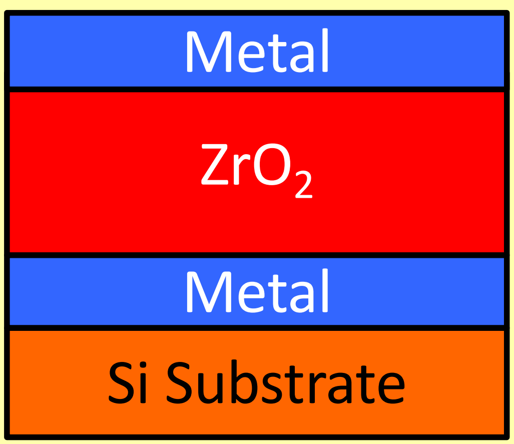

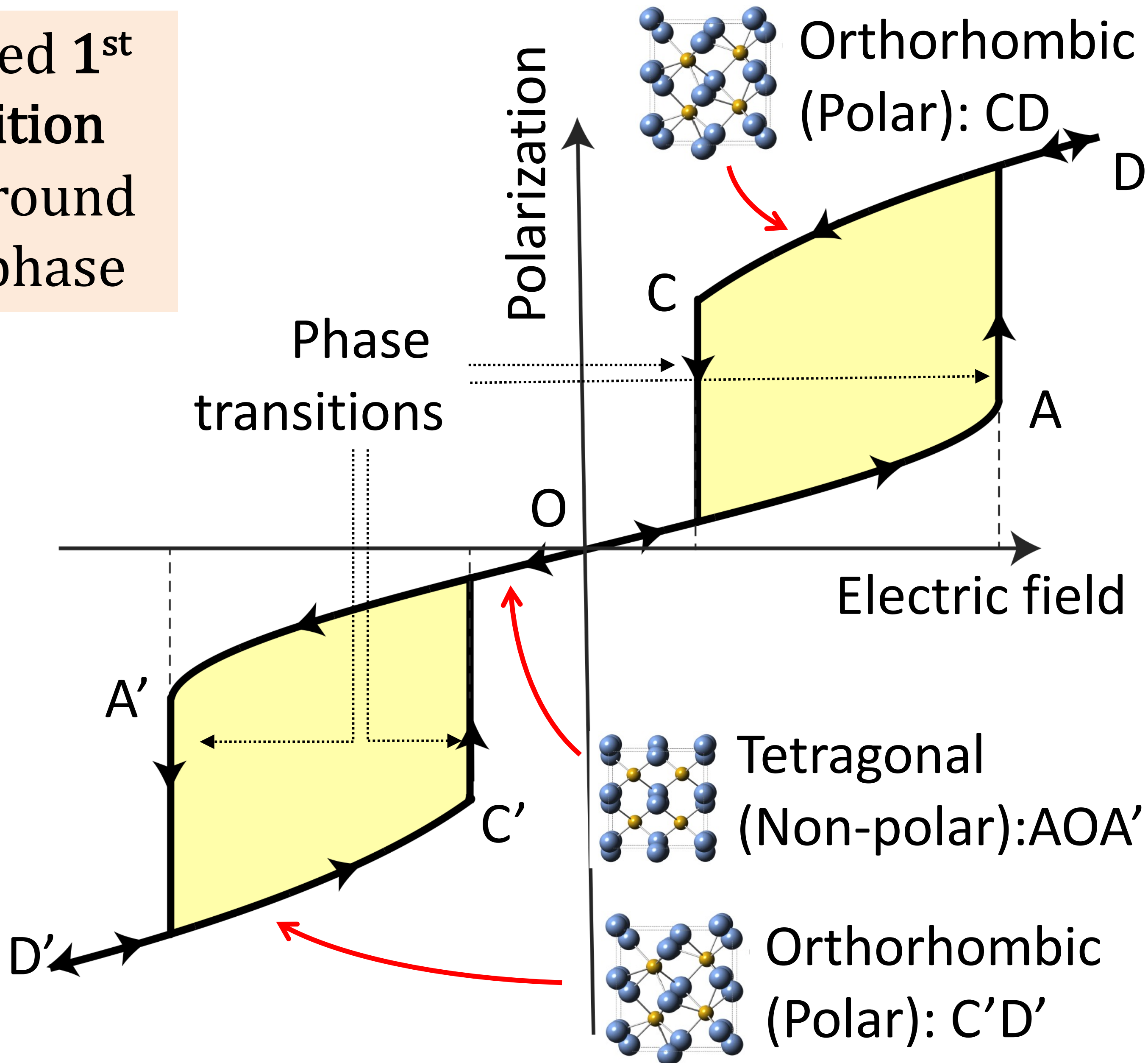

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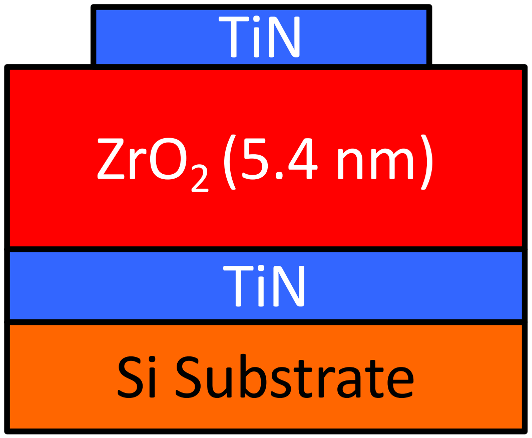
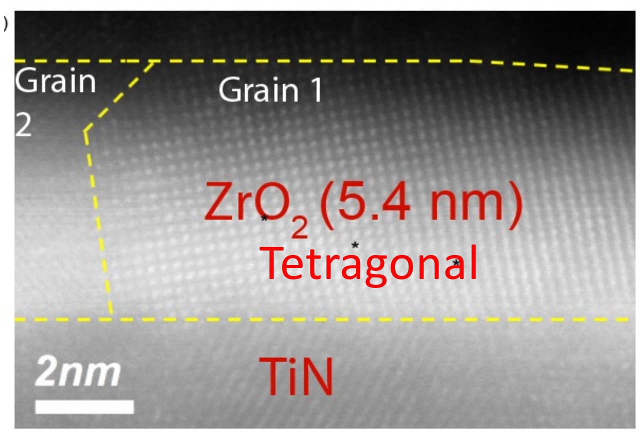
Antiferroelectricity in ZrO_2

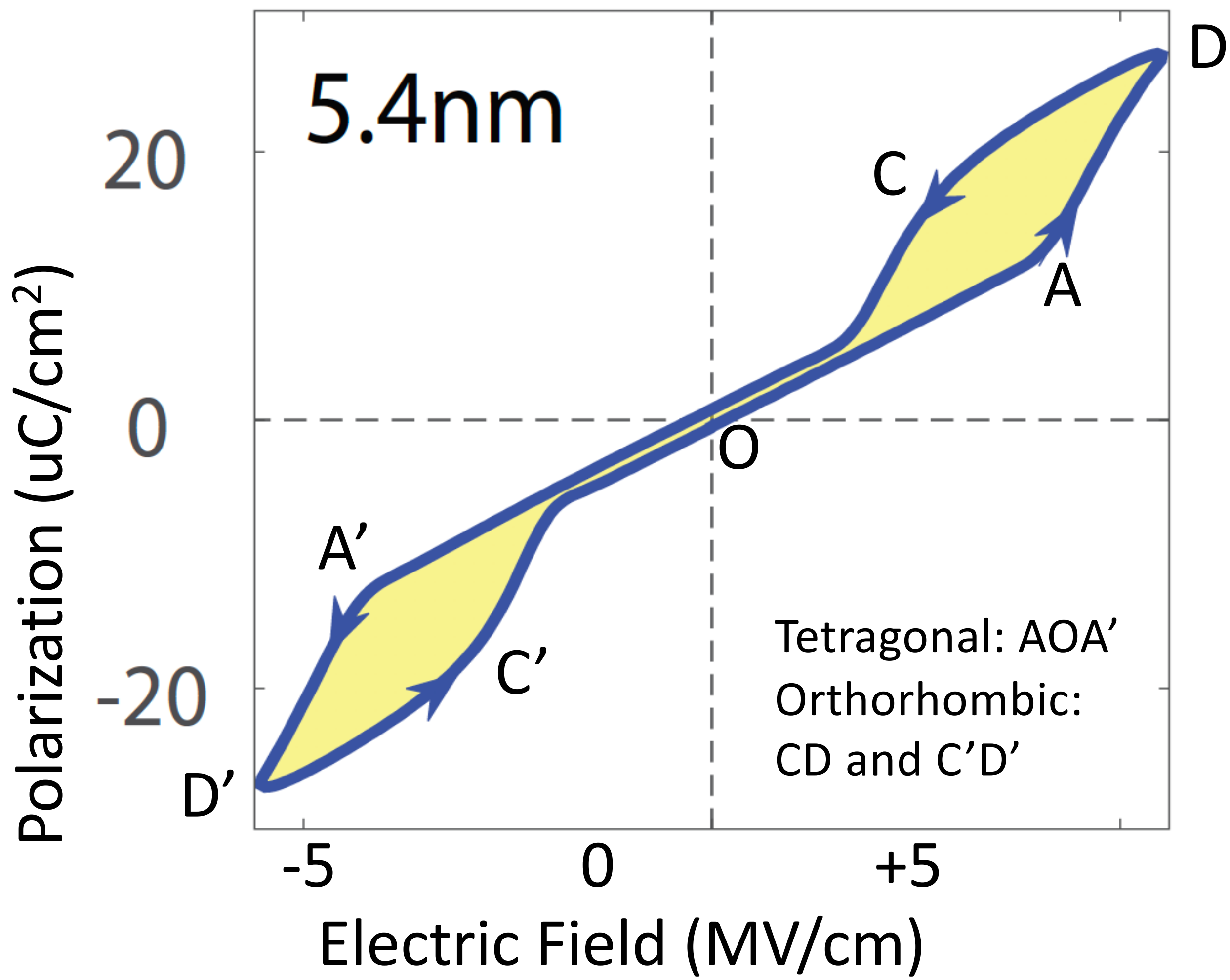
Structure



HAADF STEM



Hysteresis Loops



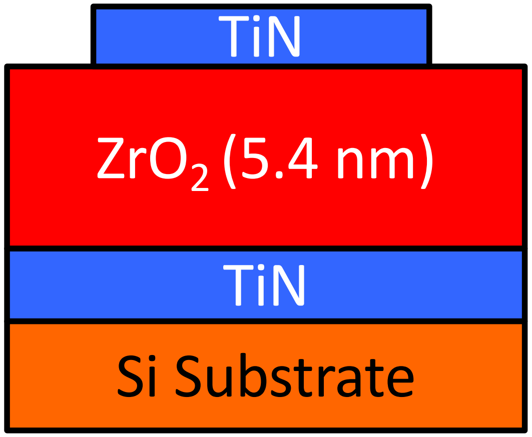
ALD grown ZrO_2 at Georgia Tech shows robust antiferroelectricity at a thickness as low as **5.4 nm**.

Tasneem et al. (in prep)

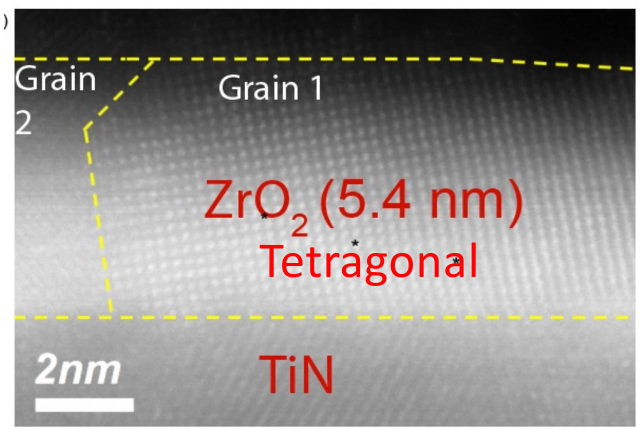
Georgia Tech

Antiferroelectricity in ZrO_2

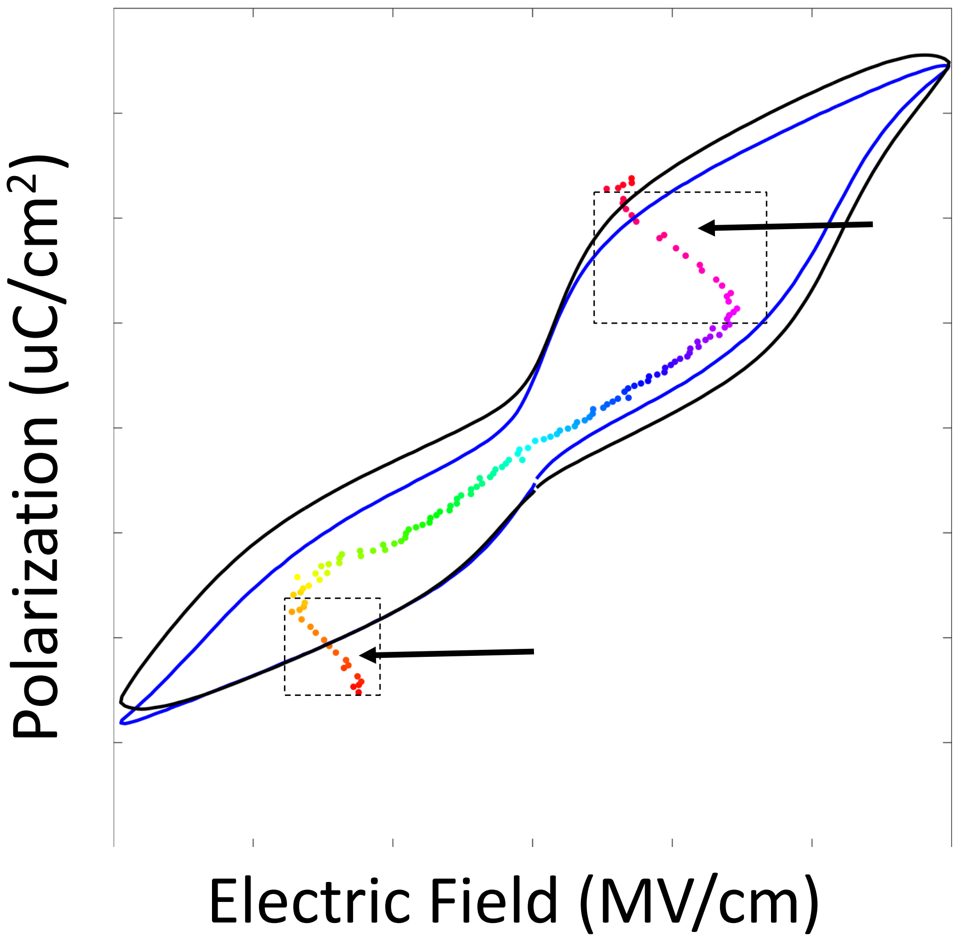
Structure



HAADF STEM



Hysteresis Loops



Unstable phase transition states in antiferroelectrics observed!

Tasneem et al. (in prep)

Why are we interested?

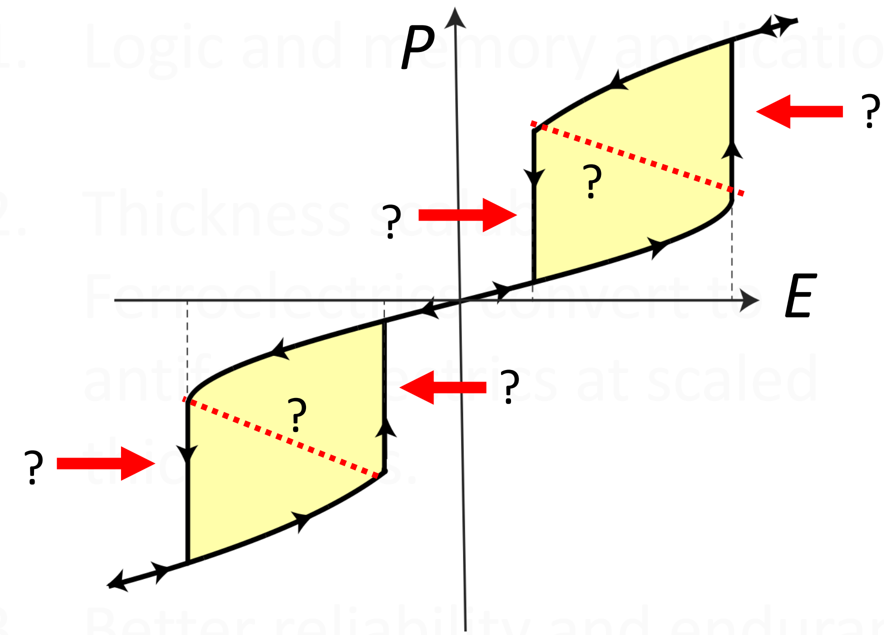
Science

1. Can we control the phase transition?

2. Nucleation and growth mechanisms during phase transition?

3. Is there a thickness limit to antiferroelectricity?

And many more…



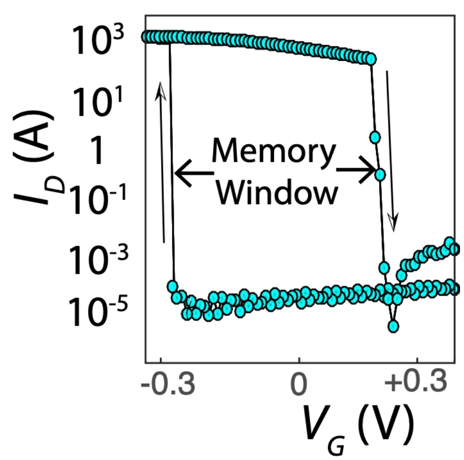
Why are we interested?

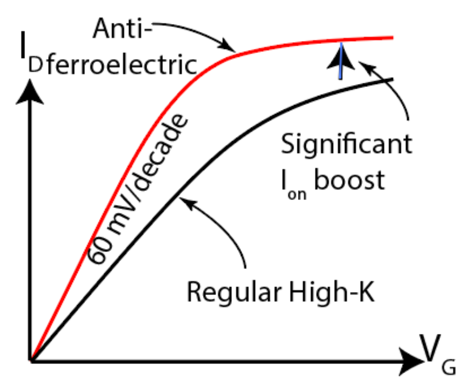
Science	Technology
1. Can we control the phase transition?	1. Logic and memory applications.
2. Nucleation and growth mechanisms during phase transition?	2. Thickness scalability: Ferroelectrics convert to antiferroelectrics at scaled thicknesses.
3. Is there a thickness limit to antiferroelectricity?	3. Better reliability and endurance

And many more…

Semiconductor Research Corporation

JUMP





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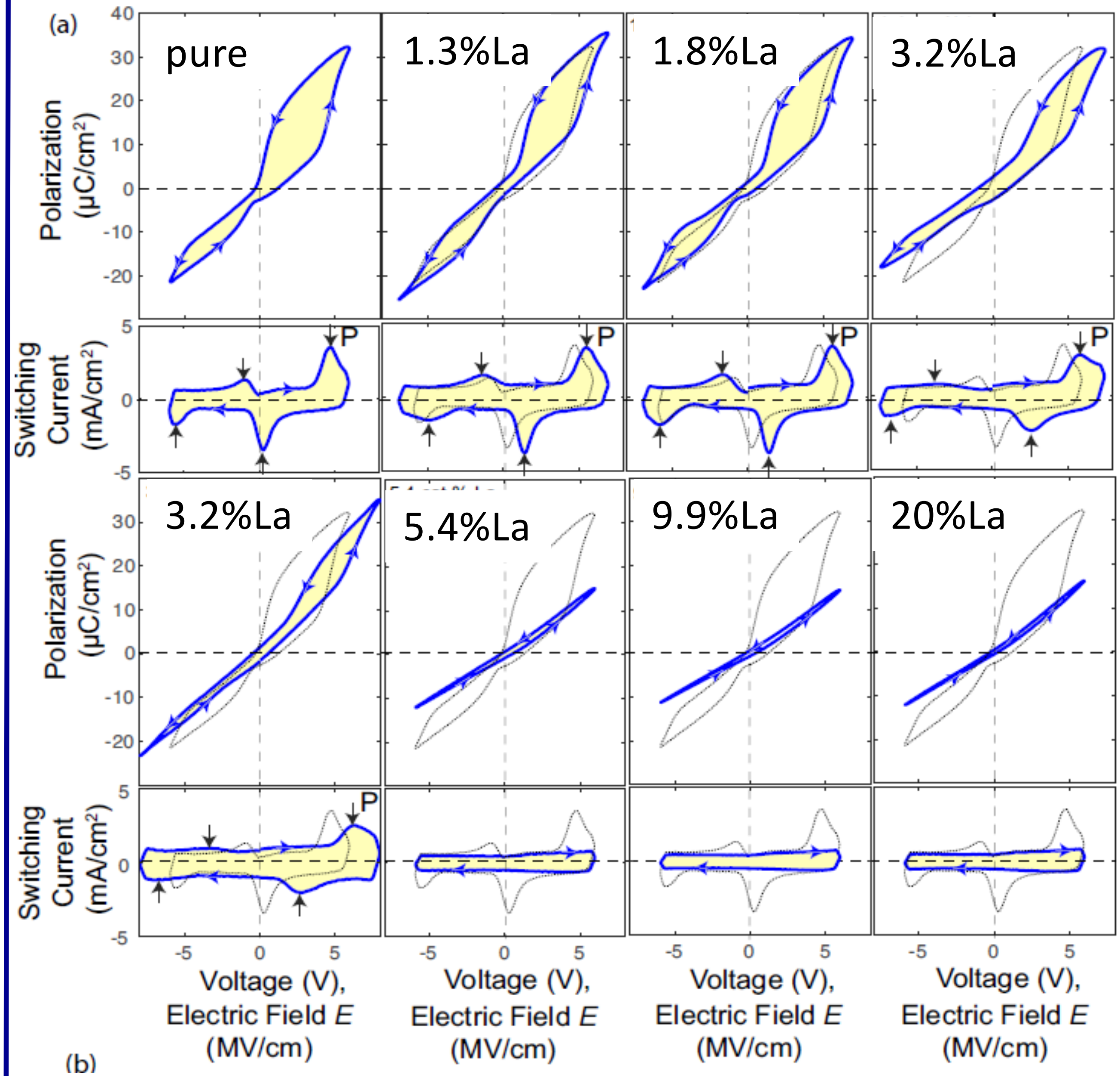
Effects of doping on Antiferroelectricity

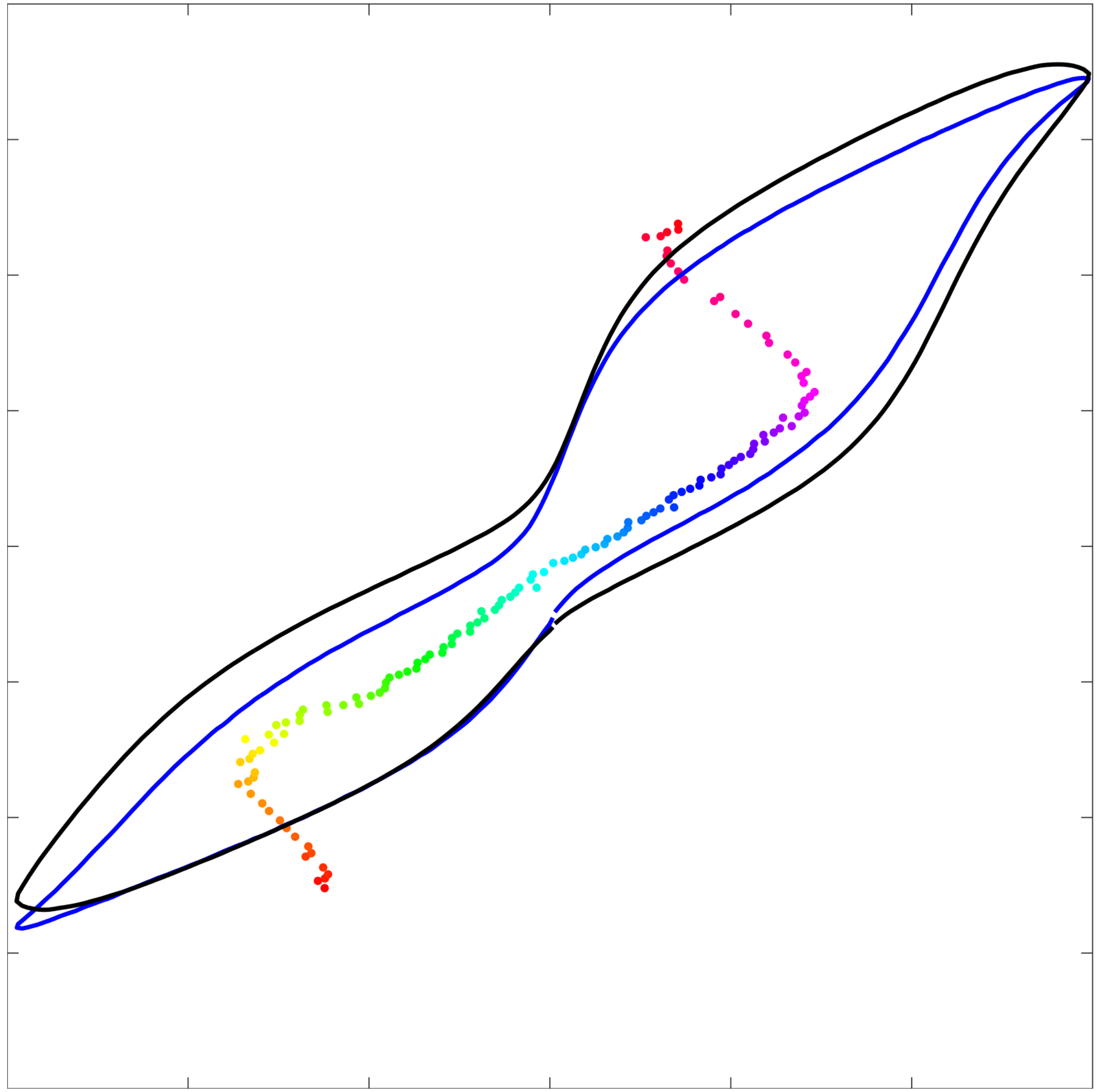


Increase in %La leads to

1. Narrowing of AFE Double Hysteresis Loops
2. Increase in Critical Voltage or Electric Field required for AFE→FE transition.

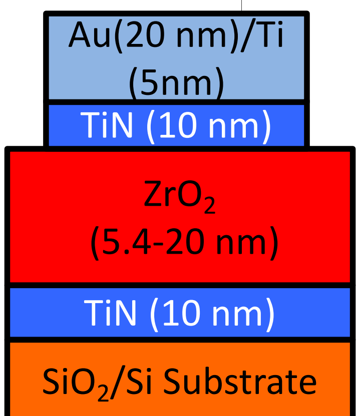
Wang, Zheng, et al. , *Applied Physics Letters* 112.22 (2018): 222902.

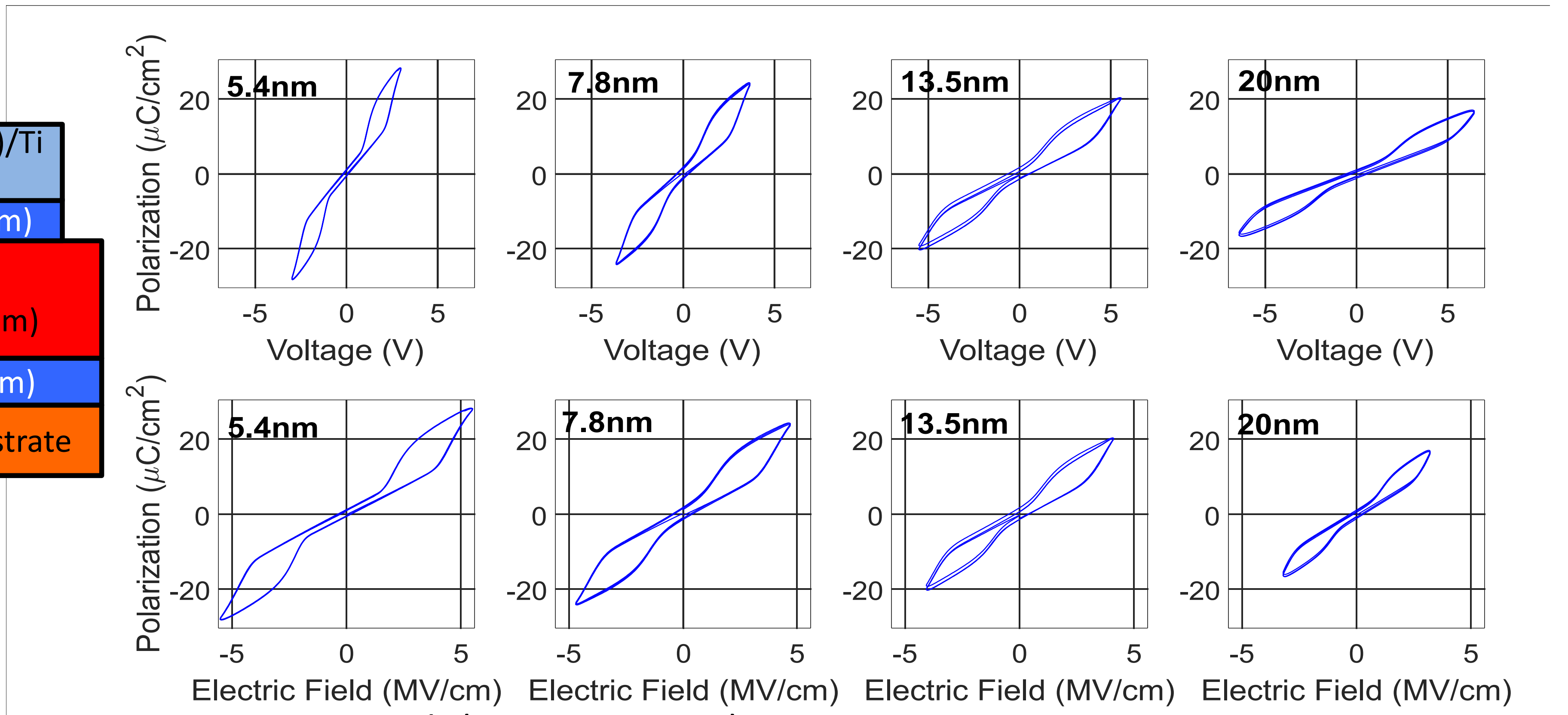
Georgia Tech



Results: Scaling of AFE ZrO_2

- ZrO_2 ALD recipe and anneal condition optimized.
  - ALD tool: Cambridge NanoTech Plasma ALD Fiji-F202 at Georgia Tech.
- Robust AFE double hysteresis loop obtained for thickness as low as 5.4 nm ZrO_2.

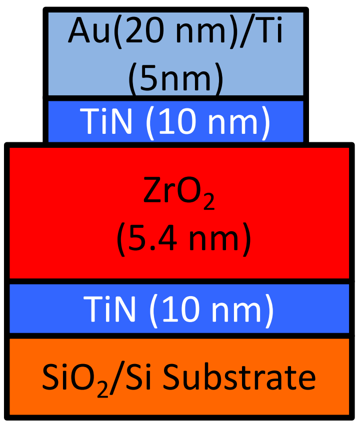


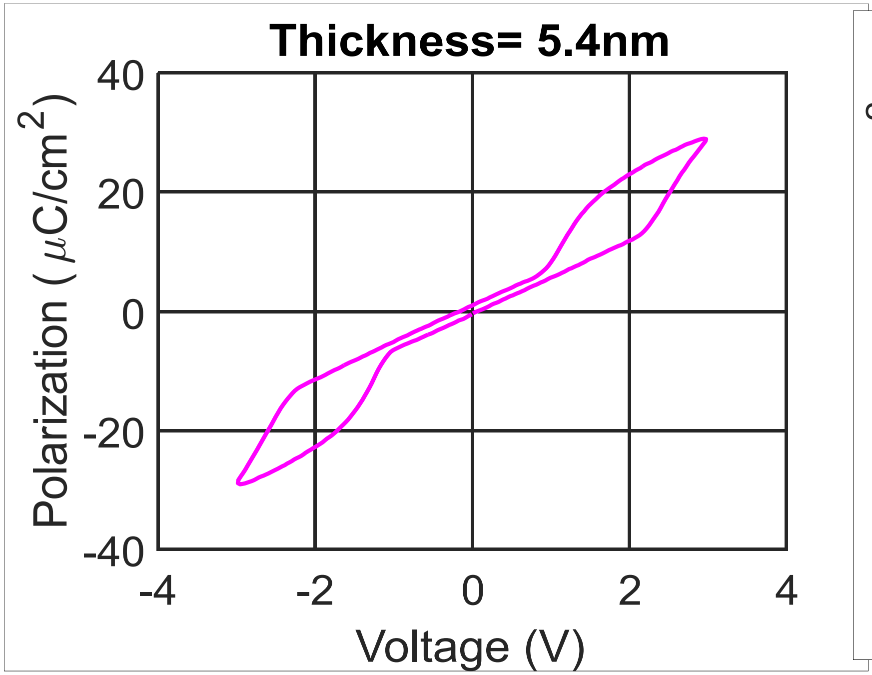


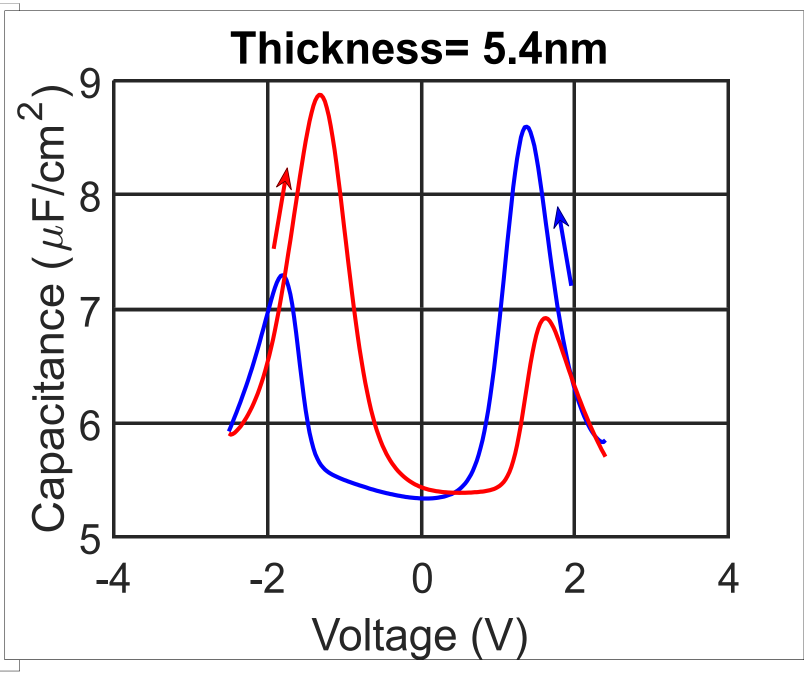
Tasneem et al. (in preparation)

Results: Scaling of AFE ZrO_2 (5.4 nm)

- Robust AFE double hysteresis loop obtained for thickness as low as 5.4 nm ZrO_2.
- Capacitance-voltage characteristics show AFE type double butterfly loops.



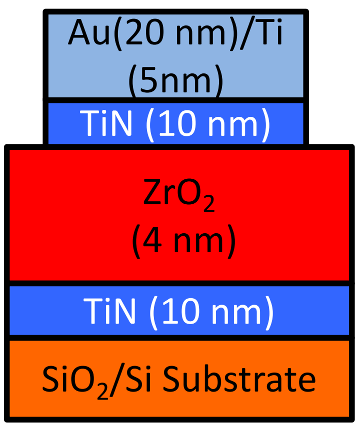


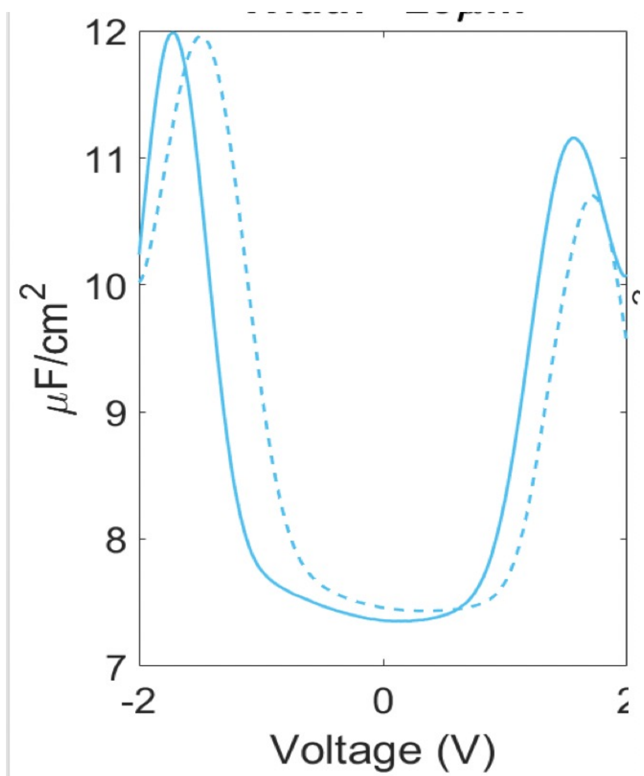


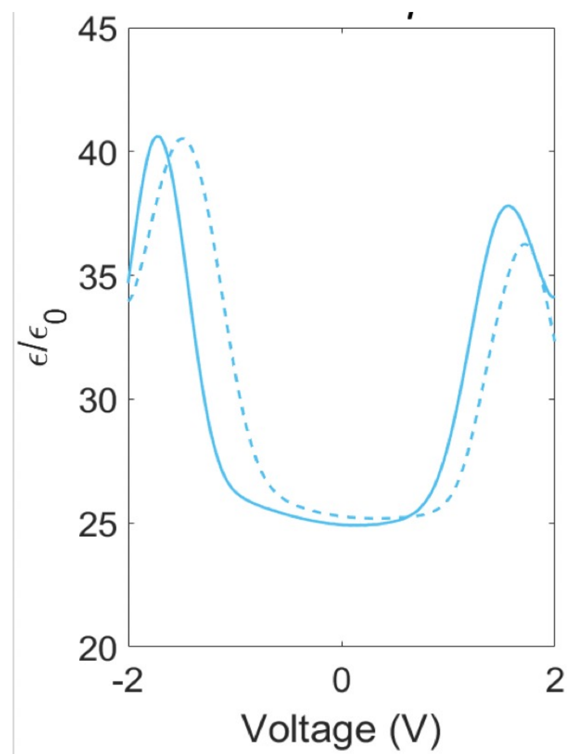
Tasneem et al. (in preparation)

Results: Scaling of AFE ZrO_2 (4 nm)

- 4 nm ZrO_2: Capacitance-voltage characteristics show AFE type double butterfly loops, but polarization vs. voltage hysteresis could not be measured due to high leakage.



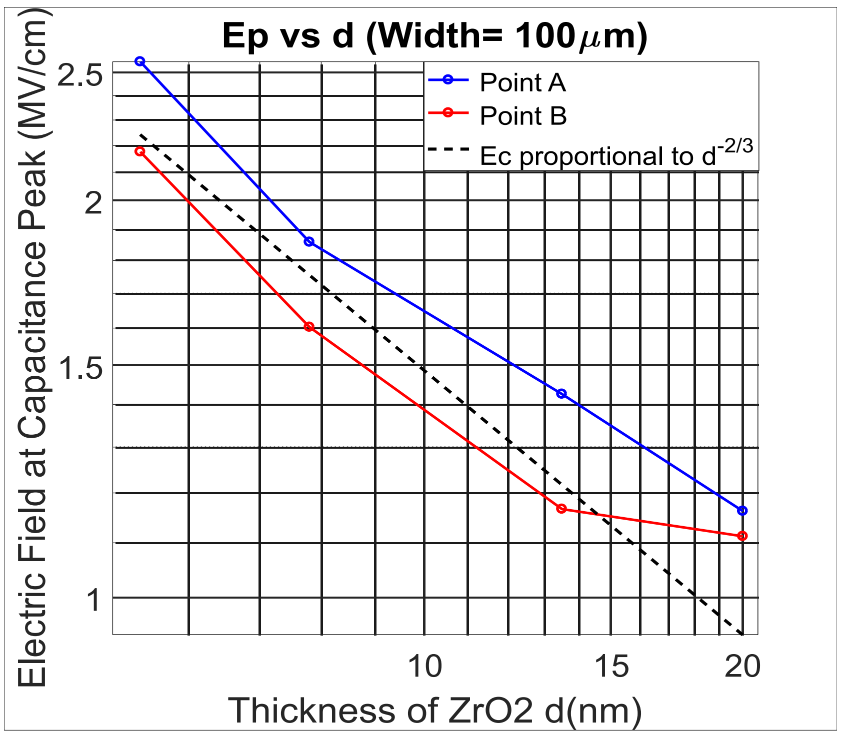


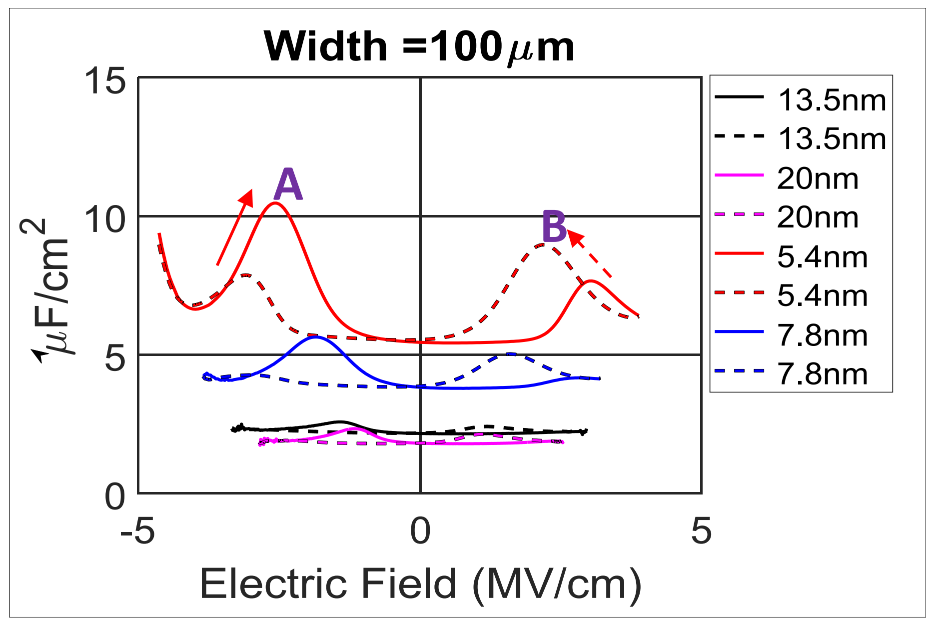


Tasneem et al. (in preparation)

Results: Scaling of AFE ZrO_2 (Electrical properties)

- Coercive Electric Field, Ec decreases as we increase the thickness of ZrO_2 layer.
- Change in Electric Field with ZrO_2 layer thickness seems to follow the J-K-D Law:
- $E_c \propto d^{-\frac{2}{3}}$ (Jenovec-Kay-Dunn Law for ferroelectric)





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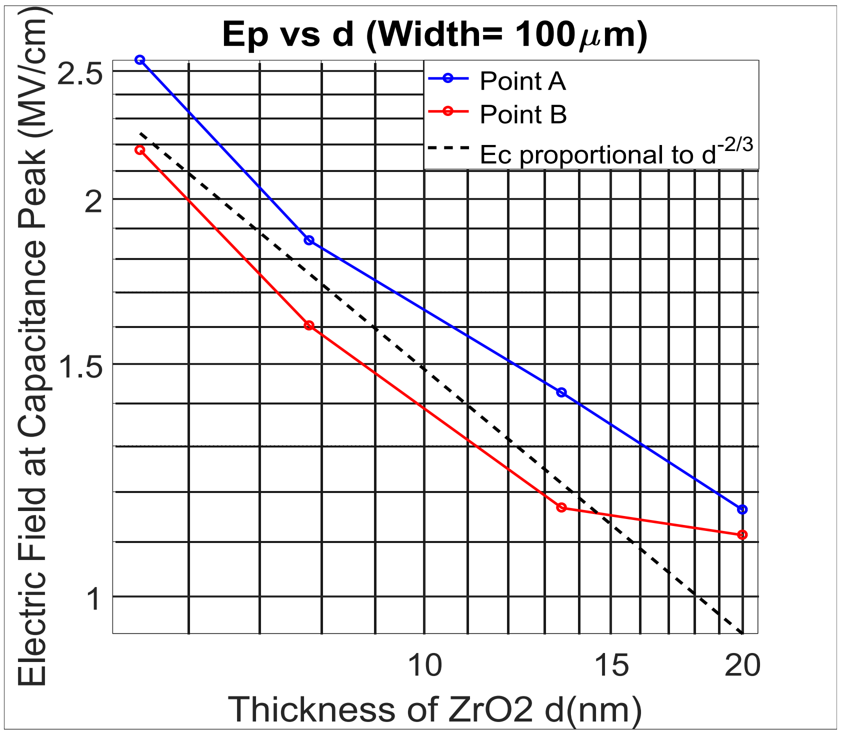
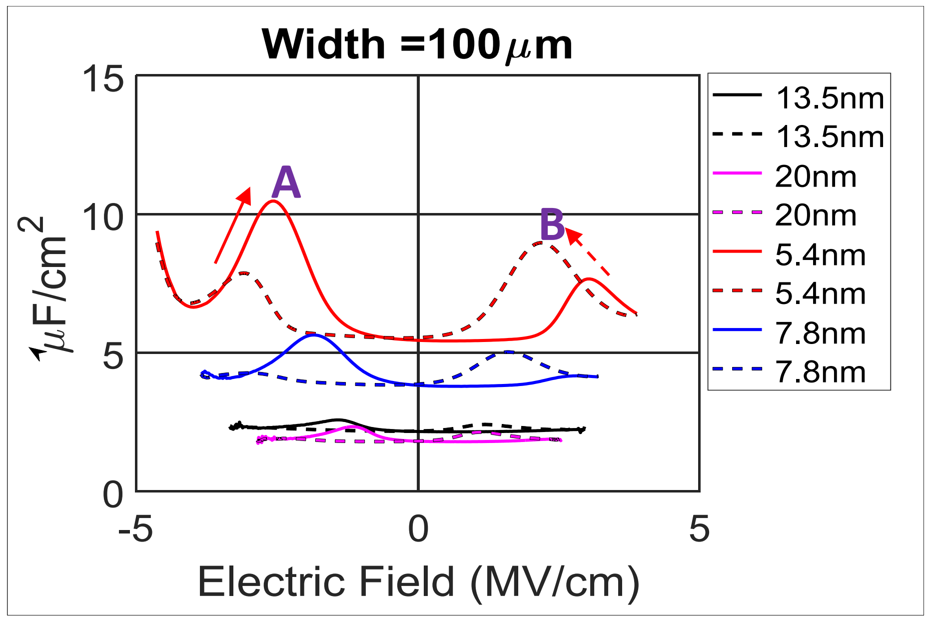
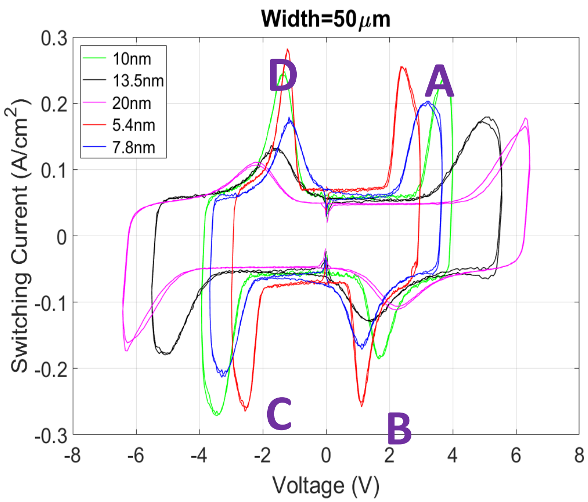


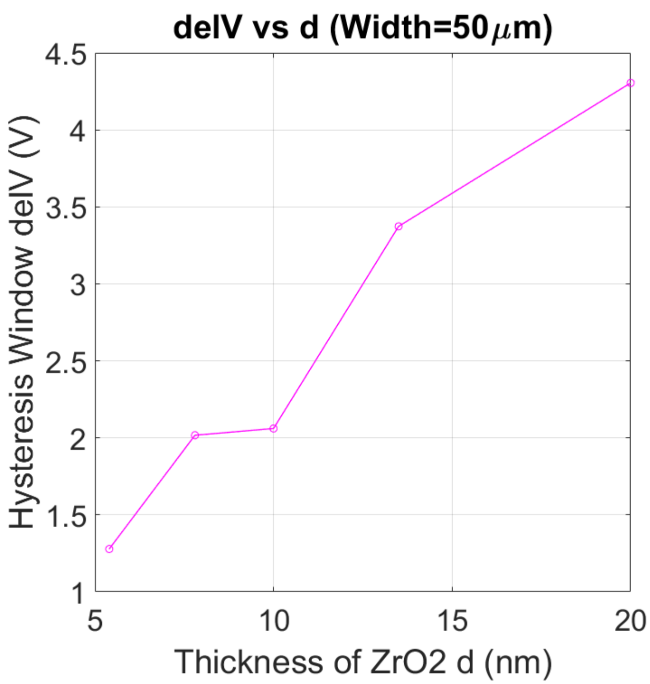


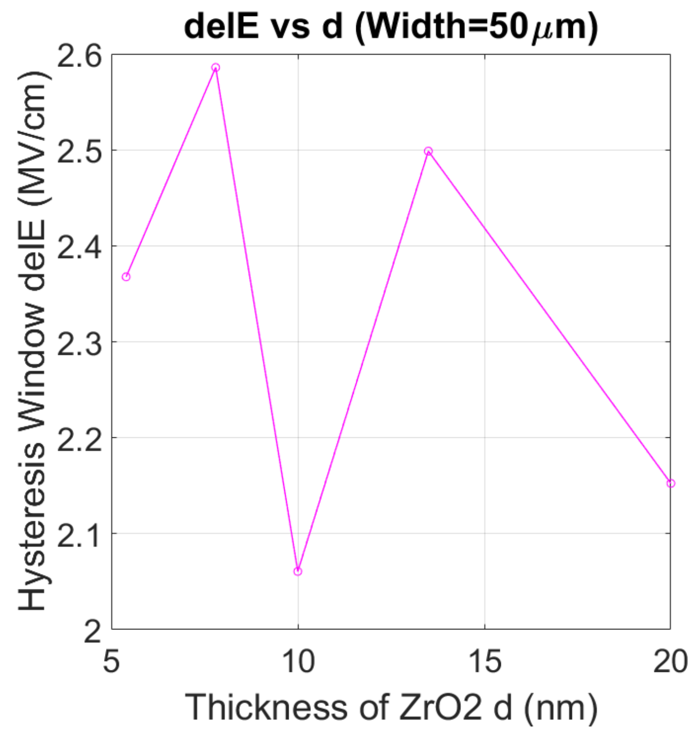
Tasneem et al. (in preparation)

Results: Scaling of AFE ZrO_2 (Electrical properties)

- Voltage Width of the hysteresis window changes linearly with the thickness.
- Electric field width of the hysteresis window stays constant with thickness.



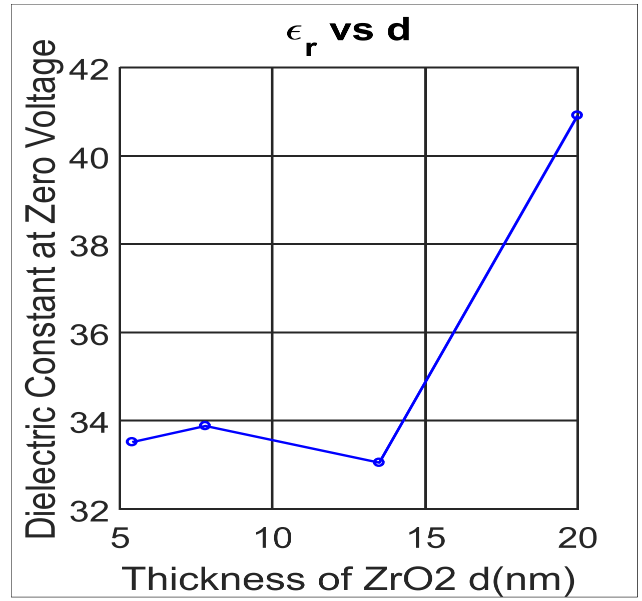


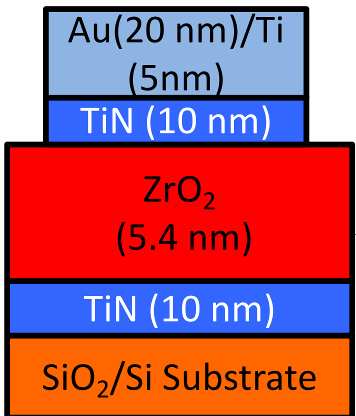


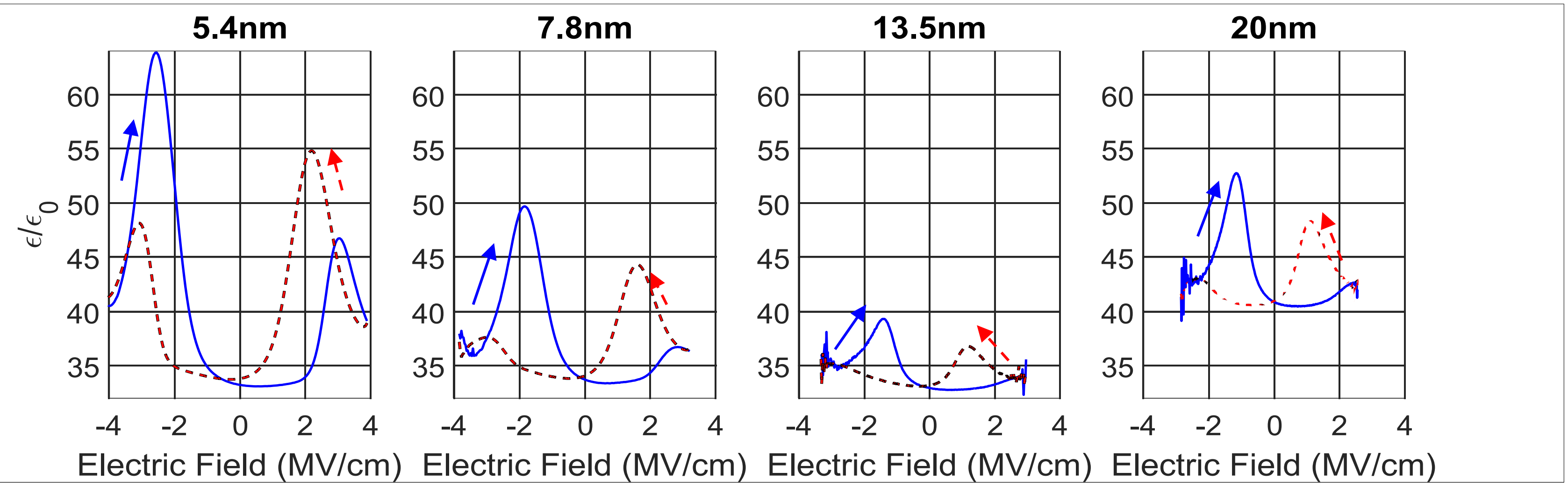
Tasneem et al. (in preparation)

Results: Scaling of AFE ZrO_2 (Electrical properties)

- Dielectric constant at crossing seems remain constant at ~35 until 13 nm

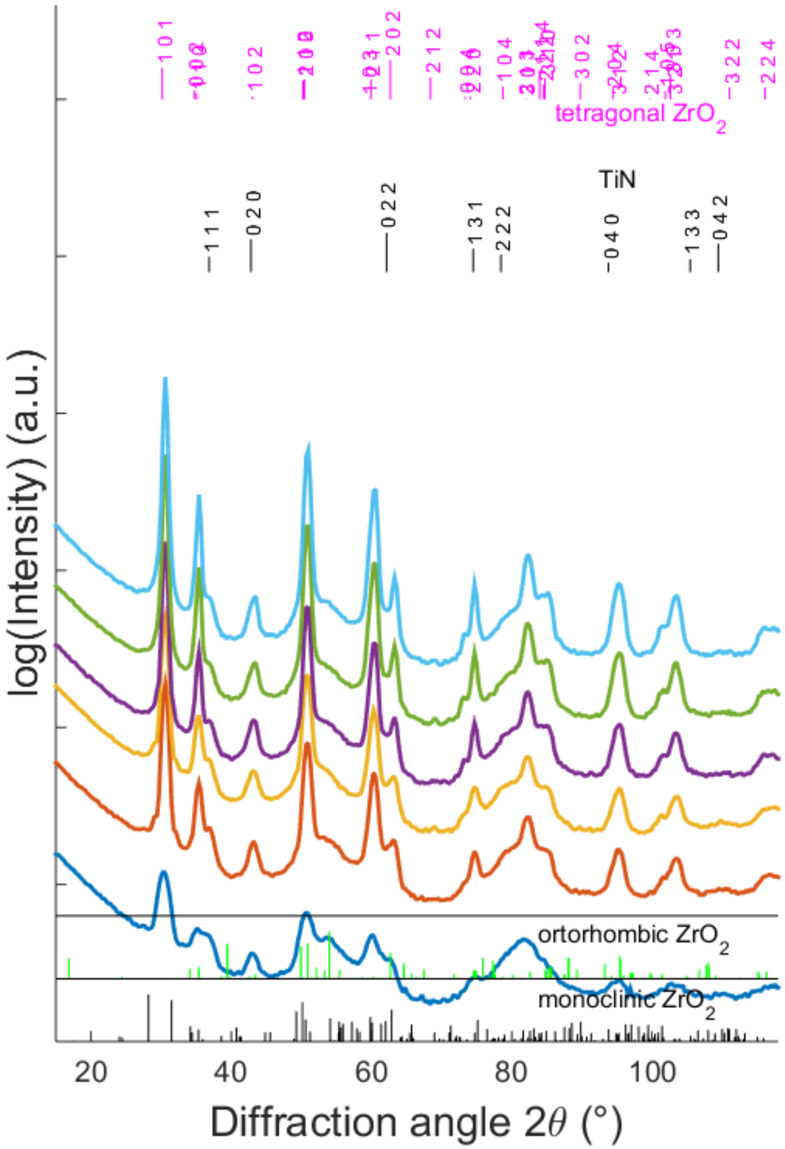






Tasneem et al. (in preparation)

Results: Scaling of AFE ZrO_2 (Structural properties)



20 nm
17 nm
13.5 nm
10 nm
7.8 nm
5.4 nm

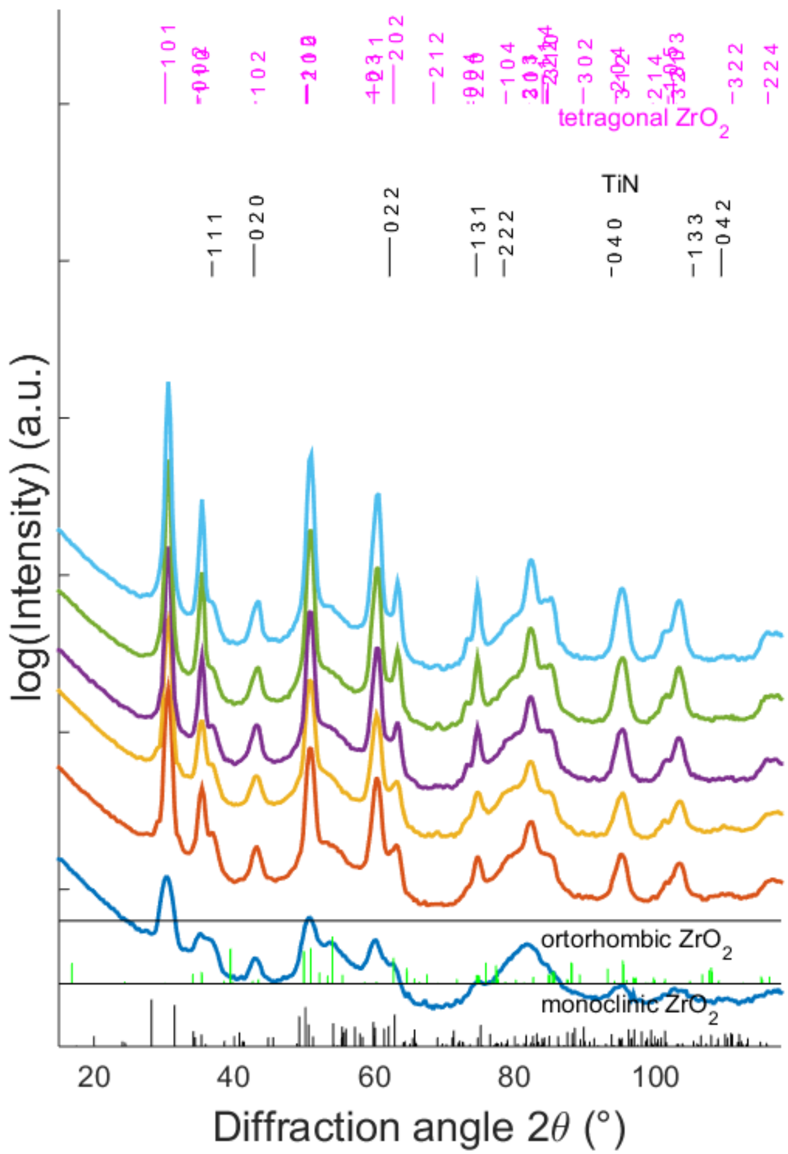
In 5.4 nm and 7.8 nm no monoclinic and orthorhombic phases detected
(pure tetragonal phase)

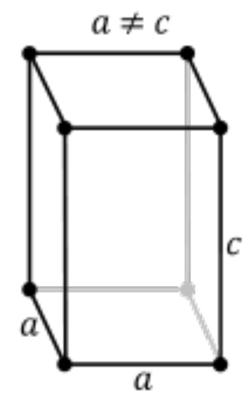
Refer to slide 6 last point

Collaboration with Charles University, Czech Republic

Tasneem et al. (in preparation)

Results: Scaling of AFE ZrO_2 (Structural properties)





20 nm

17 nm

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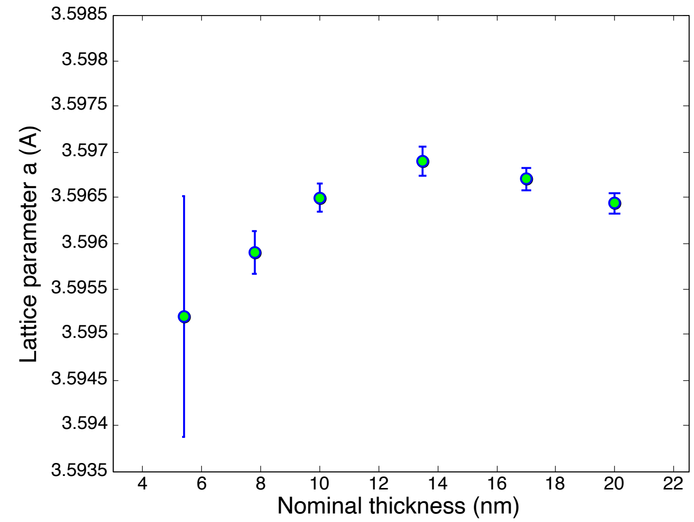
7.8 nm

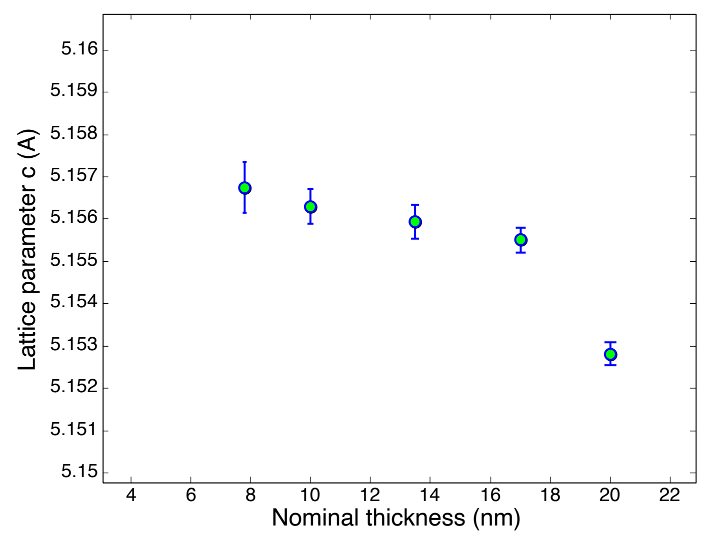
5.4 nm

Tasneem et al. (in preparation)

a-axis Lattice Parameter

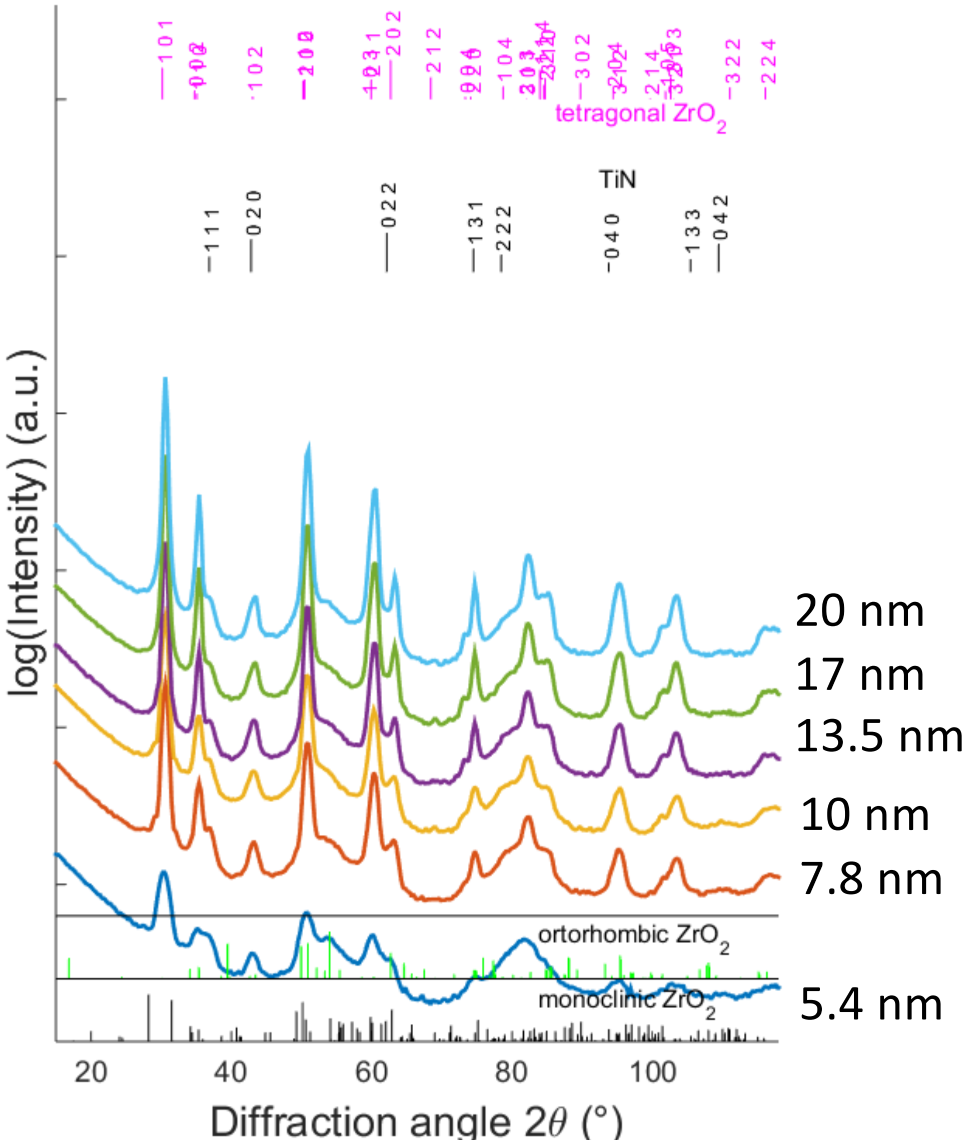


c-axis Lattice Parameter

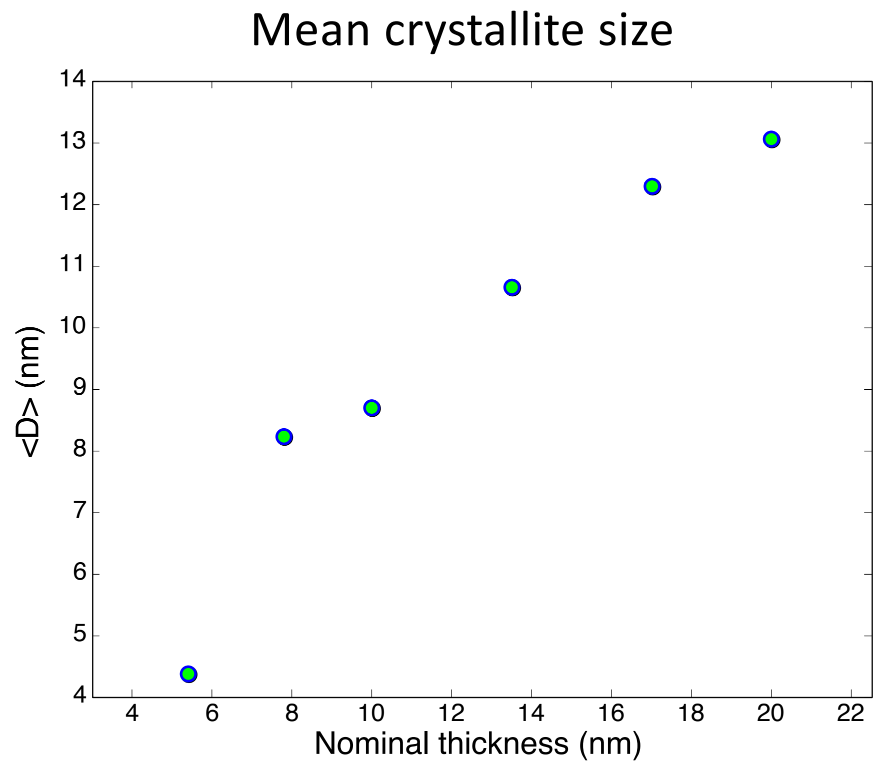


Standard: (a, c)= (3.595 A, 5.19 A)

Results: Scaling of AFE ZrO_2 (Grain size evolution)

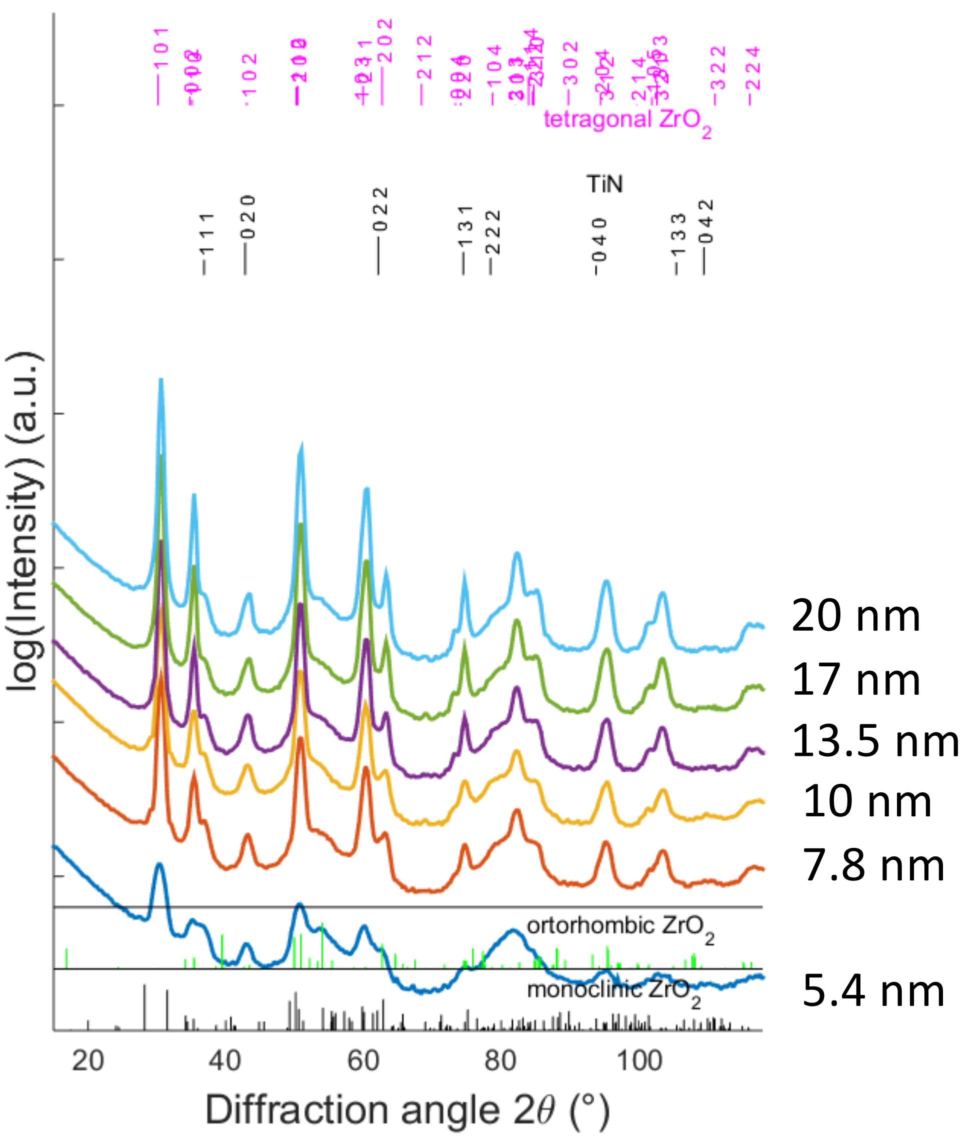


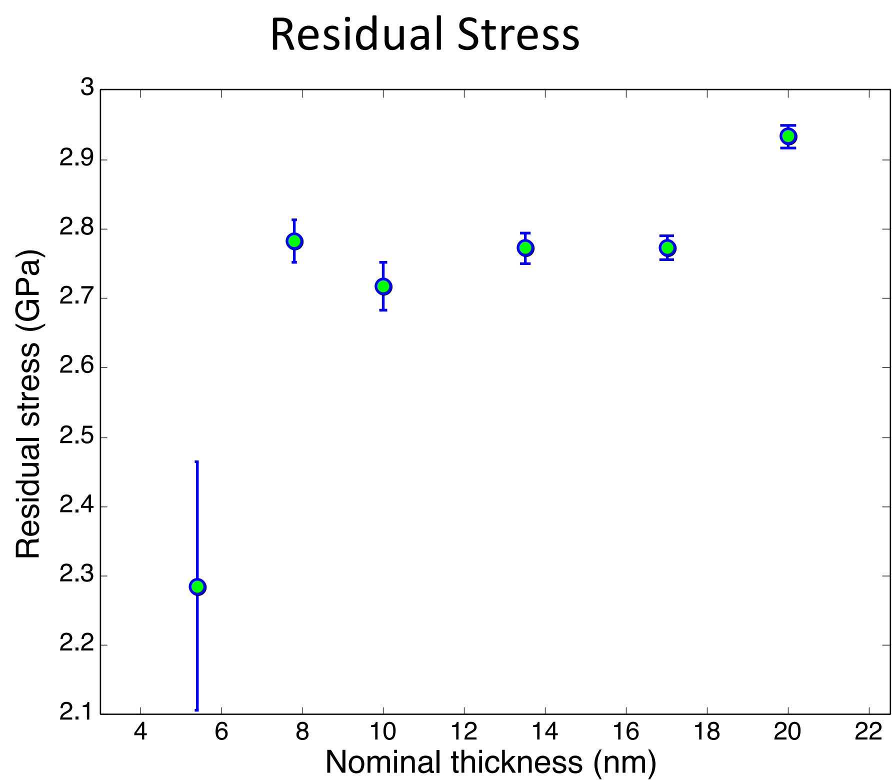
Tasneem et al. (in preparation)



Mean crystallite size (i.e., grain size) decreases with decreasing thickness.

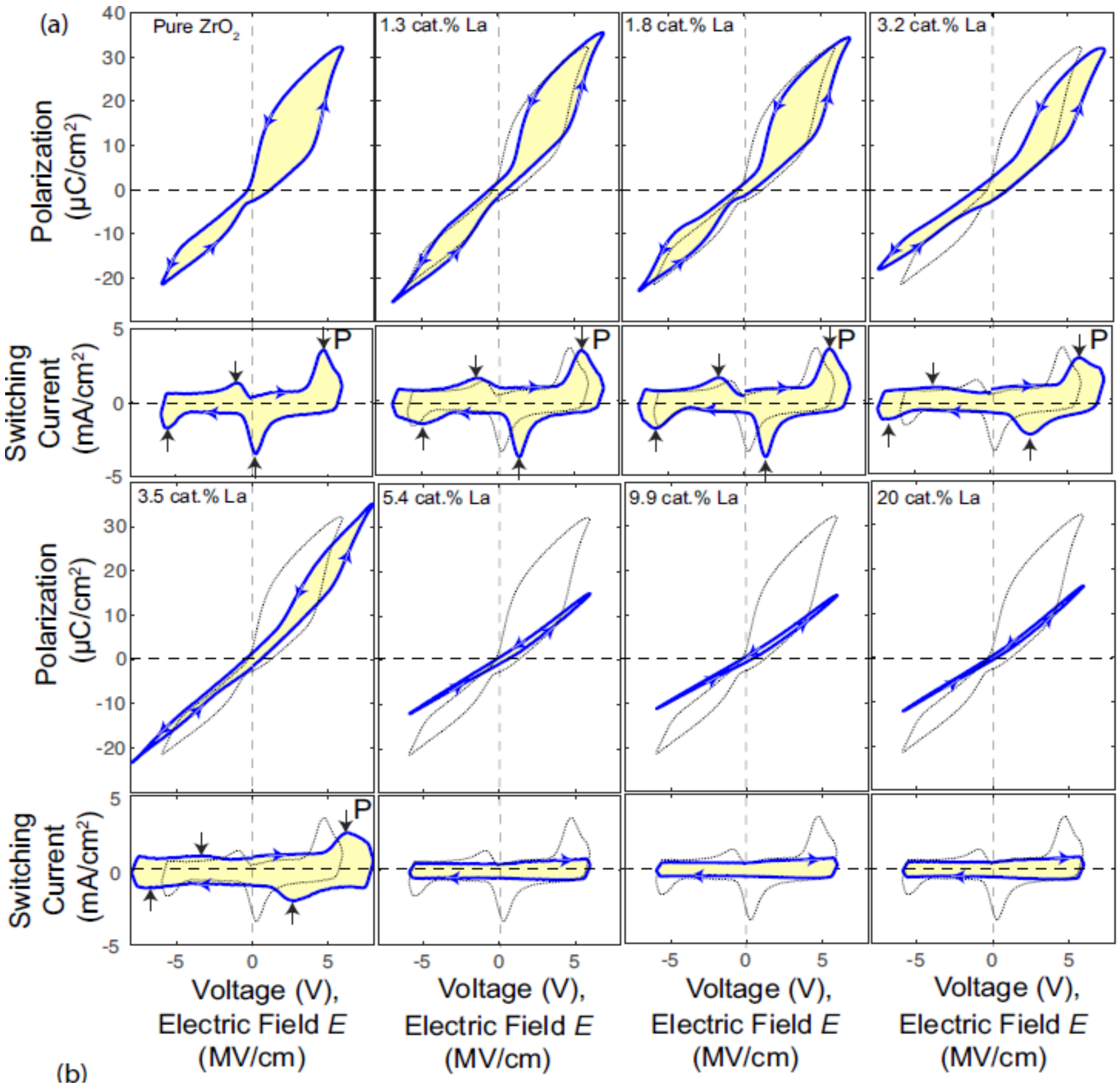
Results: Scaling of AFE ZrO_2 (Residual stress)





Significant residual stress observed in our ZrO_2 samples.

Comparison to our prior work (Pre-GRC)



Increase in La Doping leads to

1. Narrowing of AFE Double Hysteresis Loops
2. Increase in Critical Voltage or Electric Field required for AFE→FE transition.

Wang, Zheng, et al. , *Applied Physics Letters* 112.22 (2018): 222902.
Collaboration with AIXTRON (now Eugenus)

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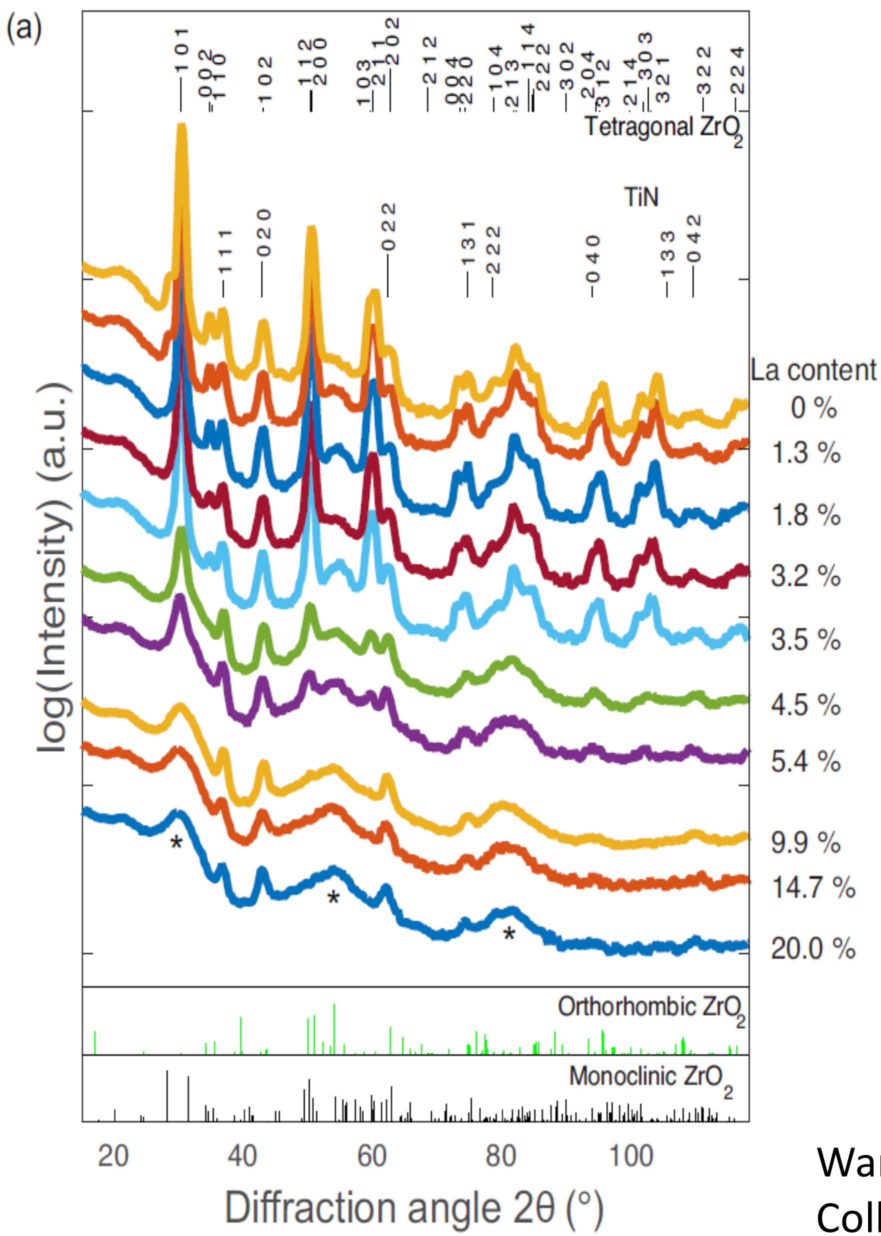
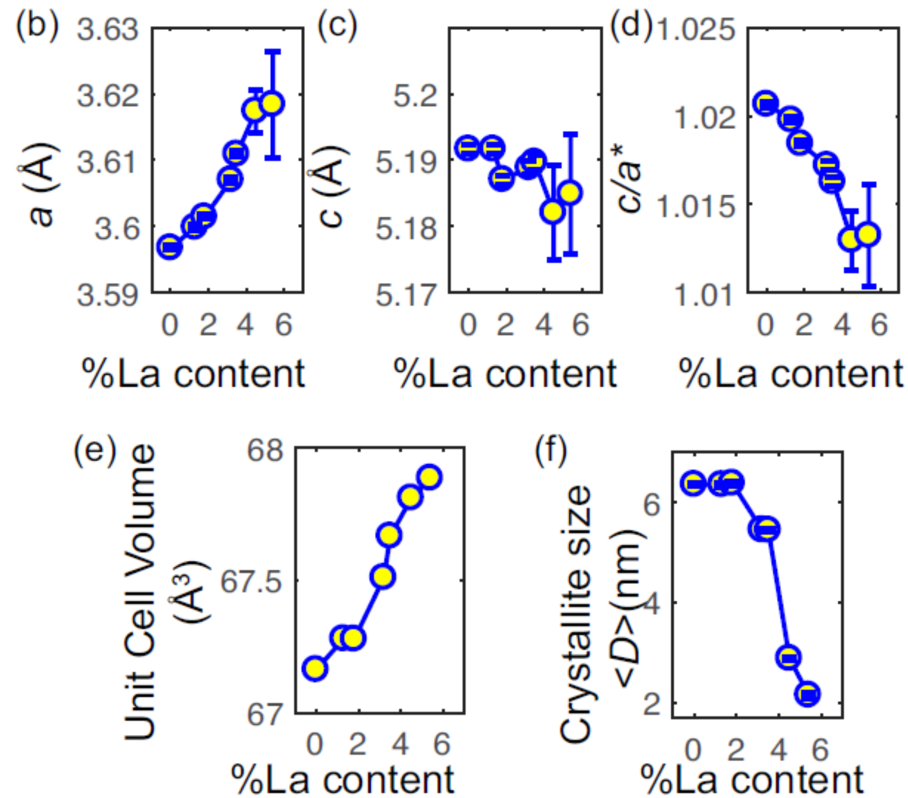


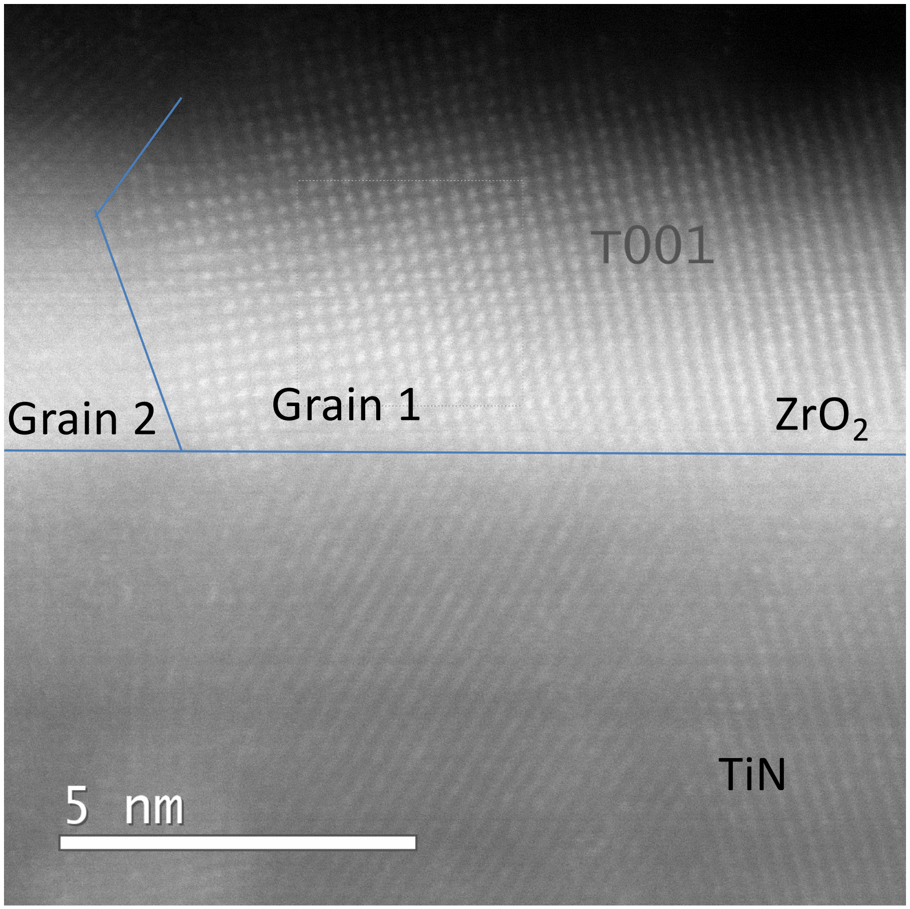


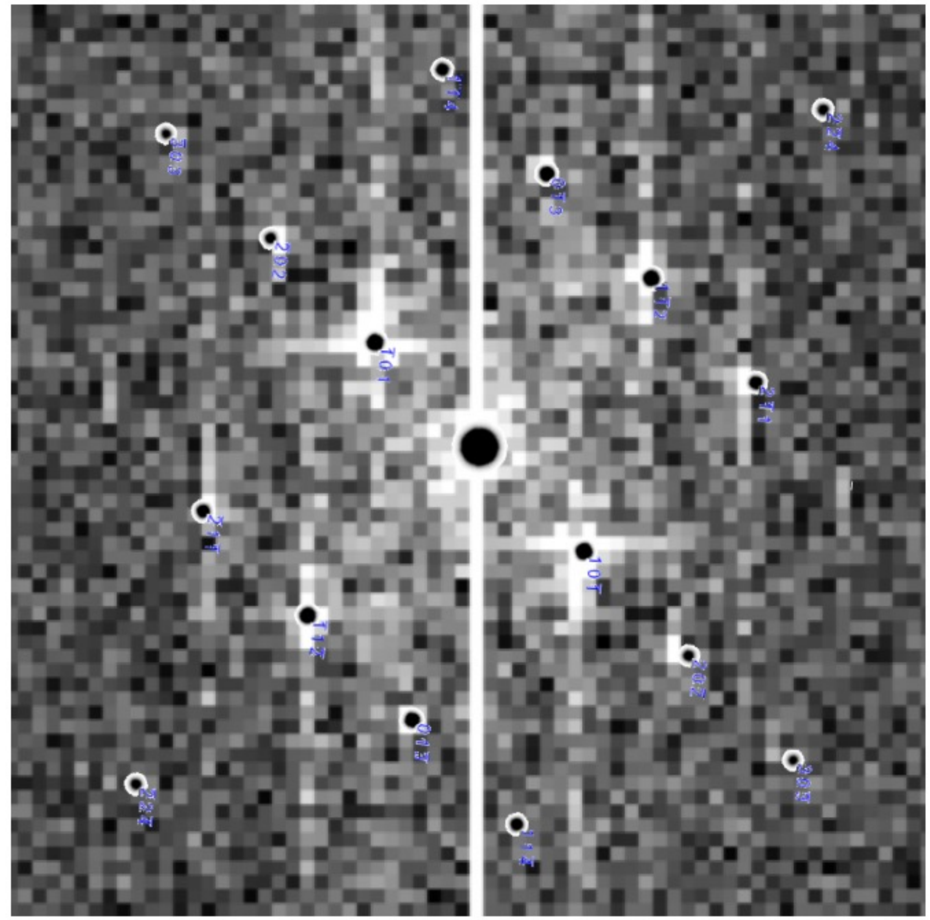
Increase in La Doping leads to:

- Decrease of Tetragonality (c/a^*)
- Decrease of the (nano-) crystallite size
- Increase in unit cell volume

Wang, Zheng, et al. , *Applied Physics Letters* 112.22 (2018): 222902.
Collaboration with AIXTRON (now Eugenus)

Atomic resolution STEM Imaging of 5.4 nm ZrO_2



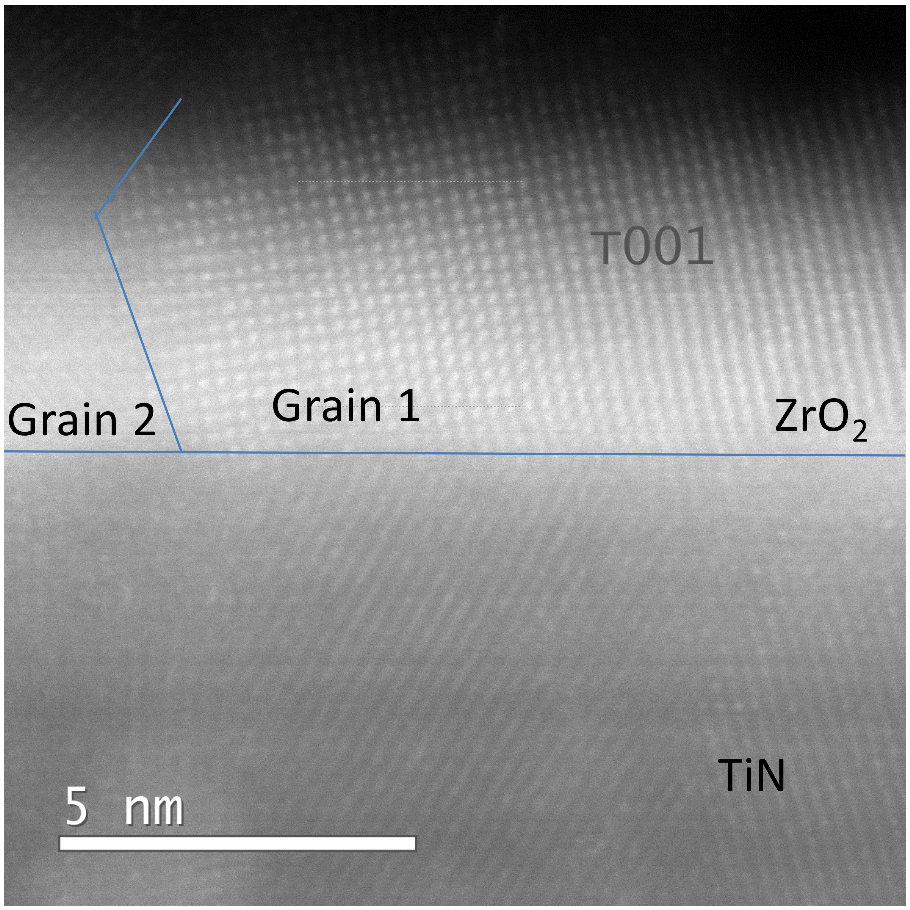


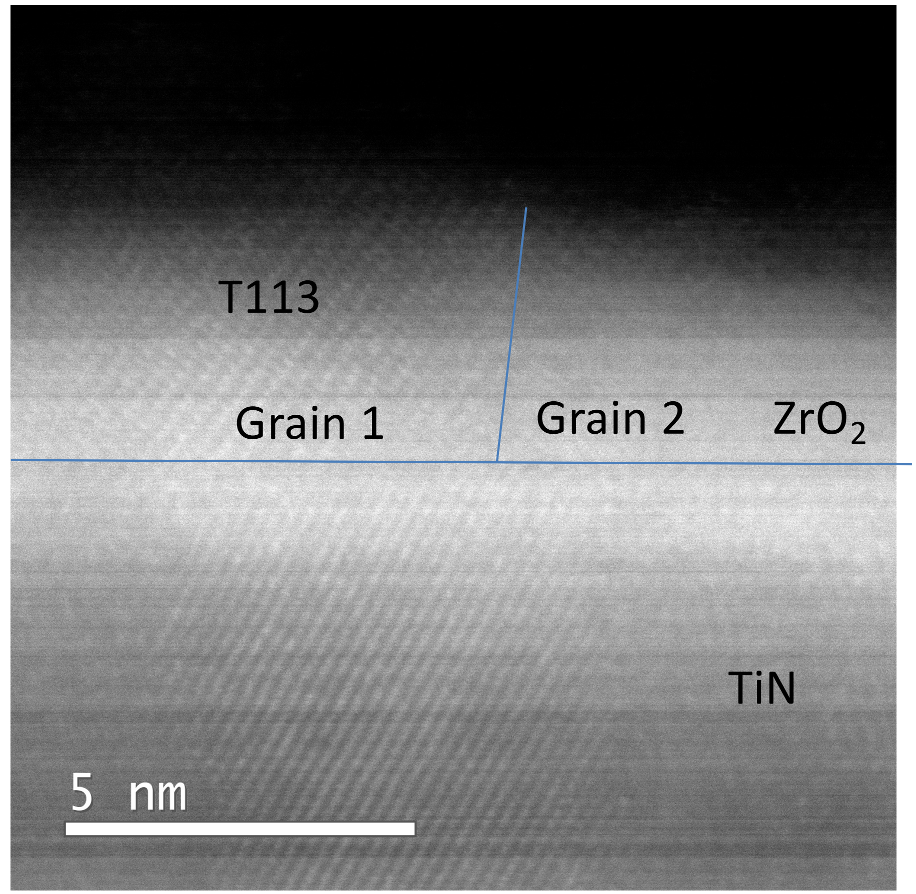
High Angle Annual Dark Field (HAADF) STEM done at Georgia Tech

Done by co-PI: Joshua Kacher group

If the d-spacings and angle match perfectly, the reflection points in FFT (white dots) MUST match the simulated diffraction patterns (black dots) perfectly.

Atomic resolution STEM Imaging of 5.4 nm ZrO_2





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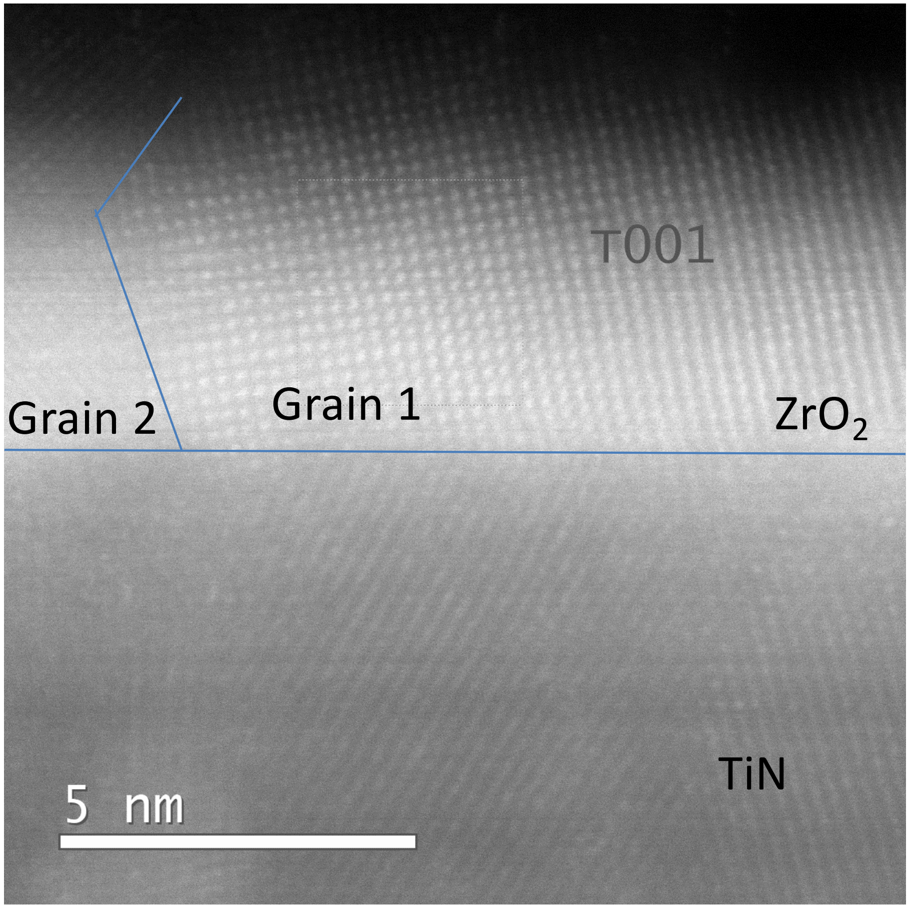

Zone axis	frequencies
100	1
001	1
110	1
111	1
311	3

All the grains were observed to be tetragonal.

Why are we doing Atomic Scale Microscopy?

- Because the crystal structure of ferroelectric HfO_2 and antiferroelectric ZrO_2 is not known yet in a AFE/DE heterostructure.
  - Depolarization field.
  - Stabilized negative capacitance.
  - Micro-Strain and grain boundary effects.
  - And so on…