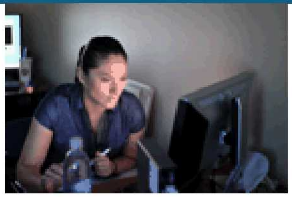
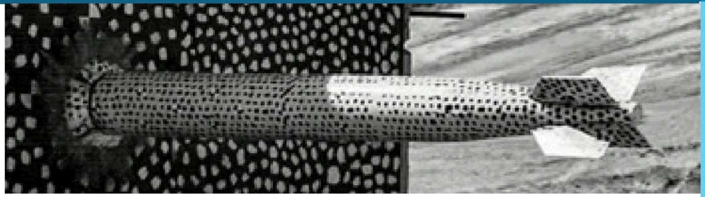
SAND2019-0651C

Time Dependence of Pyroelectric Response in $Hf_{0.58}Zr_{0.42}O_2$ Films





PRESENTED BY

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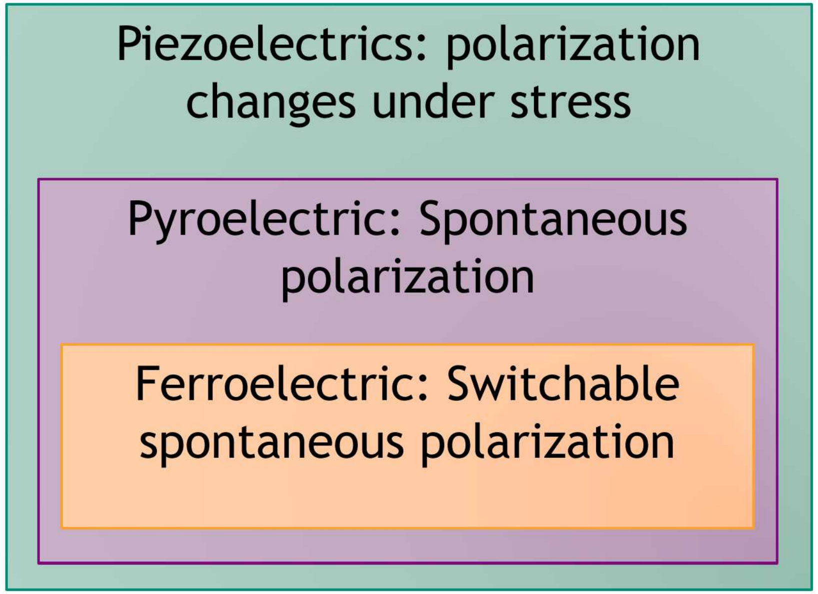
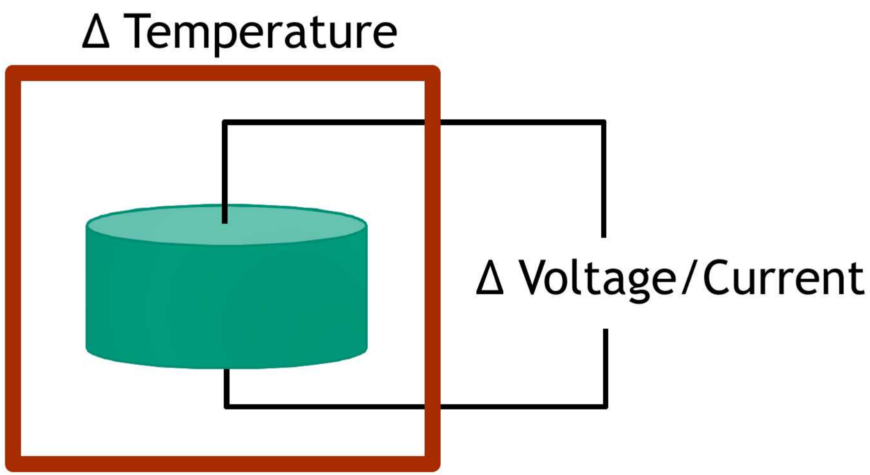
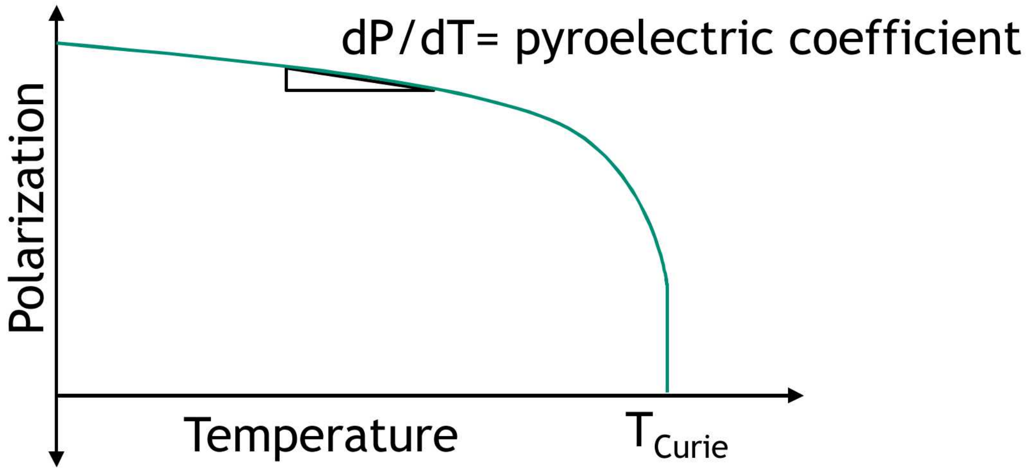
What is the Pyroelectric Effect?



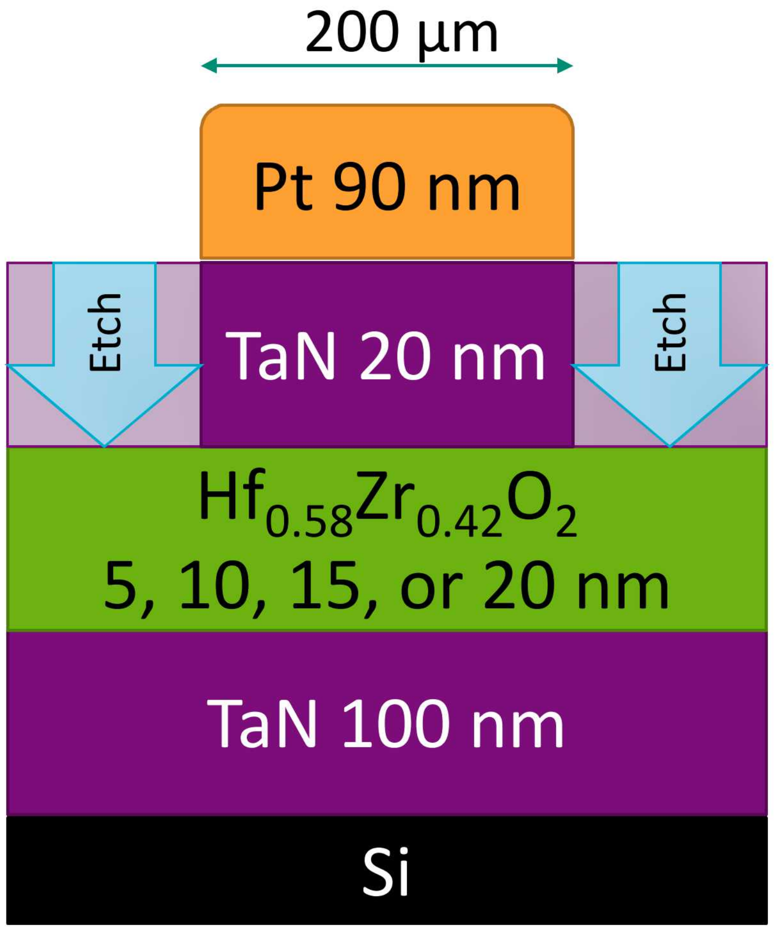
- All Ferroelectrics are also Pyroelectric
- Ferroelectric HfO_2 Thin Films
  - Potential for Night-Vision or Infrared Detector applications
  - Show consistent with other ferroelectrics
- If: spontaneous polarization
- Then: a uniform change in temperature creates a change in polarization
- Can be measured as a voltage or current





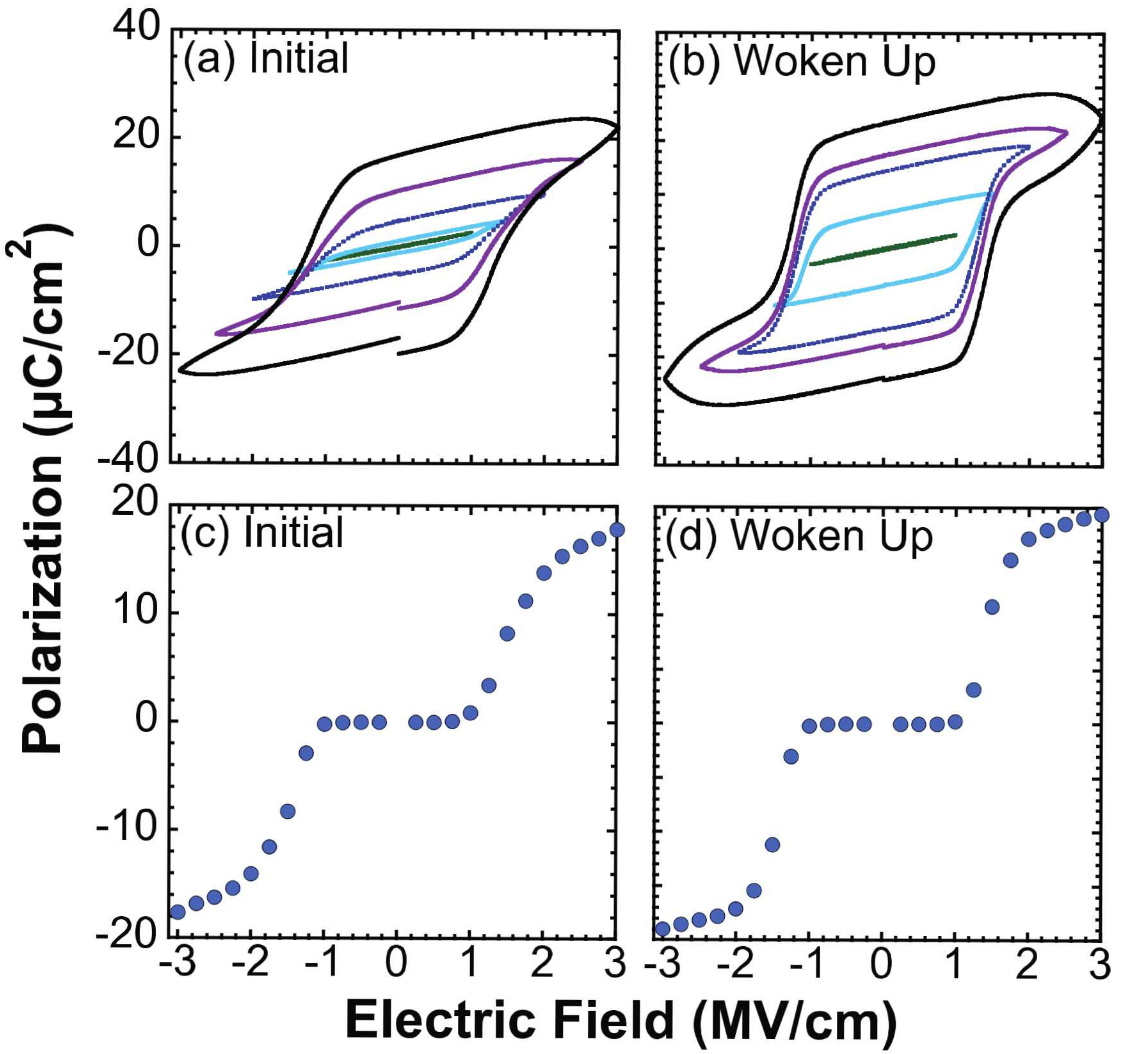
Experimental and Device Stack

- RF sputter TaN from TaN target
- Thermal ALD $Hf_{0.58}Zr_{0.42}O_2$ at 150 ℃ by TDMA Hf, TDMA Zr, and H_2O
  - HfO_2 0.109 nm GPC
  - ZrO_2 0.097 nm GPC
  - 5 cycle ZrO_2 & 5 cycle HfO_2 supercycle (~1 nm)
- Rapid thermal anneal 30s at 600 ℃ under nitrogen
- Lithographically define sputtered Pt dots
- ICP reactive ion etch
  - SF_6 and C_4F_8 atmosphere



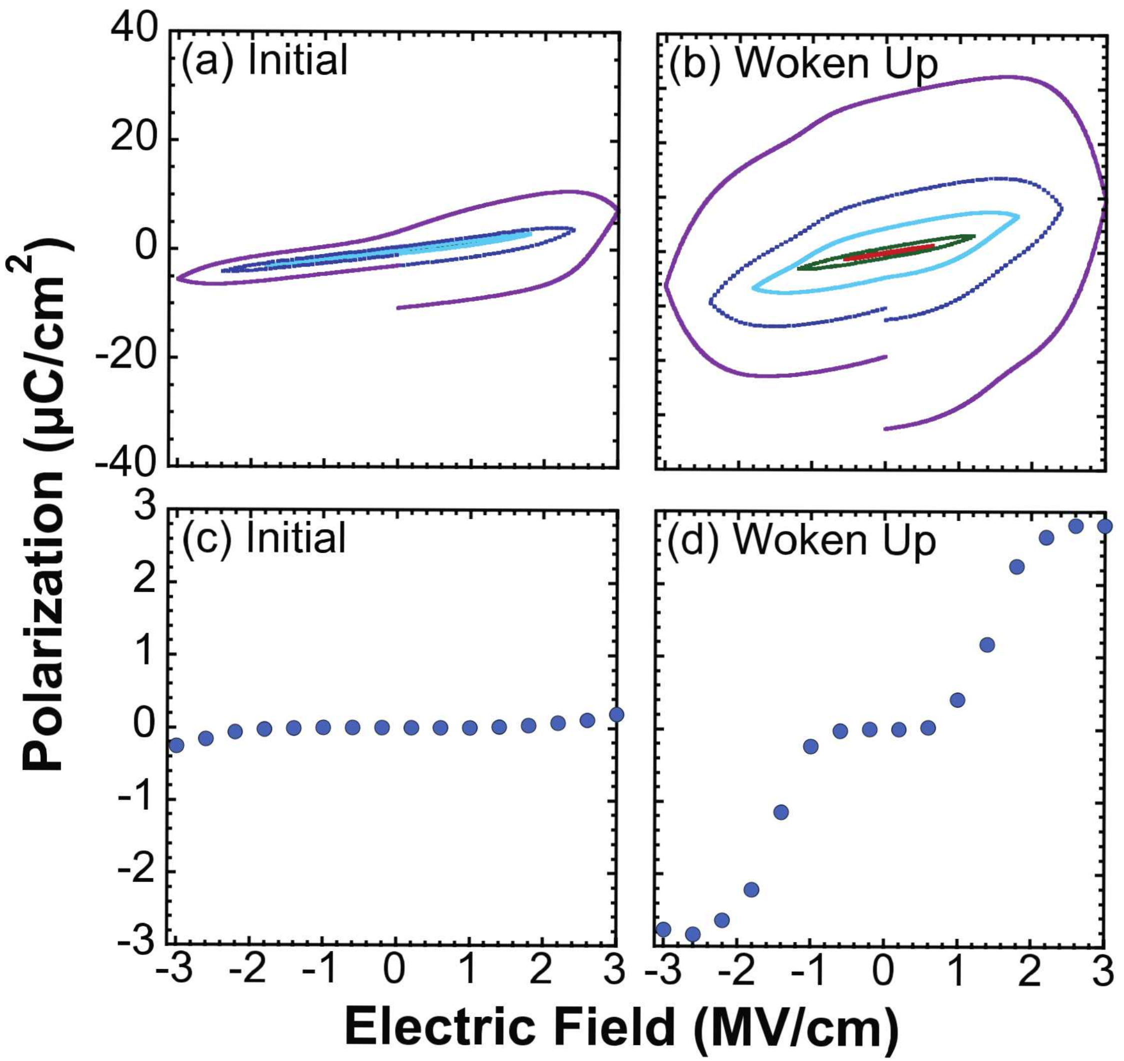
Polarization

20 nm



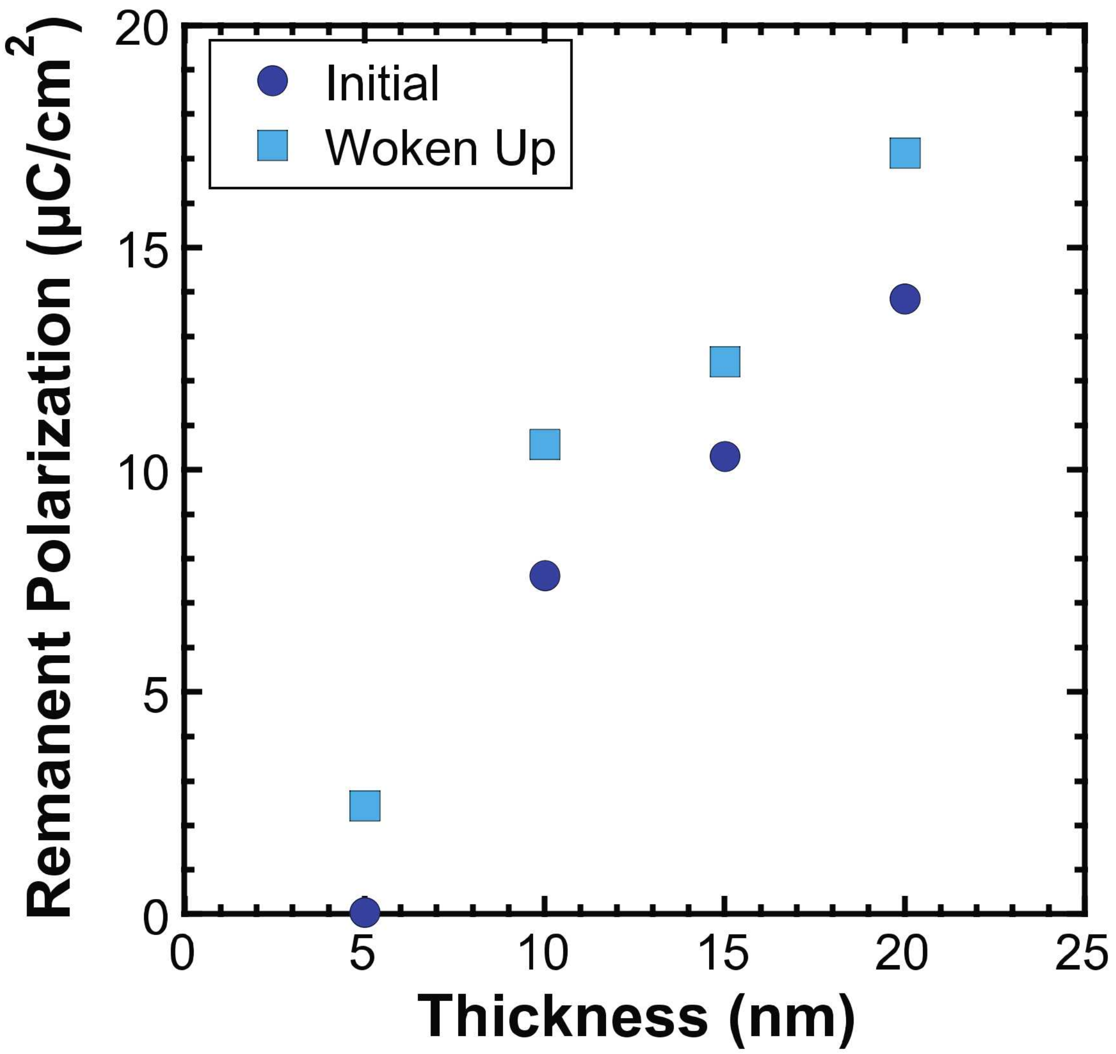
2 MV/cm Square Wave 10^3 cycles

5 nm



3 MV/cm Square Wave 10^5 cycles

Polarization: Thickness Trend



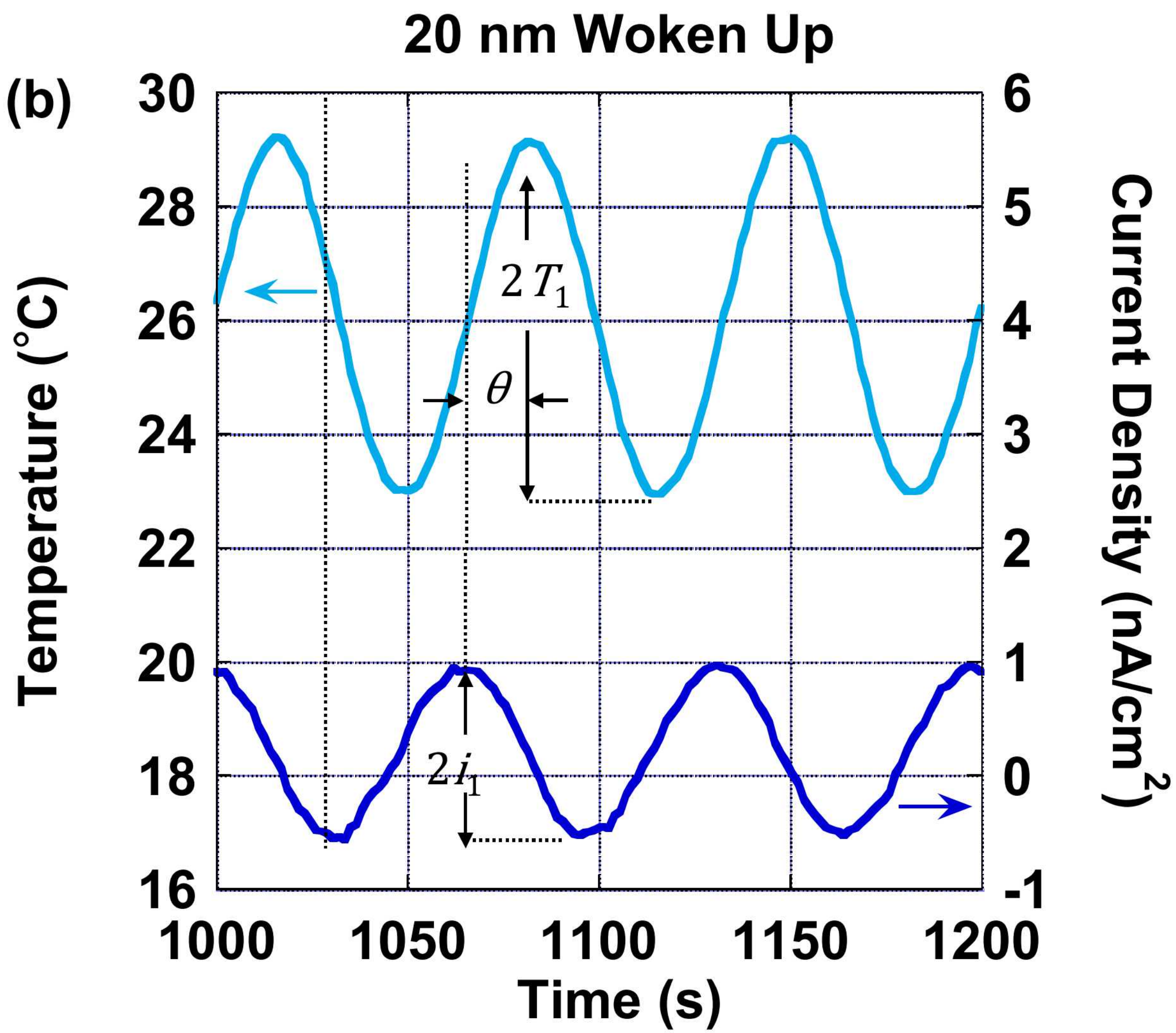
- Remanent polarization decreases with decreased thickness
- Wake up increases remanent polarization
  - Especially important in thin films

Pyroelectric Measurements

- Dynamic & Direct Measurement
  - Continuous change in temp and measure the current simultaneously
  - Sinusoidal Oscillating Temperature
    - Pyroelectric current depends on change in temperature with time
    - 90°out of phase

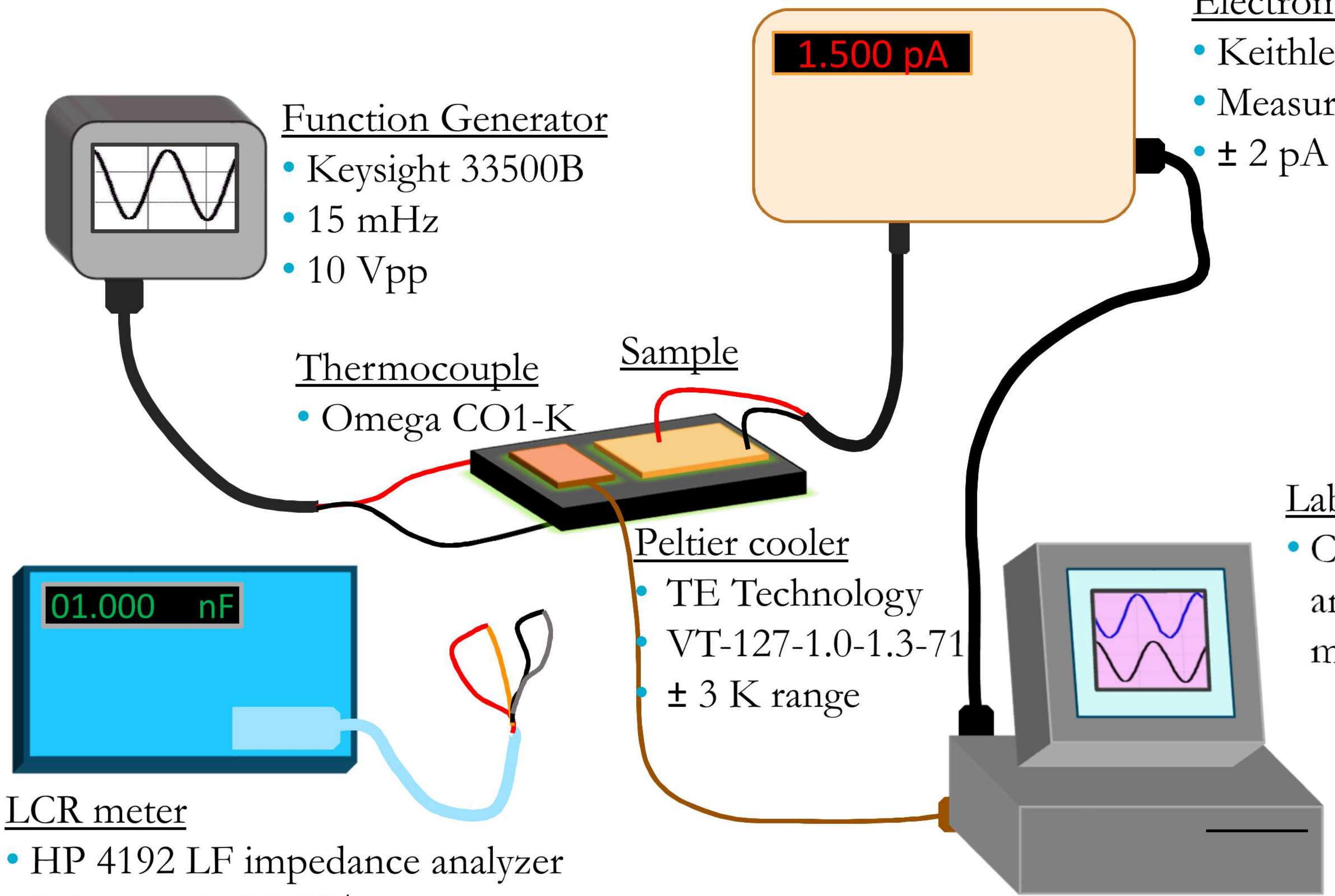
$$i_1 \sin(\theta) = pA\omega T_1$$

p – pyroelectric coefficient
ω – angular frequency of temperature
A – area of device



E. J. Sharp and L. E. Garn, J Appl. Phys. **53**, 8980 (1982); doi: 10.1063/1.330455

Pyroelectric Setup



Electrometer
- Keithley 6512
- Measures current
- ± 2 pA range

Function Generator
- Keysight 33500B
- 15 mHz
- 10 Vpp

Thermocouple
- Omega CO1-K

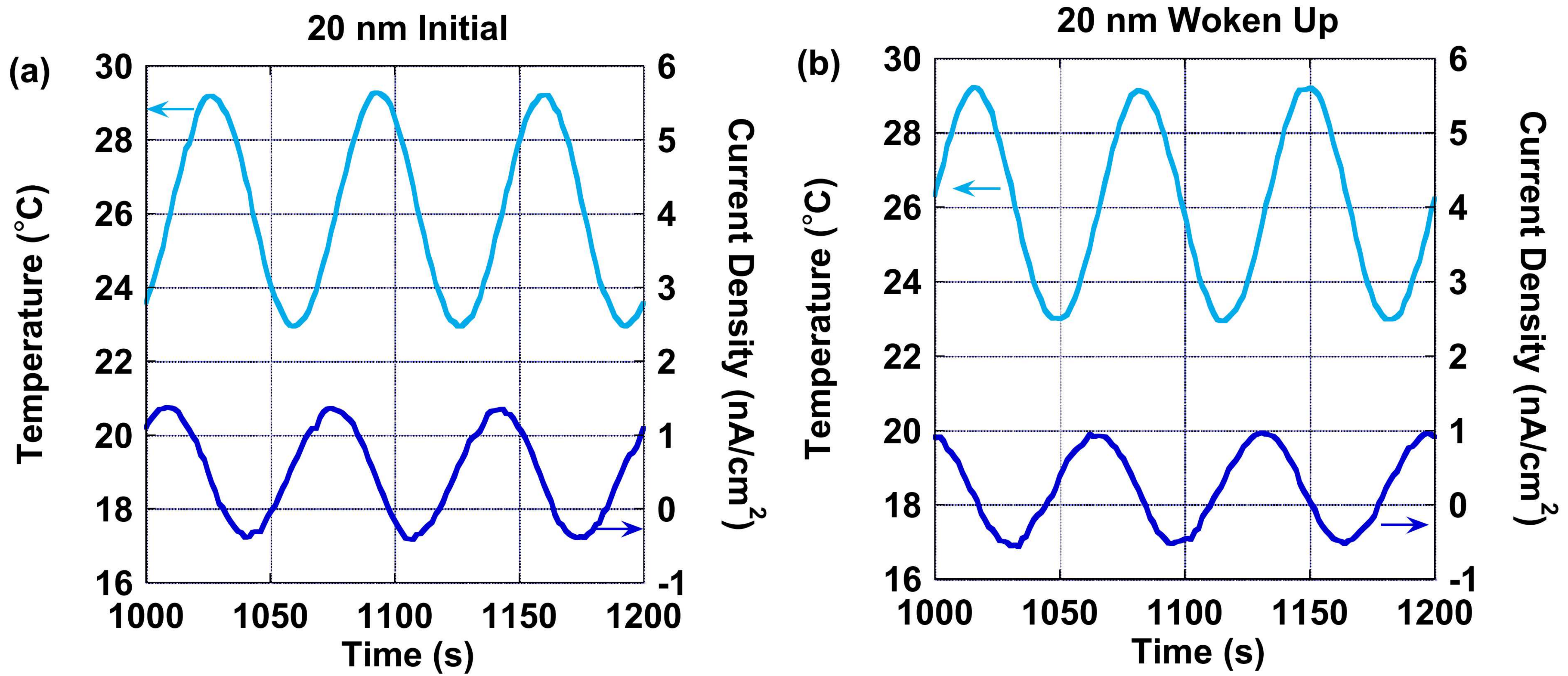
Sample

Peltier cooler
- TE Technology
- VT-127-1.0-1.3-71
- ± 3 K range

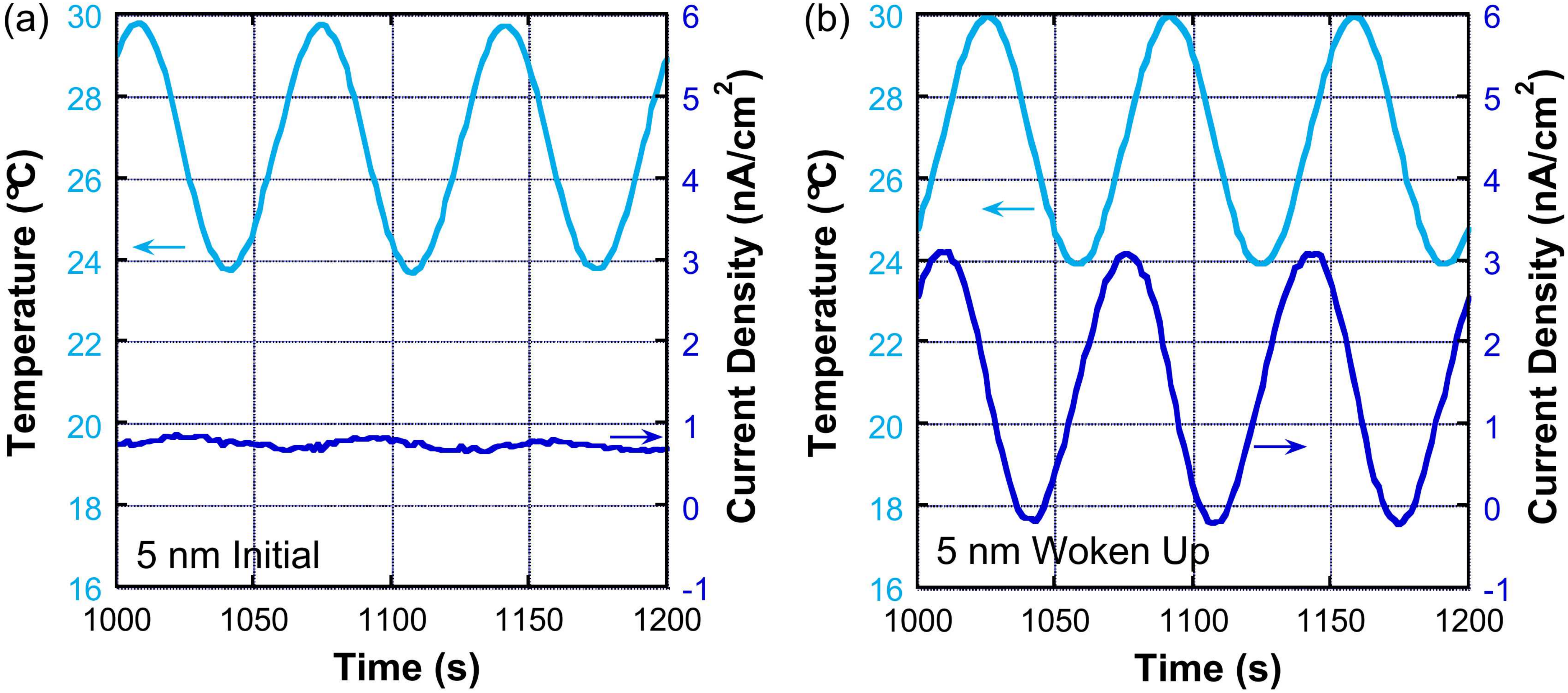
Labview
- Collects current and temperature measurement

LCR meter
- HP 4192 LF impedance analyzer
- Pole sample 2 MV/cm
- Check capacitance and loss tangent at 1 kHz

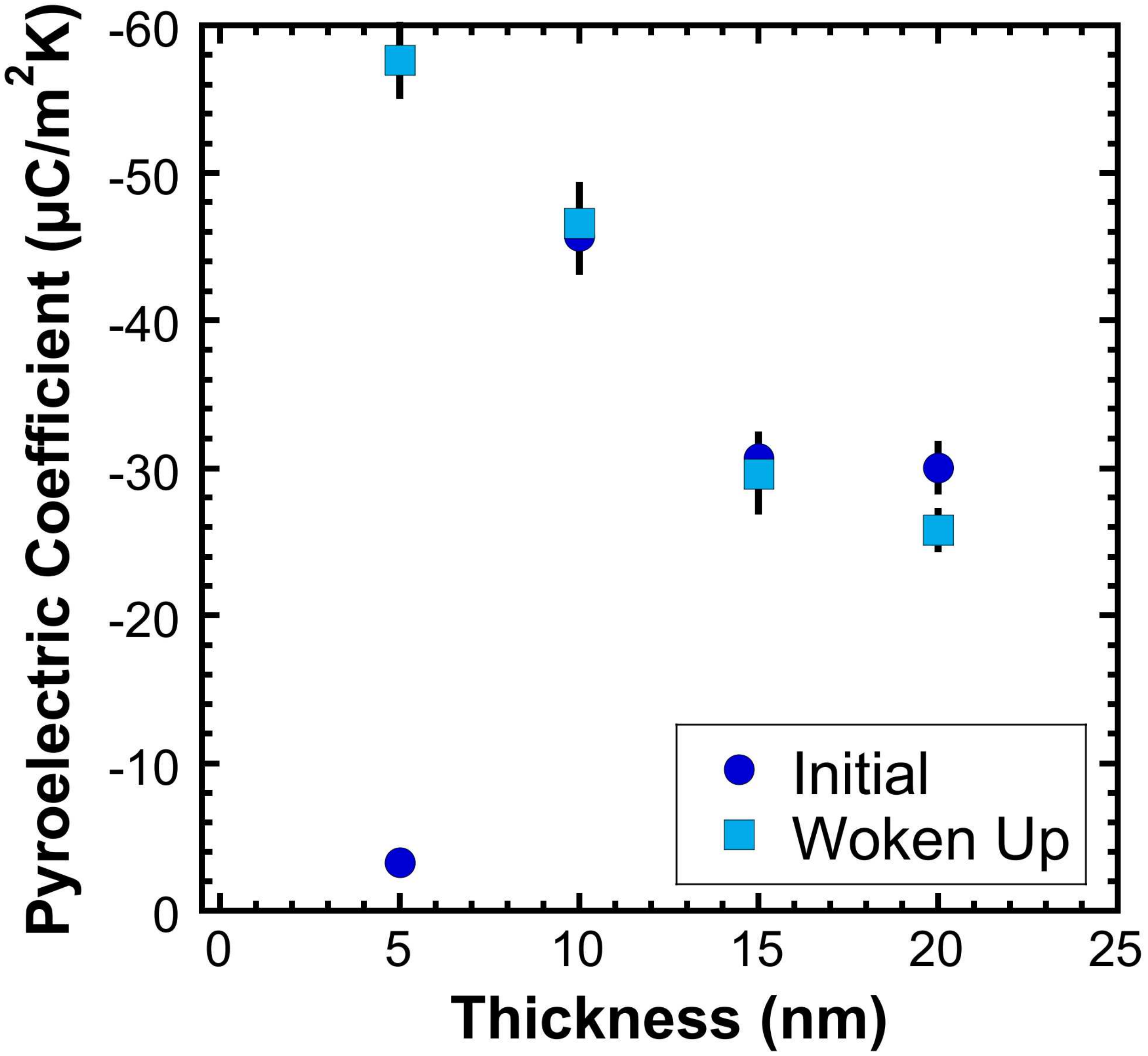
Pyroelectric Measurement 20 nm



Pyroelectric Measurement 5 nm

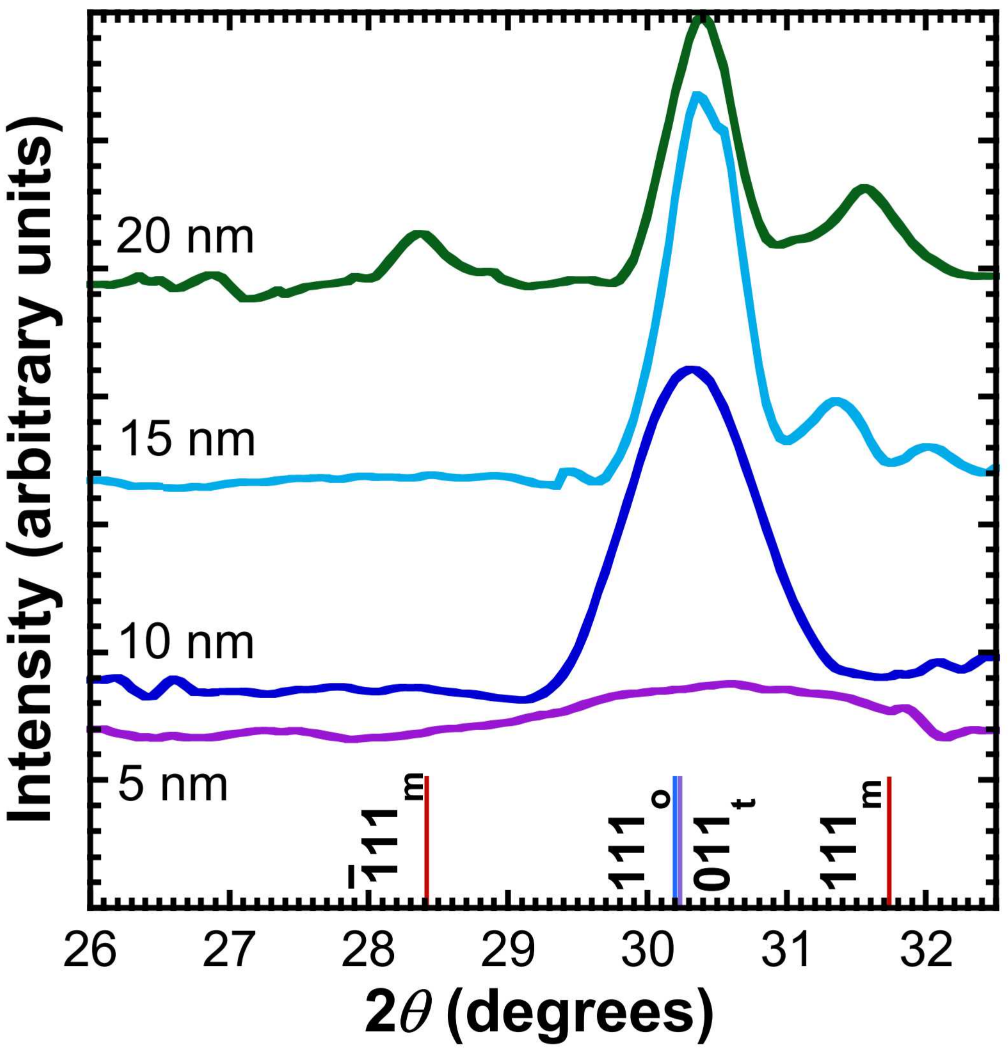


Pyroelectric Coefficient with Thickness



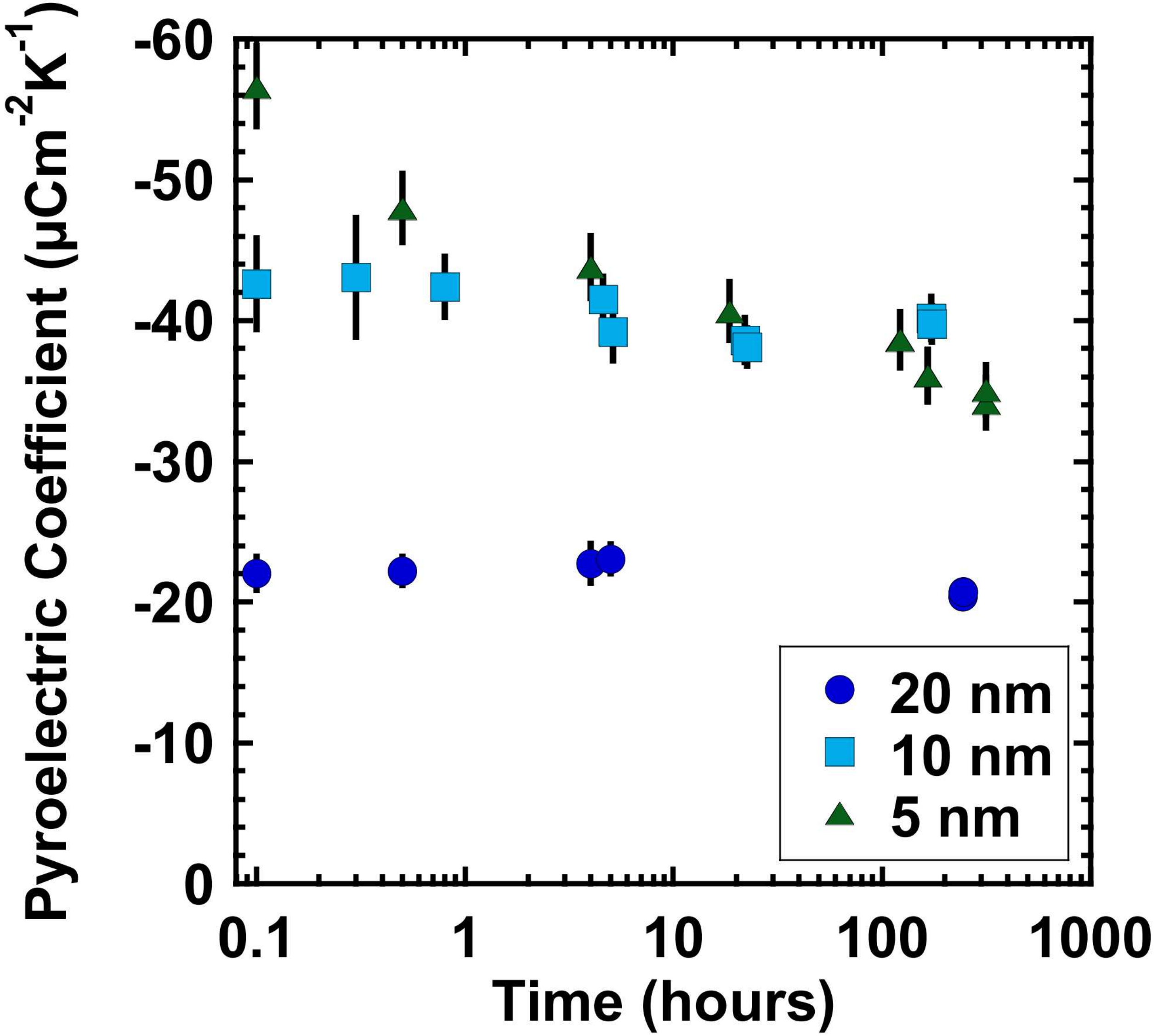
- Wake up makes little difference
  - Except 5 nm
- Pyroelectric coefficient increases as thickness decreases
- Increasing pyroelectric coefficient with decreasing polarization may indicate phase transition

Grazing Incident X-ray Diffraction



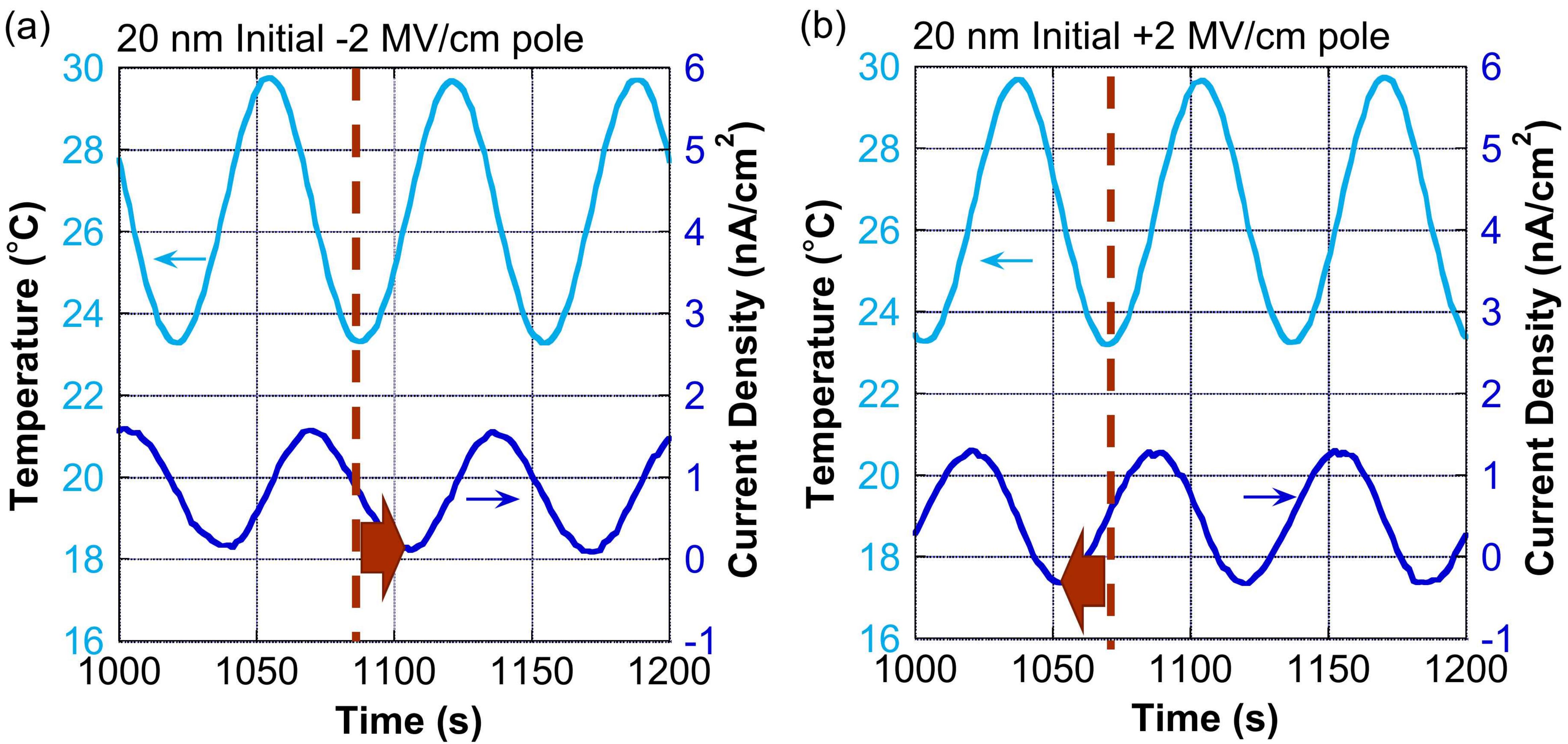
- Increasing Orthorhombic/tetragonal phase fraction with decreased thickness
  - 5 nm too broad to be conclusive
- Fitted grain sizes were consistent with film thickness
- Don’t seem to be losing orthorhombic phase
  - Likely not phase change

Pyroelectric Coefficient Over Time



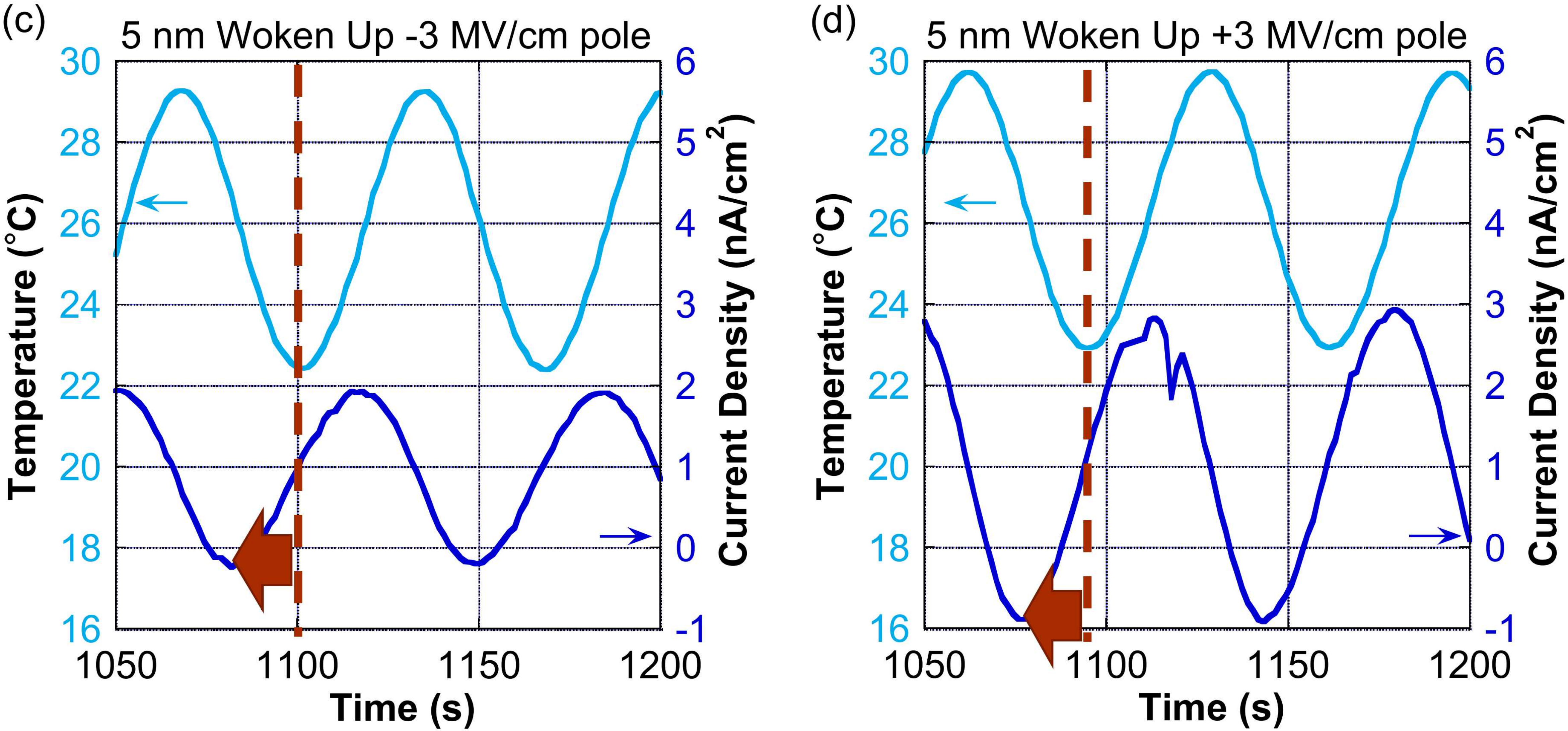
- 5 nm pyroelectric response decays
  - Not typical of ferroelectric
  - May be trapped charge contributing to response
- Similar decrease reported by Lane Martin's group in Berkeley with 10 nm Si:HfO_2, increased as a function of wake up.
  - S. Pandya et al., Physical Review Materials **2**, 124405 (2018)
- Decrease in polarization with time of 3 nm Y:HfO_2 with Ge bottom electrode mentioned, but not shown.
  - X. Tian et al., Appl. Phys. Lett. **112**, 102902 (2018)

Reversing Polarity on 20 nm Film



+85°, 24 μC/m^{-2}K^{-1} **-93°, -27 μC/m^{-2}K^{-1}**

Reversing Polarity on a 5 nm Film



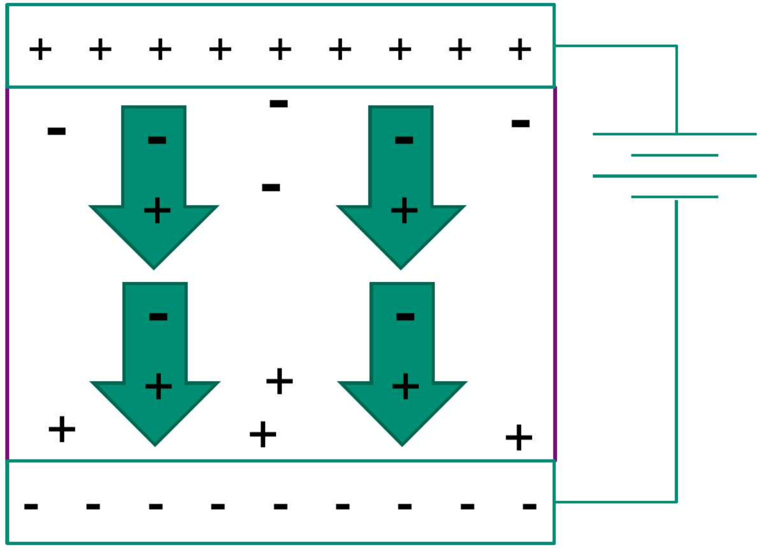
-100°, -34 μC/m^{-2}K^{-1}

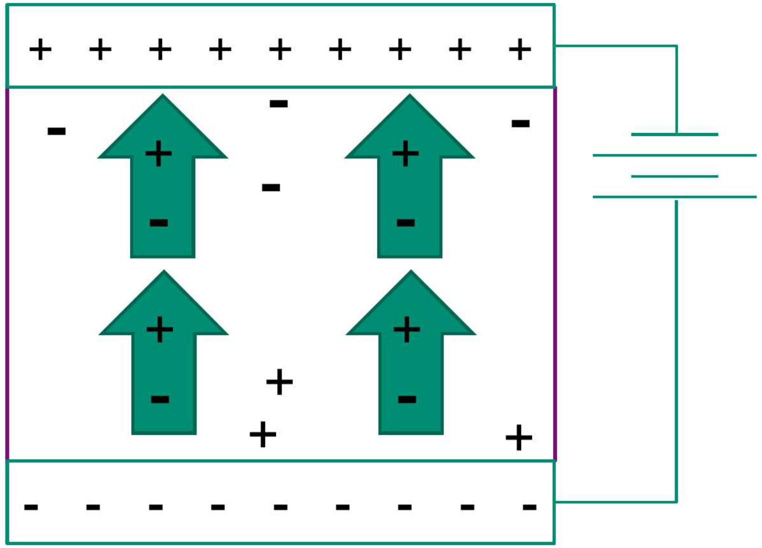
-94°, -59 μC/m^{-2}K^{-1}

Electrets Like Behavior

Thick (nm)	Negative Bias		Positive Bias		Delta Offset (°)
	Offset (°)	p ($\mu C/m^{-2}K^{-1}$)	Offset (°)	p ($\mu C/m^{-2}K^{-1}$)	
5	-100	-34	-94	-59	+6
10	+83	+31	-95	-42	-178
20	+85	+24	-93	-27	-178

- Electret: point and/or dipole charge trapped in polymer or oxide
- Non-switchable charge contributing to the pyroelectric response
  - Likely injected during wake up cycling
  - Dominates switchable charge in 5 nm sample
  - Some present in 20 and 10 nm samples as well

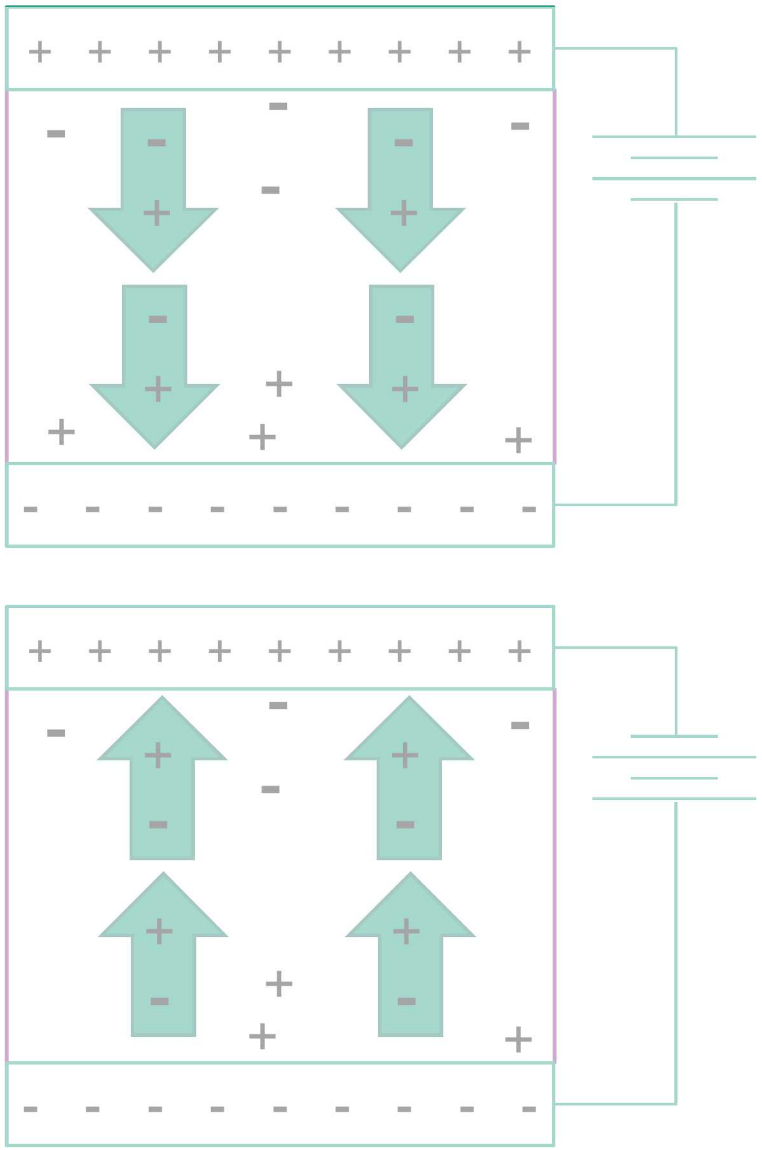




Summary

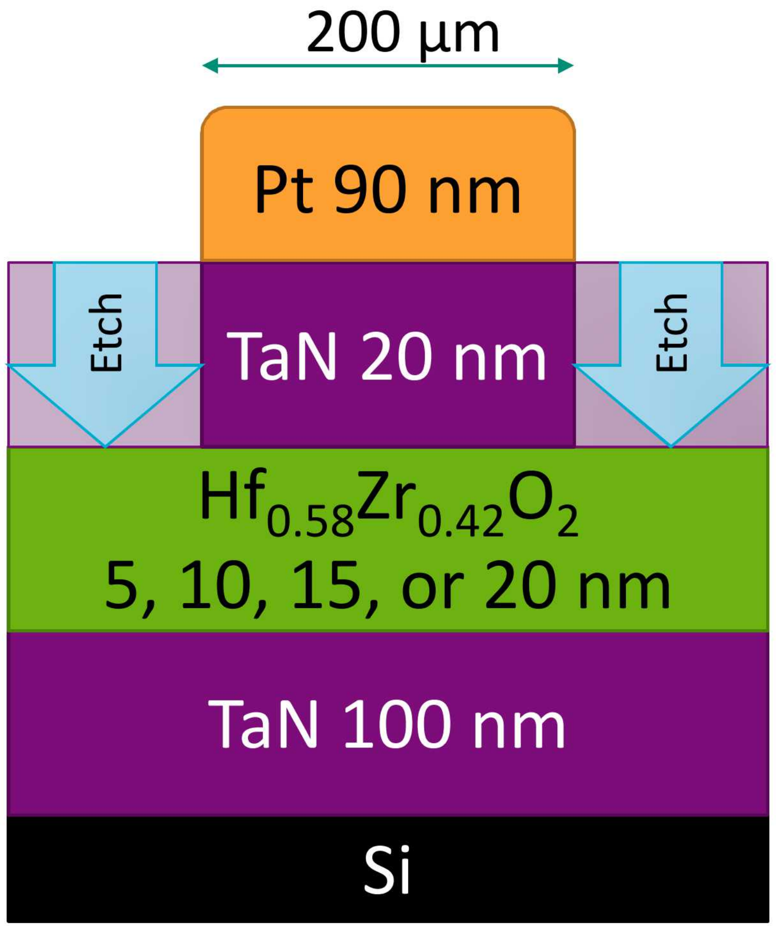
- Non switchable charge is contributing to the pyroelectric response in 5 nm $Hf_{1-x}Zr_xO_2$ films
  - Decays with time after poling
  - Not present prior to wake up
  - Present in 10 and 20 nm thick films as well but makes smaller contribution
- Unstable pyroelectric coefficient a problem for infrared detector applications
  - 10 nm $Hf_{1-x}Zr_xO_2$ seems OK
- May be dependent on the interface and wake up cycling

Thick (nm)	Negative Bias		Positive Bias		Delta Offset (°)
	Offset (°)	p (μC/m^{-2}K^{-1})	Offset (°)	p (μC/m^{-2}K^{-1})	
5	-100	-34	-94	-59	+6
10	+83	+31	-95	-42	-178
20	+85	+24	-93	-27	-178

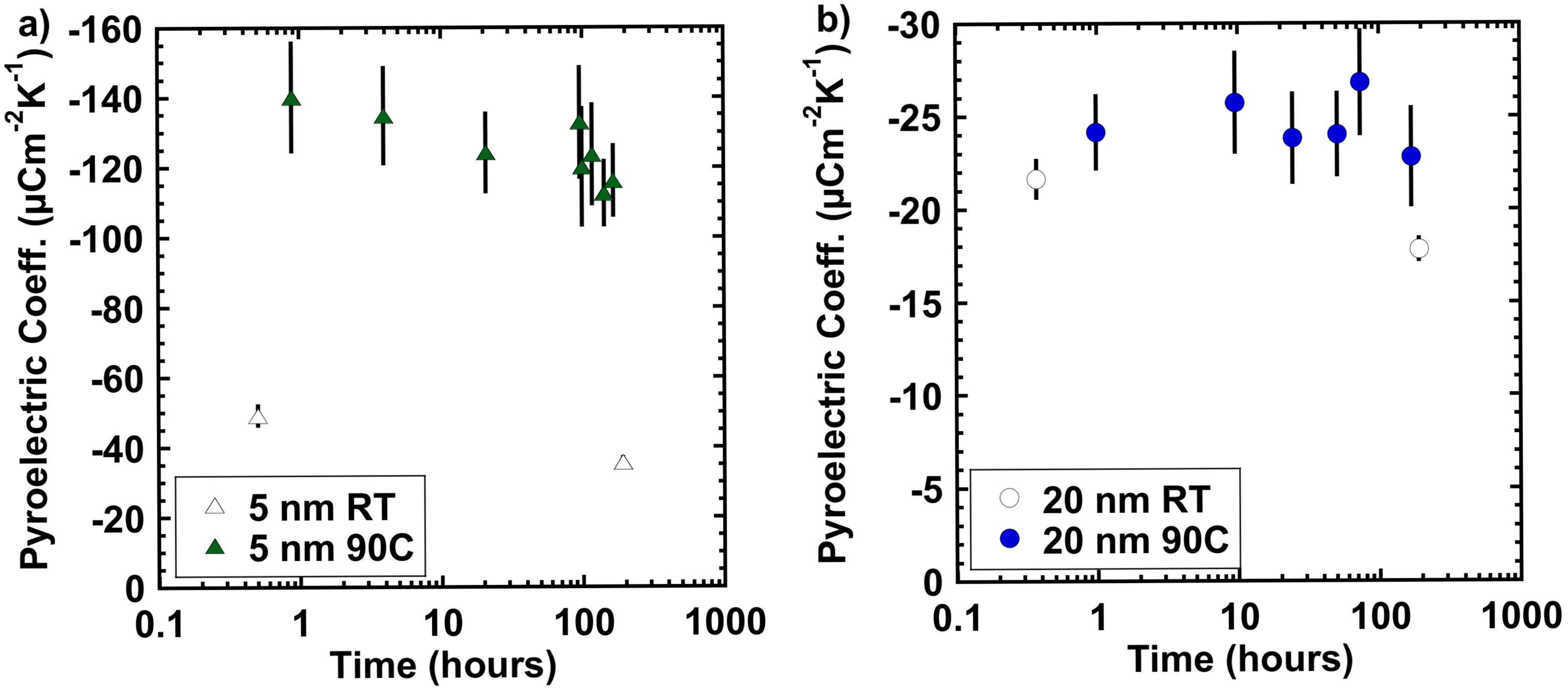


Backup Slides

Thick (nm)	Negative Bias		Positive Bias		Delta Offset (°)
	Offset (°)	p (μC/m^{-2}K^{-1})	Offset (°)	p (μC/m^{-2}K^{-1})	
5	+100	-34	+94	-59	+6
10	-83	+31	+95	-42	-178
20	-85	+24	+93	-27	-178



90 °C Pyroelectric Response Over Time

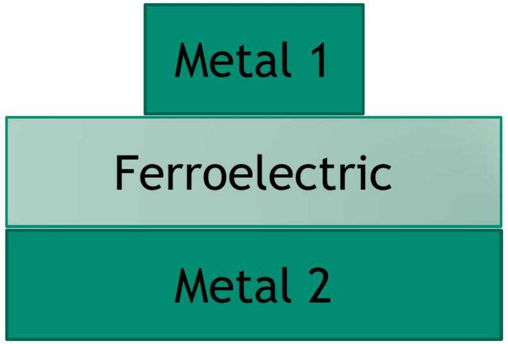


Ferroelectric Tunnel Junction

A switchable, permanent polarization enables switchable tunneling resistances*

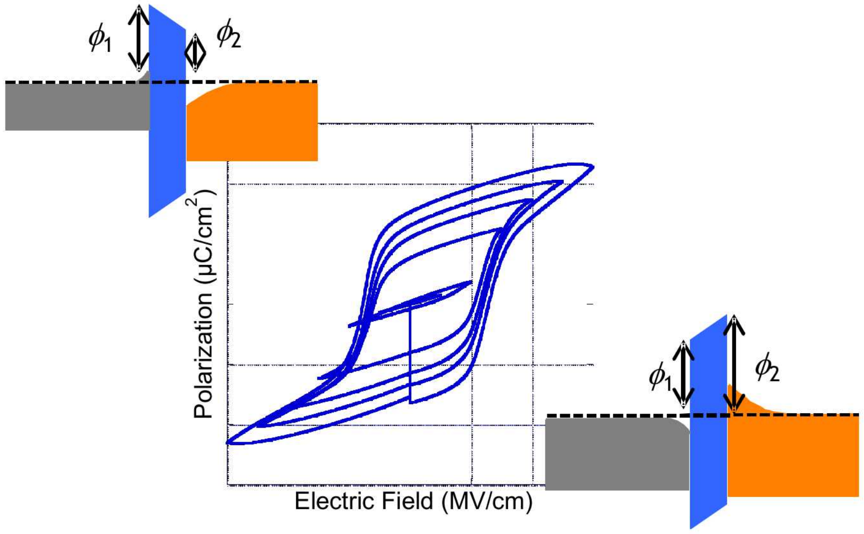
- Must be thin enough for tunneling (<5nm)

Recently discovered ferroelectric HfO_2 offers low cost, Si compatible option

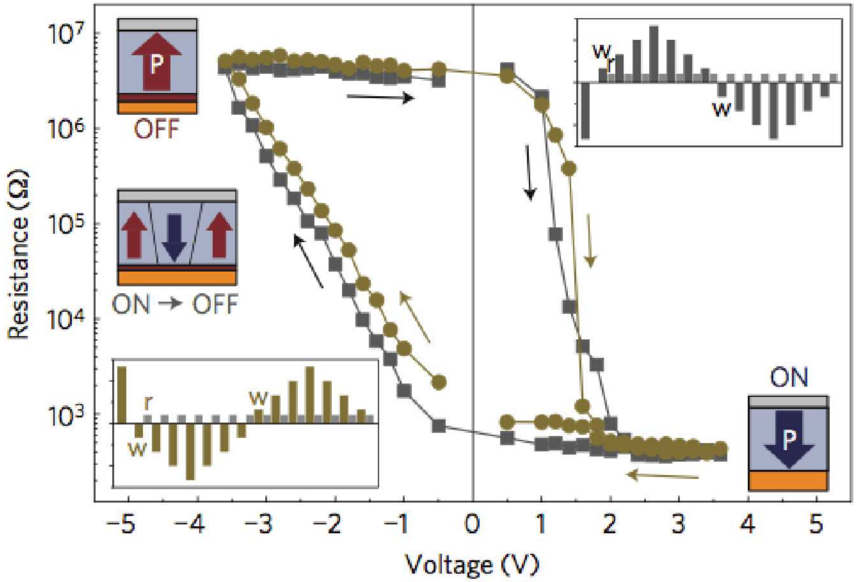


*Kohlstedt, et al. Phys. Rev. B **72**, 125341 (2005)

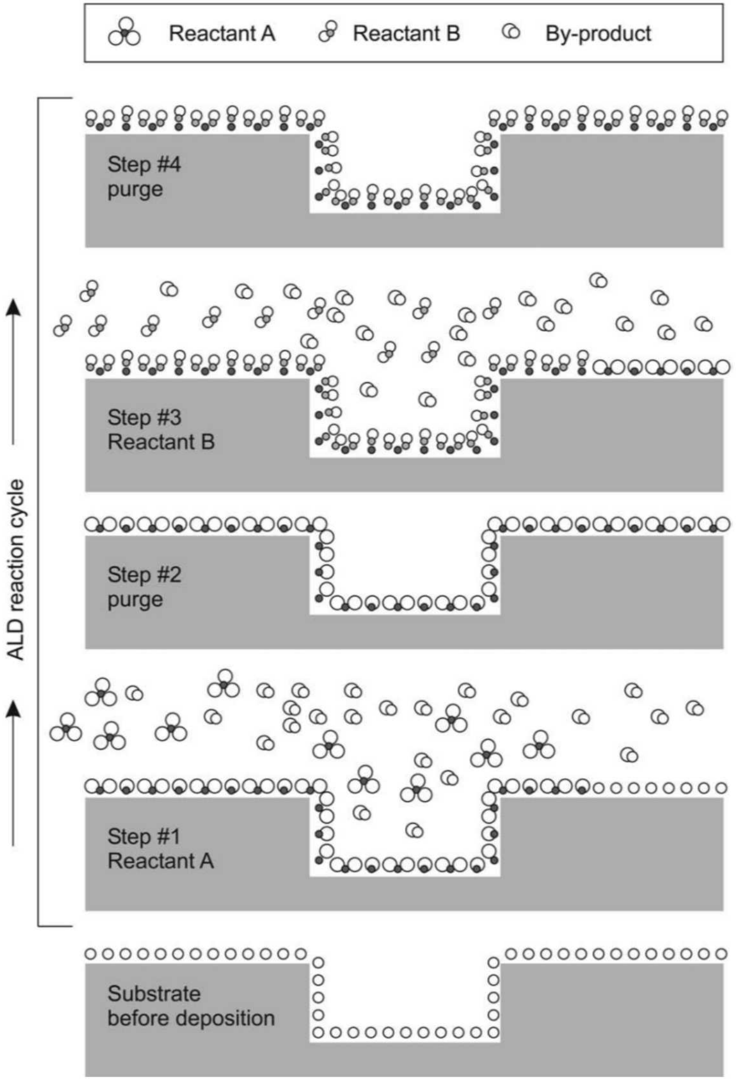
Wen *et al.*, Nat. Mater. 12, 617 (2013)



Pt/$BaTiO_3$/Nb:$SrTiO_3$



Atomic Layer Deposition



Schematic of ALD process

R. L. Puurunen J. Appl. Phys. **97**, 121301 (2005)

Variant of Chemical Vapor Deposition

Reactants separated by inert gas purge

Reaction limited to chemisorbed surface layer

Conformal over high aspect ratios

Precise thickness control with sub-monolayer growth per cycle

Multicomponent and graded compositions

Ferroelectric HfO_2

2011 Boscke *et al.* – Namlab

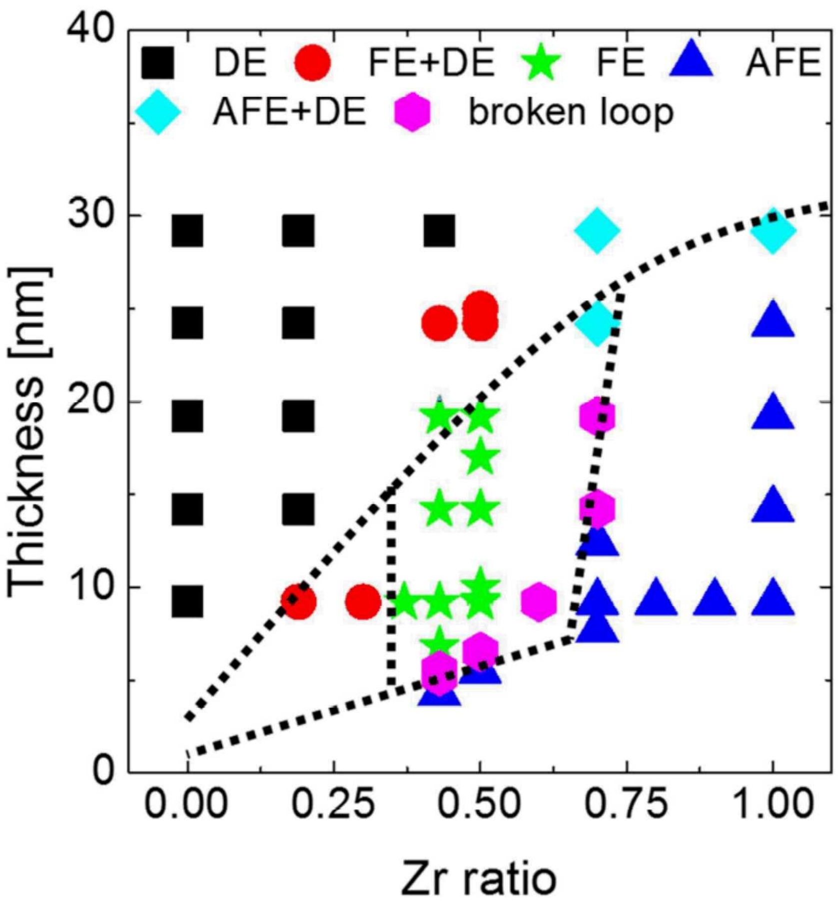
- 2 to 5% $Si:HfO_2$ via ALD with TiN top and bottom electrodes and anneal.
- Proposed metastable orthorhombic crystal structure.

Since then:

- Dopants: Zr, Gd, Al, none,…
- Electrodes: Mostly TiN, TaN, Pt, Ir, Ru Si, …
- Thickness: 25 to ~5 nm, maybe less

CMOS compatible ferroelectric stable at <20 nm thickness.

- Applications: ferroelectric memory, energy storage & harvesting, low power FETs.

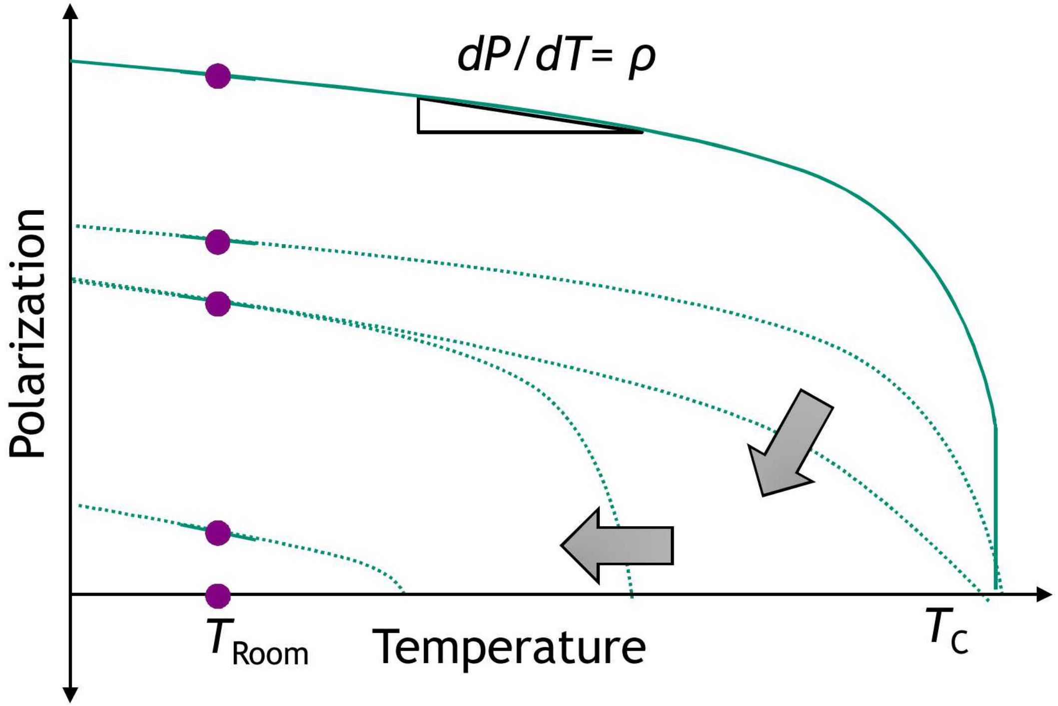


DE-dielectric
FE-ferroelectric
AFE-antiferroelectric-like

Böscke, *et al., Appl. Phys. Lett.* **99**, 102903 (2011)

M.H. Park, *et al., Nanoscale,* June 2017 DOI:10.1039/C7NR02121F

Pyroelectric Coefficient with Thickness



As thickness decreases:

- Polarization decreases
- Pyroelectric coefficient increases

Polarization vs. temperature curve response:

- Phase transition becomes more gradual
- T_C decreases

What is a Ferroelectric Material?

Spontaneous polarization which can be reoriented by an electric field

Noncentrosymmetric ionic crystals

- Centers of positive and negative charge do not coincide

Applications

- Memory: FRAM
- Actuators: Ultrasound, Sonar, AFMs
- Capacitors: Cellphones and nearly all electronics
- Sensors: Night vision, IR cameras
  - Due to pyroelectric effect