SAND2017-12019C

# Pyroelectric Response in Thin Ferroelectric $Hf_{0.58}Zr_{0.42}O_2$

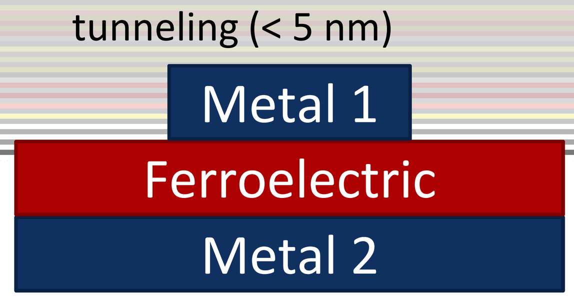
Sean W. Smith[1], M. David Henry,[1] Jeramy R. Dickerson,[1] Michael T. Brumbach,[1] and Jon F. Ihlefeld[2]

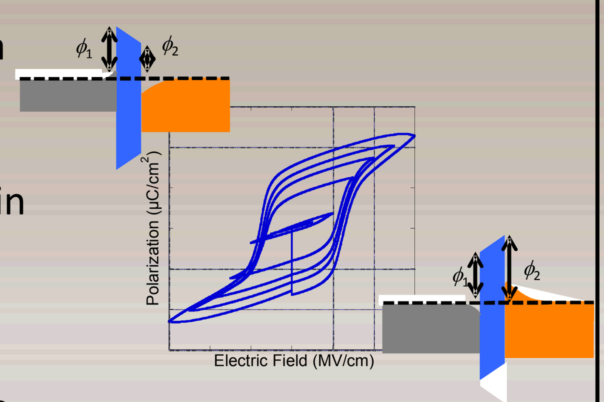
[1] Sandia National Laboratories, Albuquerque, New Mexico, USA

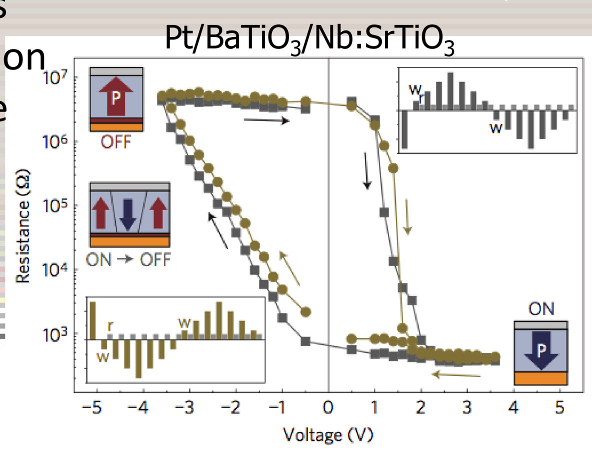
[2] University of Virginia, Charlottesville, Virginia, USA; *Corresponding Author: ssmith5@sandia.gov

## 1. Introduction

- Ferroelectric tunnel junctions are a promising memristor competitor
- Epitaxial Pt/$BaTiO_3$/Nb:$SrTiO_3$ devices have shown ~$10^4$ changes in resistance
- $HfO_2$ based ferroelectric offer potential low cost, Si process compatible route to similar devices
- Switchable, spontaneous polarization enables switchable resistance state
  - Must be thin enough for tunneling (< 5 nm)



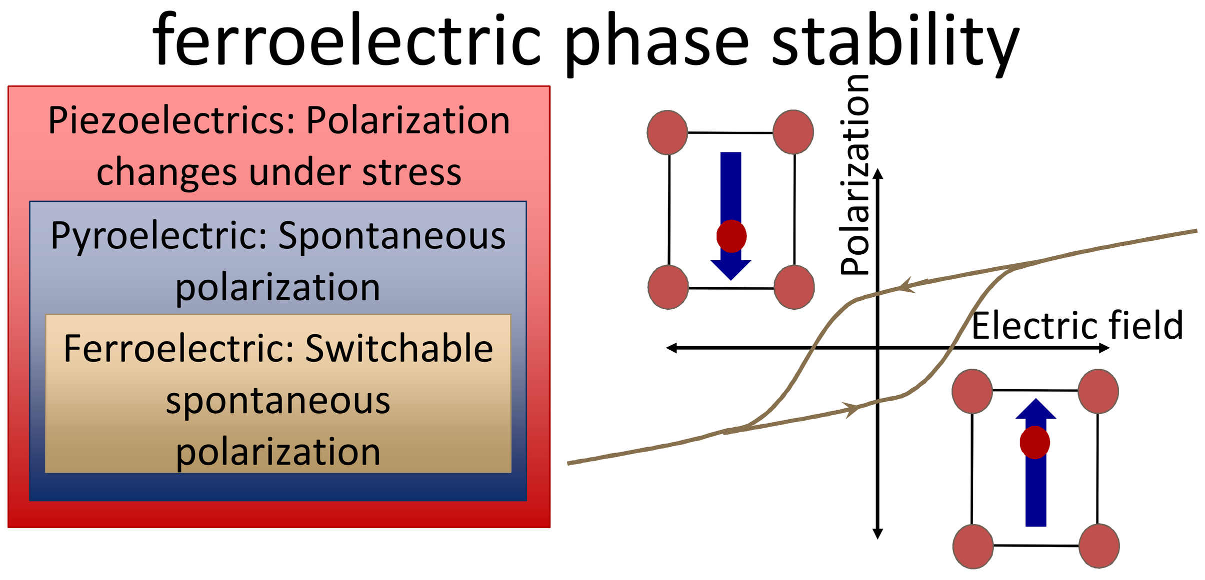




Wen *et al.*, Nat. Mater. 12, 617 (2013)

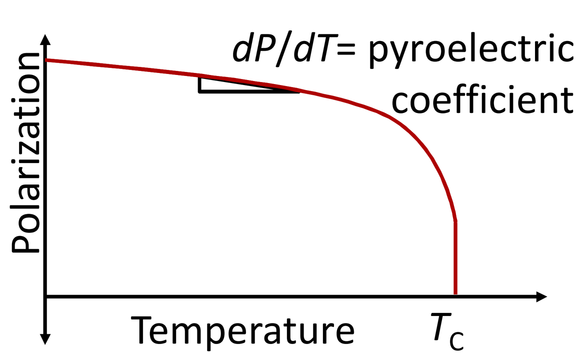
## 2. Pyroelectricity and Ferroelectricity

### Pyroelectric response gives insight to ferroelectric phase stability




Pyroelectric Effect

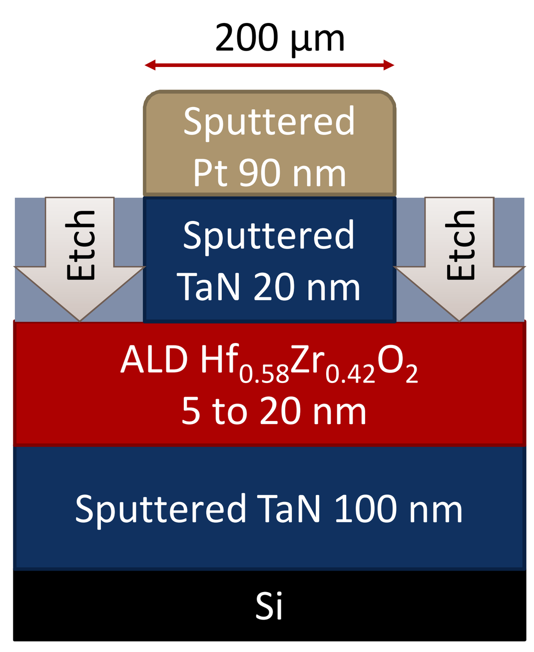
- If: spontaneous polarization
- Then: a uniform change in temperature creates a change in polarization
  - Can be measured as a voltage or current




## 3. Experimental

### Metal ferroelectric metal structure

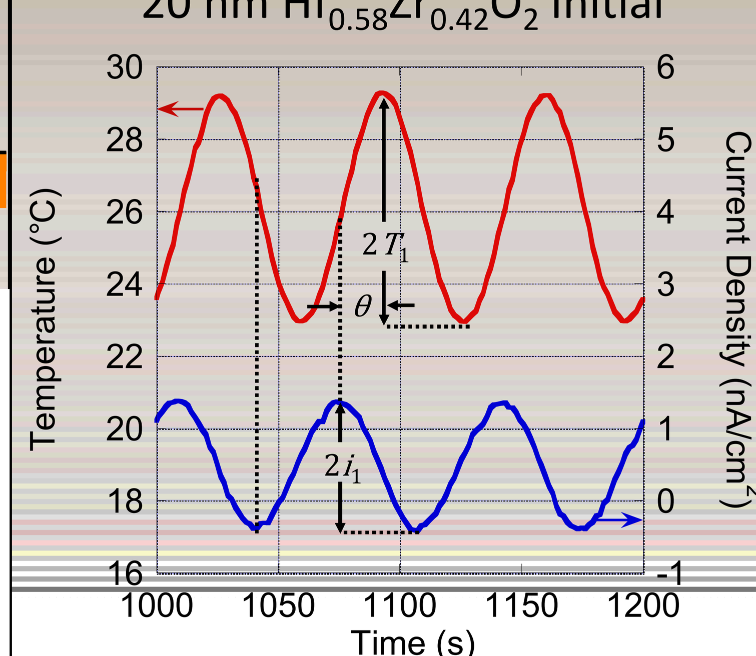
- RF sputter TaN from TaN target
- Thermal ALD $Hf_{0.58}Zr_{0.42}O_2$ at 150 °C by TDMA Hf, TDMA Zr, and H2O
  - $HfO_2$ 0.109 nm GPC
  - $ZrO_2$ 0.097 nm GPC
  - 5 cycle $ZrO_2$ & 5 cycle $HfO_2$ supercycle (~1 nm)
  - Vary number of supercycles to set thickness
- Cap with blanket TaN
- Rapid thermal anneal 30s at 600 °C under nitrogen
- Sputter Pt through shadow-mask
- ICP reactive ion etch
  - $SF_6$ and $C_4F_8$ atmosphere




Device stack schematic

## 4. Pyroelectric Measurement

### Sinusoidal temperature profile



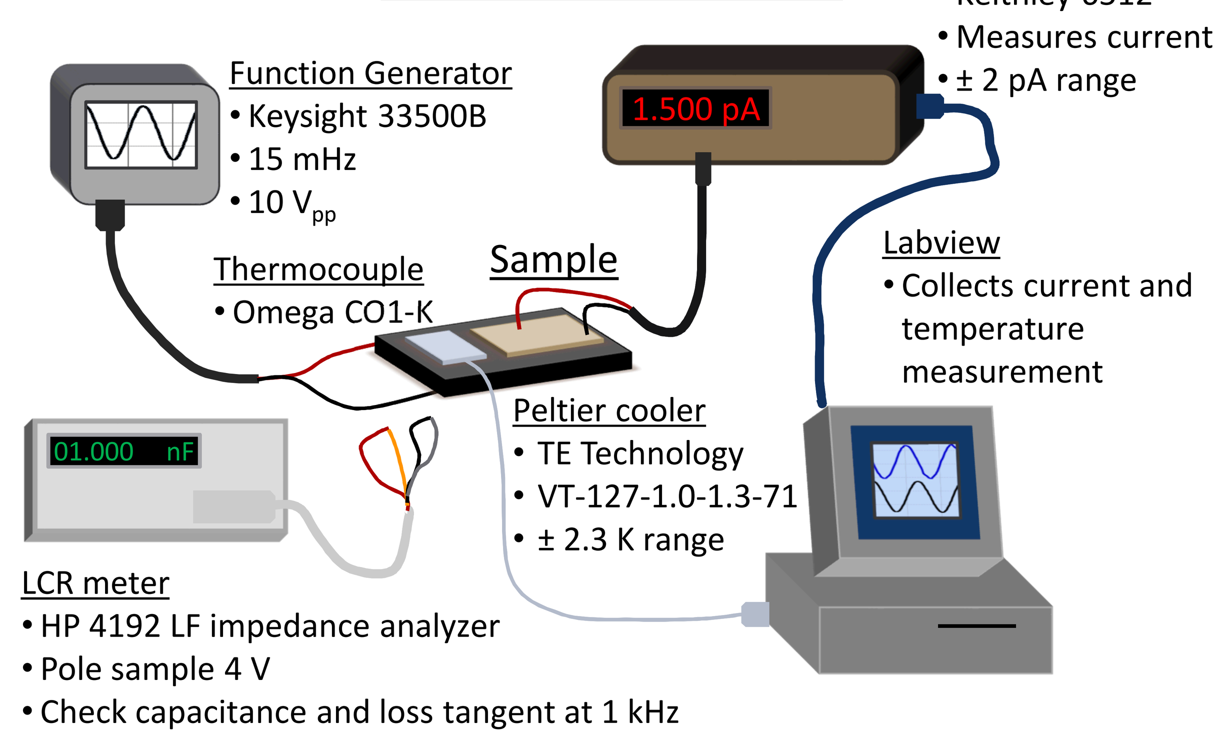

- Dynamic & Direct Measurement
  - Continuous change in temperature
  - Measure the current simultaneously
- Sinusoidal oscillating temperature to separate non-pyroelectric currents
  - Pyroelectric current depends on change in temperature with time: 90° out of phase from temperature

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

$p$ – pyroelectric coefficient
$\omega$ – angular frequency of temperature
$A$ – area of device

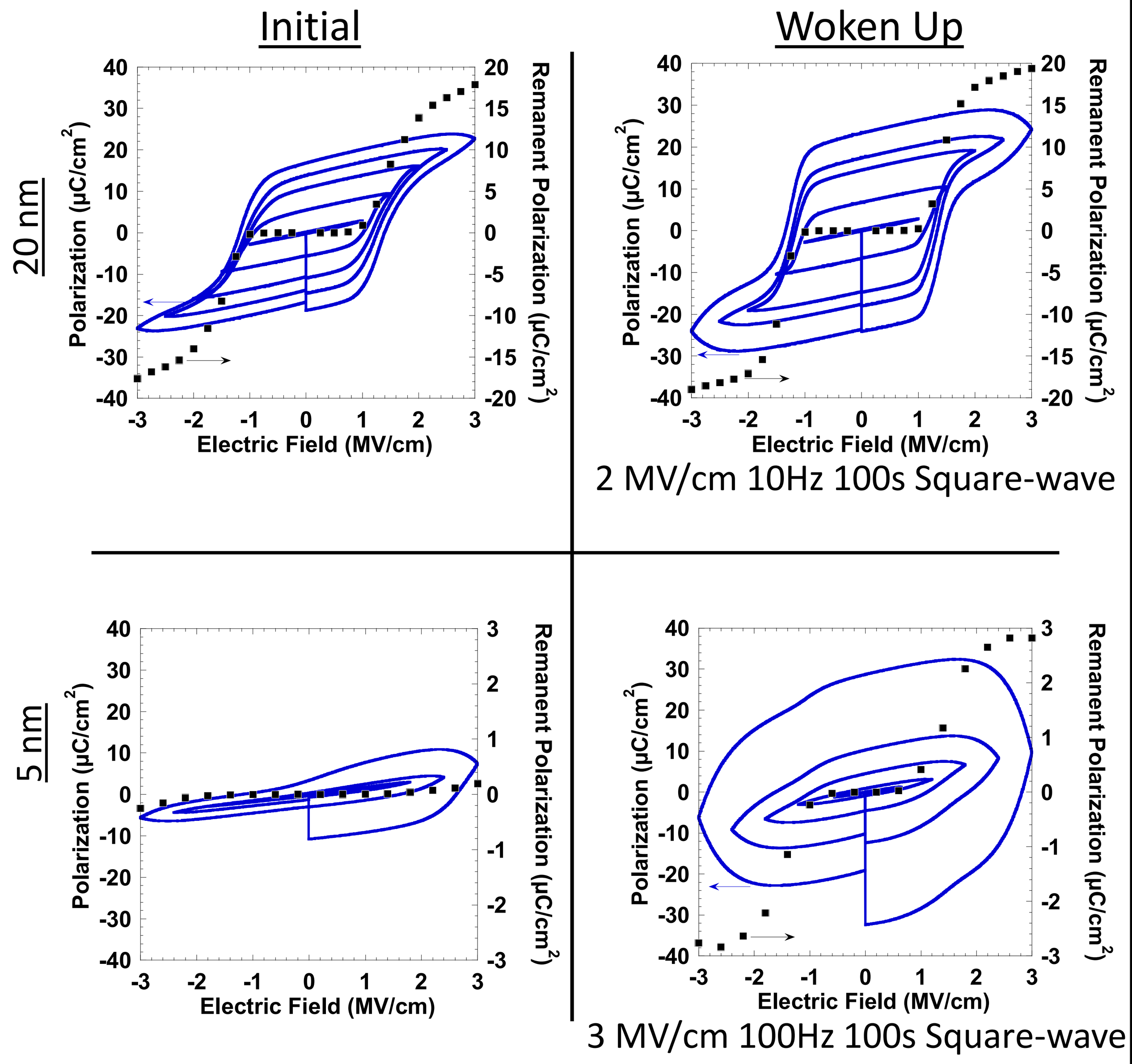
E. J. Sharp and L. E. Garn, J Appl. Phys. 53, 8980 (1982); doi: 10.1063/1.330455

Pyroelectric Test Setup




## 5. Polarization Wake Up

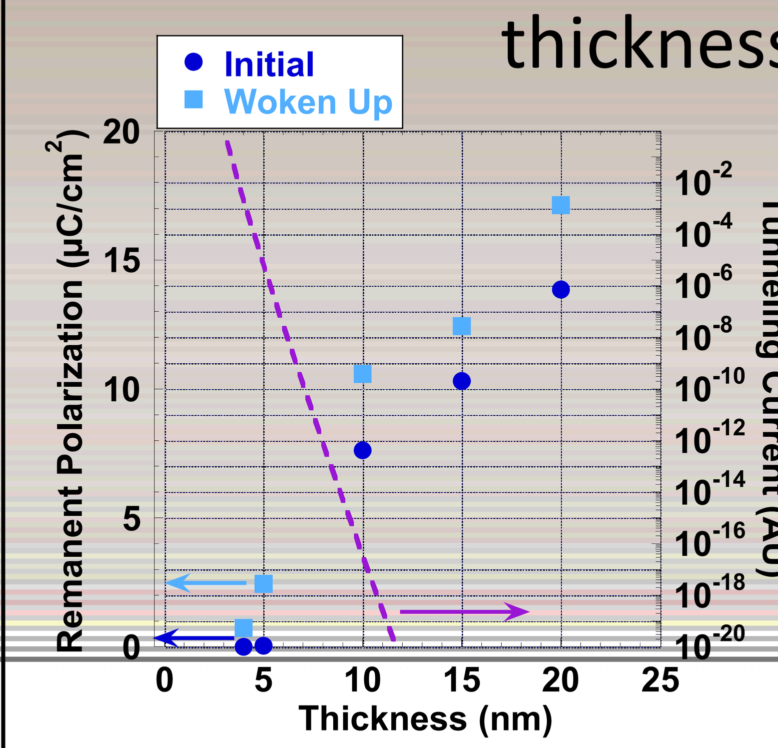
### Wake up cycling more important in thin films




Polarization electric field (100 Hz) and pulsed positive up negative down data for 20 nm and 5 nm $Hf_{0.58}Zr_{0.42}O_2$ films in the initial condition and with square wave wake up cycling.

## 6. Polarization vs. Thickness

### Remanent polarization decreases with thickness



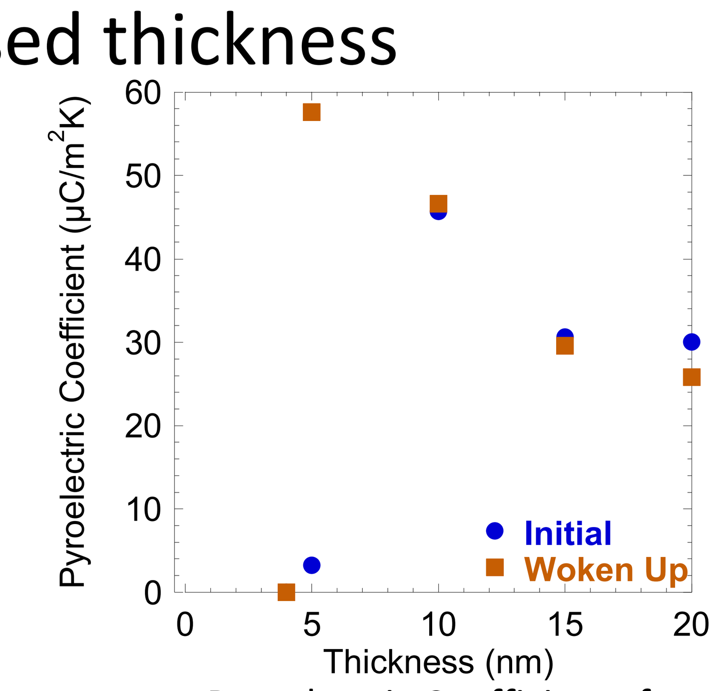

Initial and woken-up polarization response for $Hf_{0.58}Zr_{0.42}O_2$ films and normalized tunneling current magnitude as a function of thickness.

- Square waveform cycling increases remanent polarization
  - Especially important in thin films
- Remanent polarization decreases with decreased thickness
  - Drastically below 10nm
- Tunneling current decreases ~$10^{11}$ with 5 nm increase in thickness

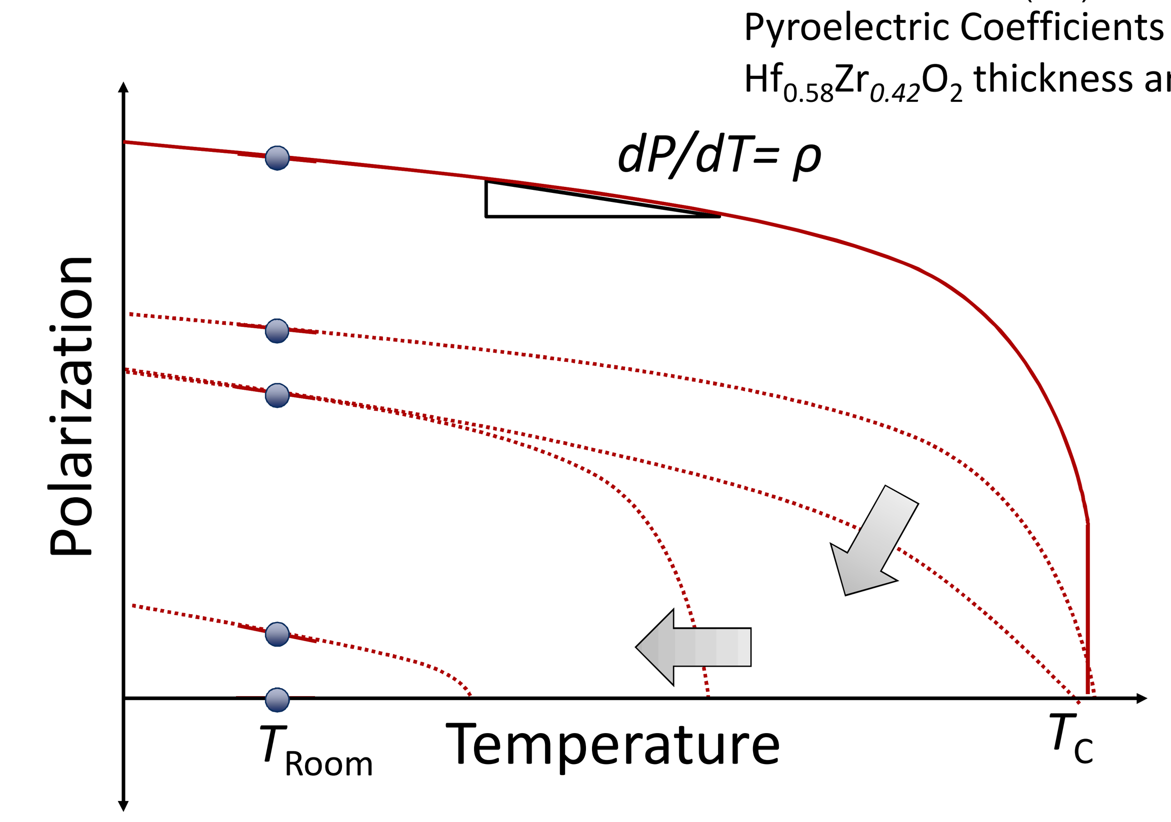
## 7. Pyroelectric Response

### Pyroelectric coefficient increases with decreased thickness

- Pyroelectric coefficient increases as thickness decreases
- Wake up makes little difference
  - Except 5 nm




Pyroelectric Coefficients for $Hf_{0.58}Zr_{0.42}O_2$ thickness array.




- Polarization vs. temperature curve possible response:
  - Phase transition becomes more gradual
  - $T_C$ decreases
- Need additional temperatures

## 8. Summary

- Observed polarization and pyroelectric response in $Hf_{0.58}Zr_{0.42}O_2$ down to 5 nm.
  - Polarization decreased with thickness
  - Pyroelectric response increased with decreased thickness
- Pyroelectric response provides insight into stability of ferroelectric phase with thickness
  - Could be decreasing $T_C$
  - Could be getting more gradual 2nd order like phase transition
- Need measurements at additional temperatures

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