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Pyroelectric Response in Thin Ferroelectric $(Hf,Zr)O_2$

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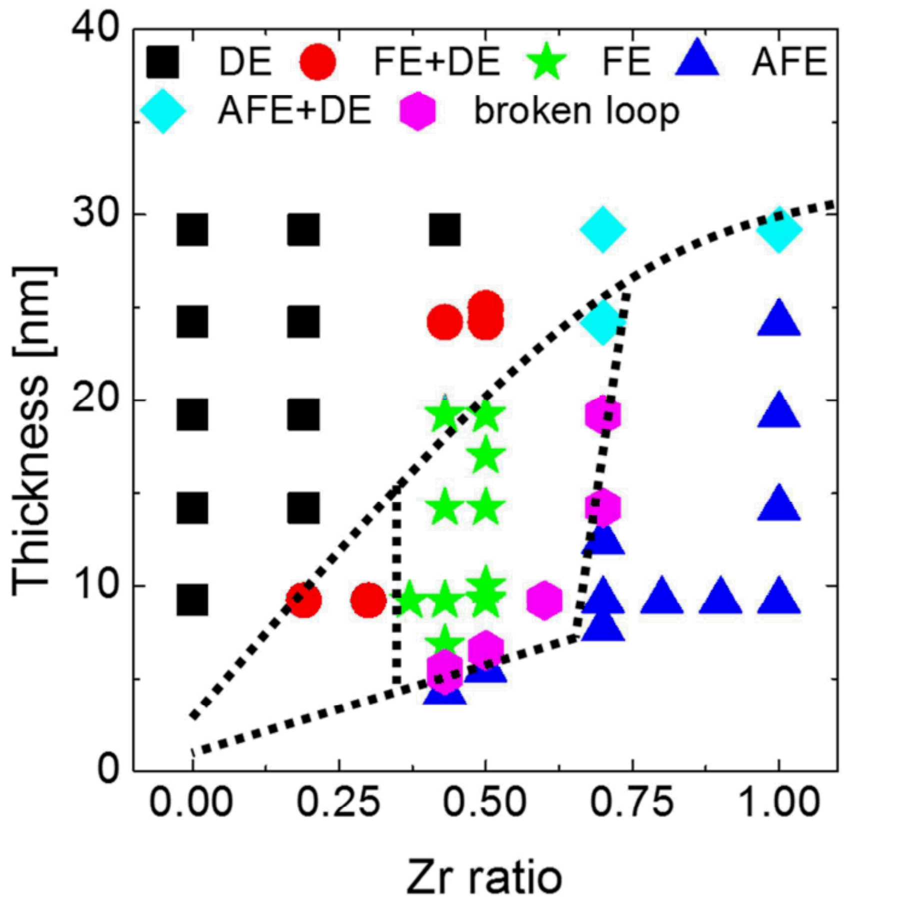
Ferroelectric HfO_2

- 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.



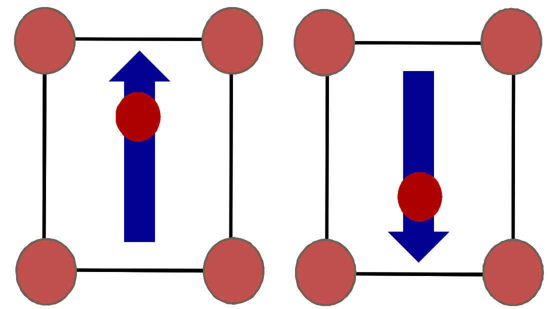
DE-dielectric
FE-ferroelectric
AFE-antiferroelectric-like

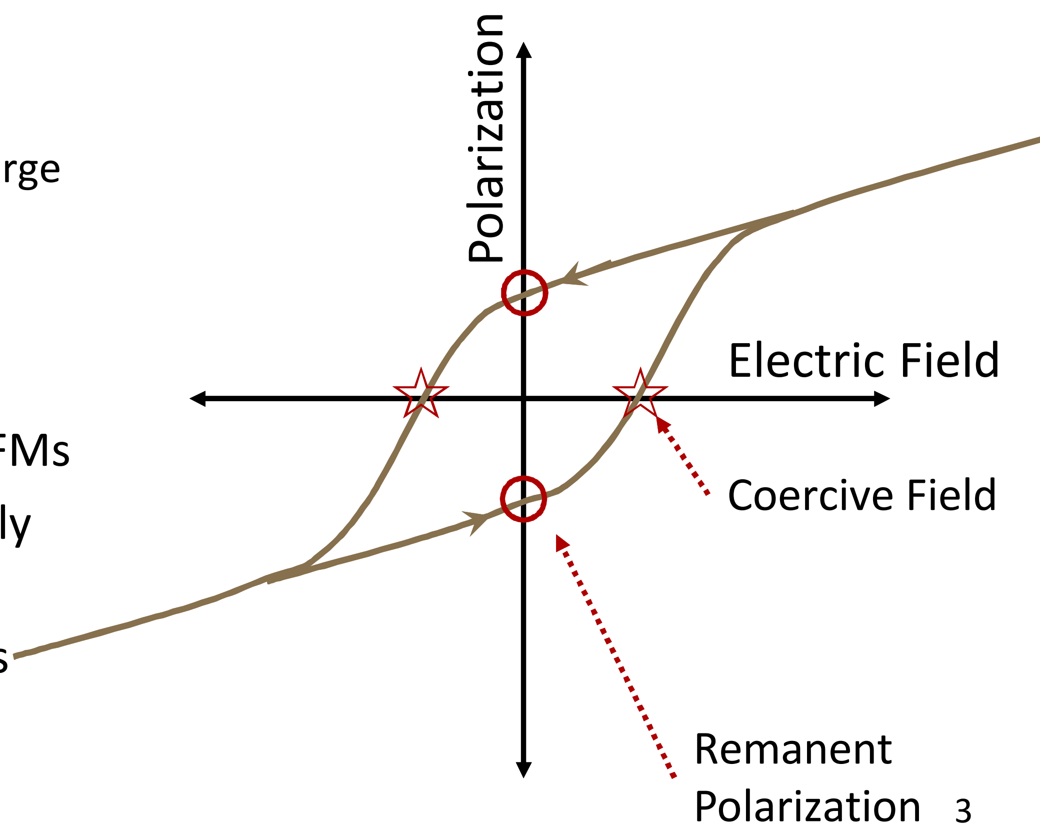
Böscke, *et al.*, *Appl. Phys. Lett.* **99**, 102903 (2011)

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

What is a Ferroelectric Material?

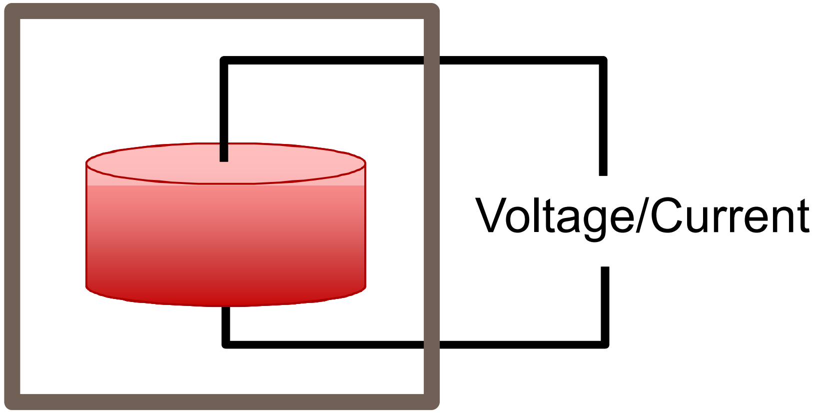
- Spontaneous polarization which can be reoriented by an electric field
- Noncentrosymmetric ionic crystals
  - Centers of positive and negative charge do not coincide
- Applications
  - Memory: FRAM
  - Actuators: Ultrasound, Sonar, AFMs
  - Capacitors: Cellphones and nearly all electronics
  - Sensors: Night vision, IR cameras
    - Due to pyroelectric effect

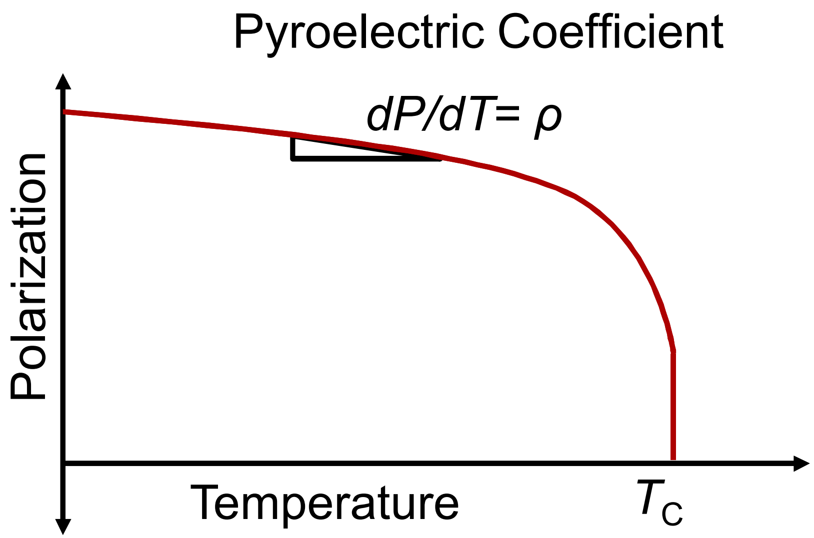




What is the Pyroelectric Effect?

- If: Spontaneous polarization
- Then: Uniform change in temperature creates a change in polarization
  - Change in polarization can be measured as a voltage or current.



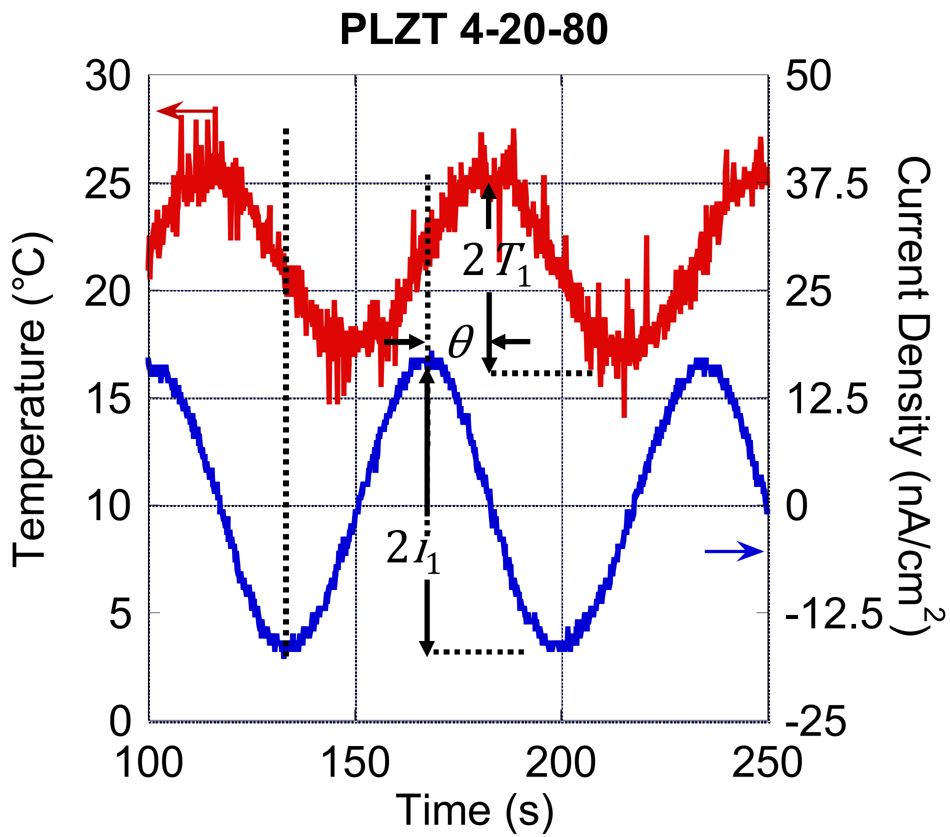


Pyroelectric Measurements

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

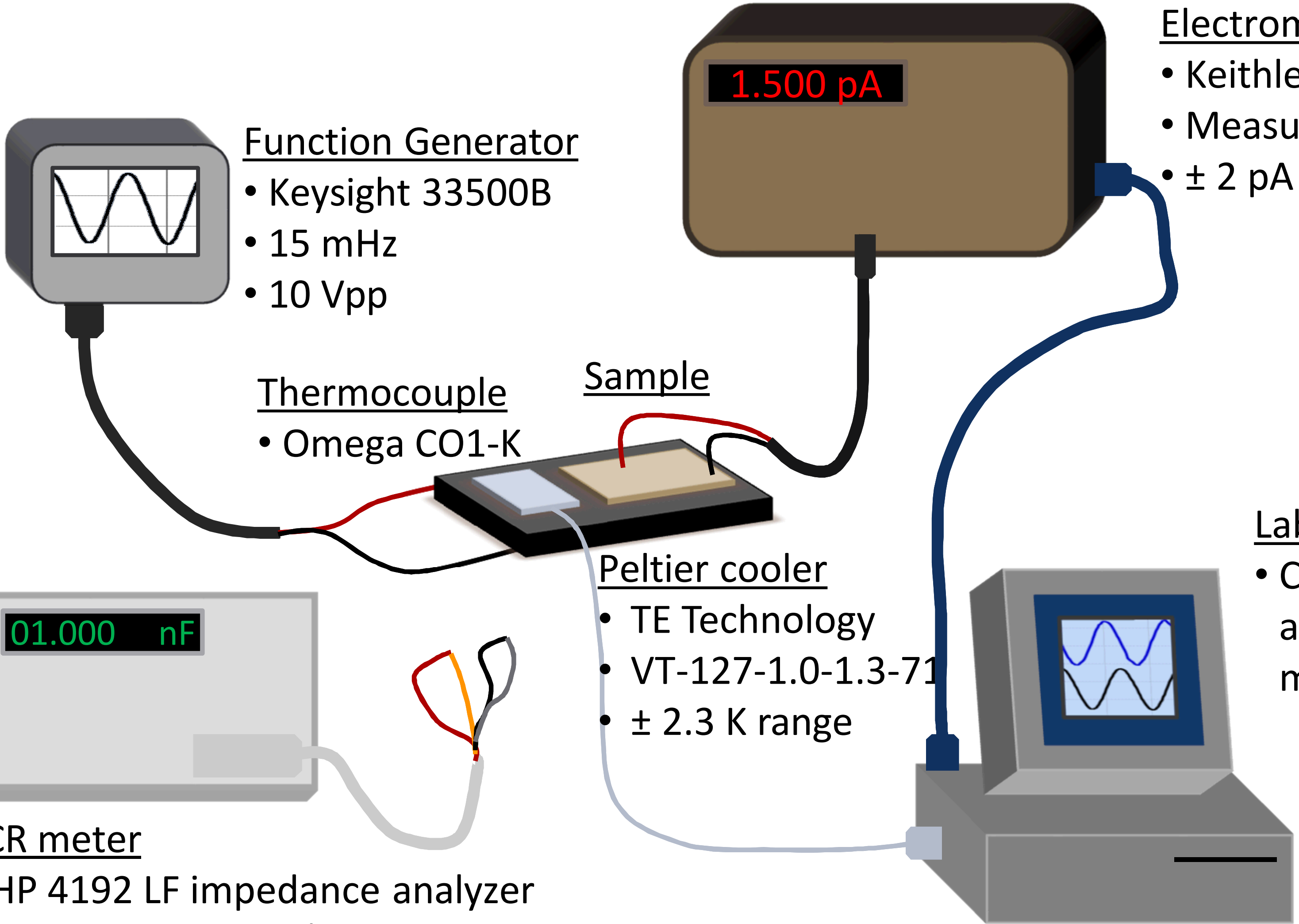
$$i_1 \sin(\theta) = pA\omega T_1$$

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

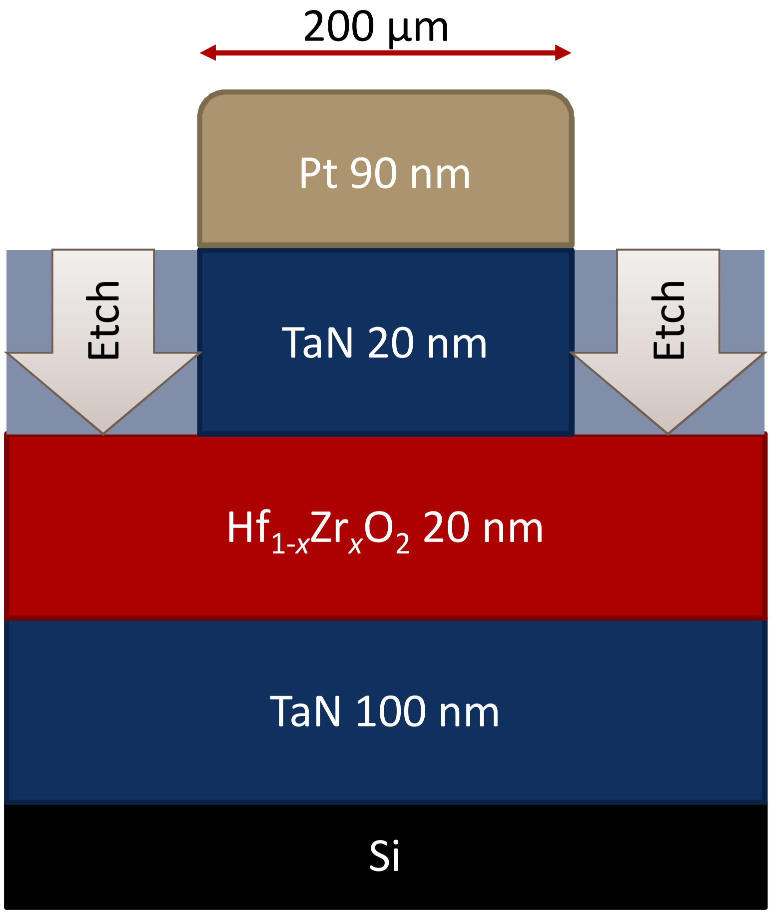
Peltier cooler
- TE Technology
- VT-127-1.0-1.3-71
- ± 2.3 K range

Labview
- Collects current and temperature measurement

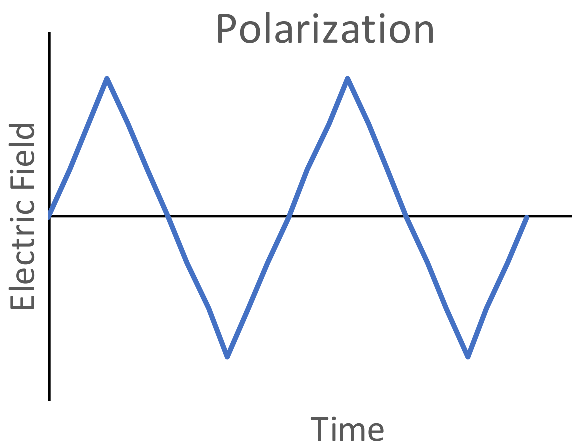
LCR meter
- HP 4192 LF impedance analyzer
- Pole sample 2 MV/cm
- Check capacitance and loss tangent at 1 kHz

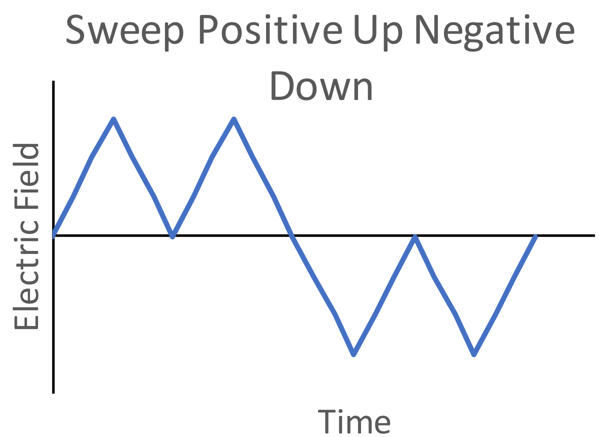
Experimental and Device Stack

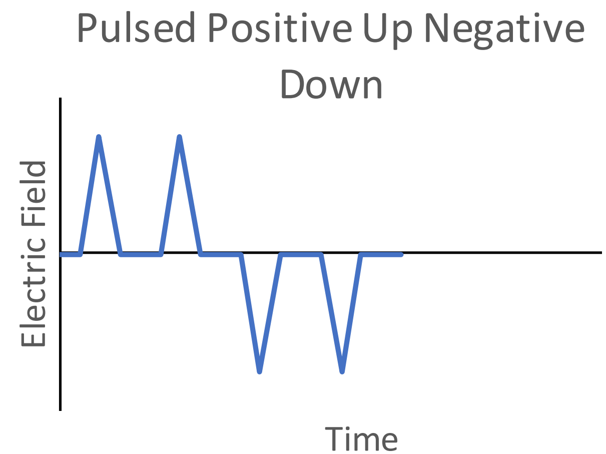
- RF sputter TaN from TaN target
- Thermal ALD $Hf_{1-x}Zr_xO_2$ at 150 °C by TDMA Hf, TDMA Zr, and H_2O
  - HfO_2 1.01 nm GPC
  - ZrO_2 0.99 nm GPC
  - 5 cycle ZrO_2 & 5 cycle HfO_2 supercycle (~1 nm)
- Rapid thermal anneal 30s at 600 °C under nitrogen
- Sputter Pt through shadow-mask
- ICP reactive ion etch
  - SF_6 and C_4F_8 atmosphere

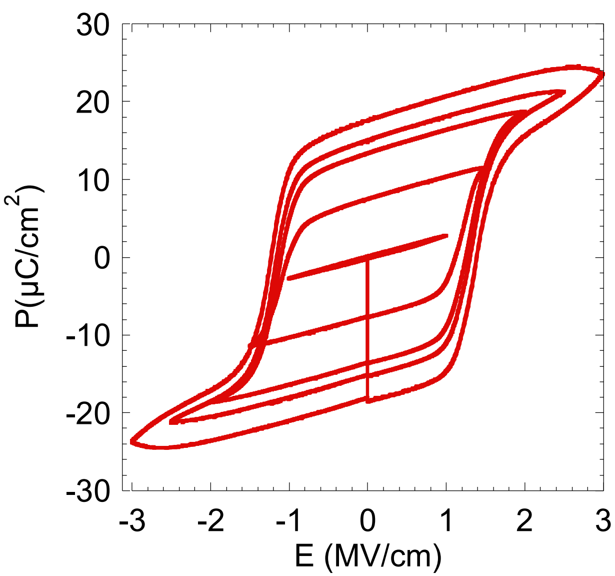


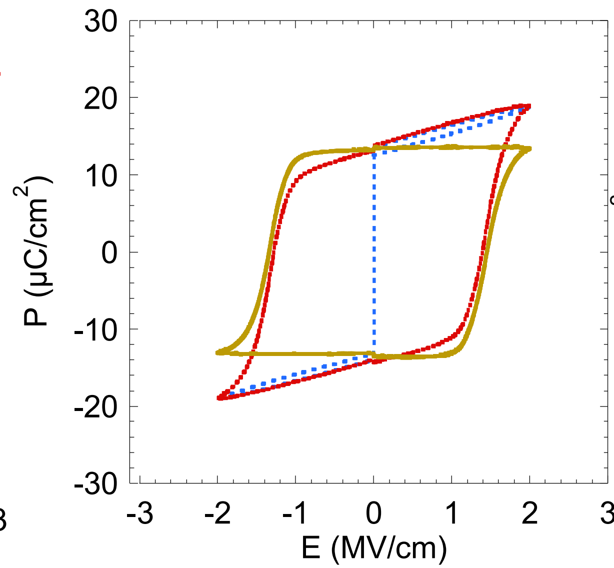
Polarization: Test Profiles

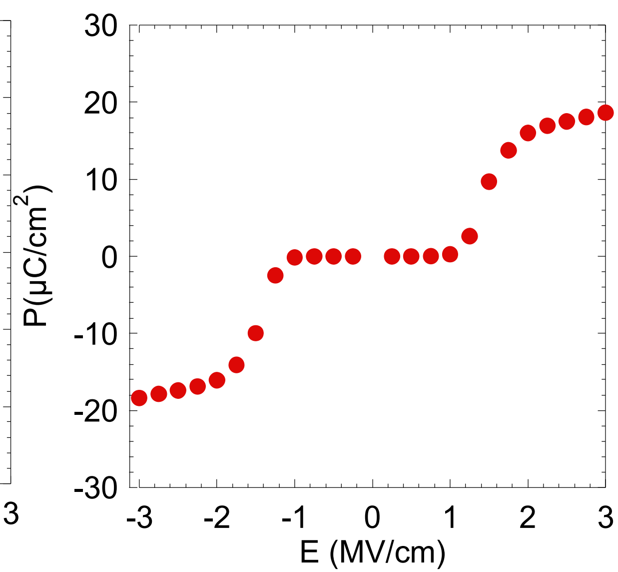






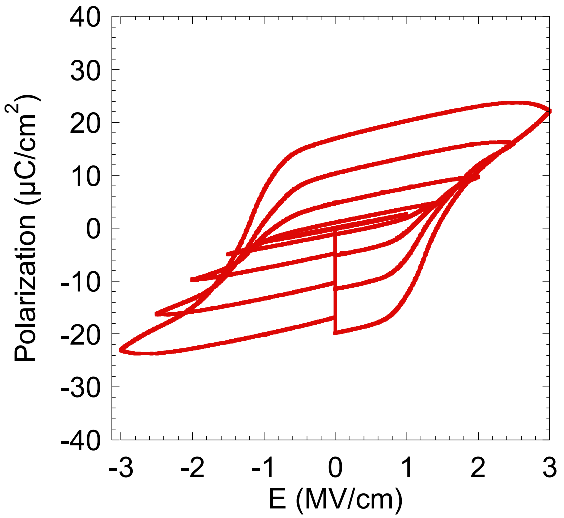


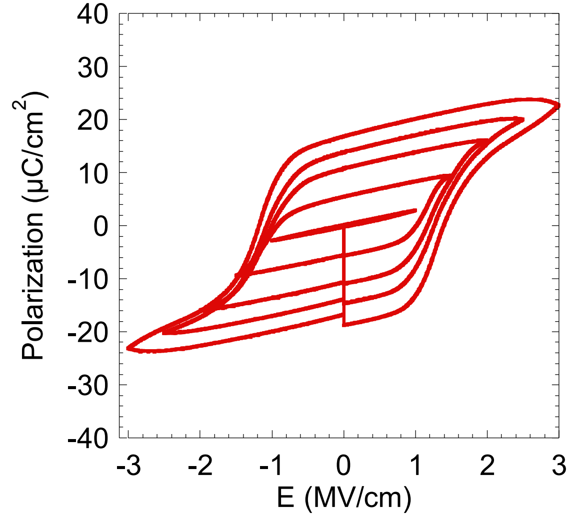


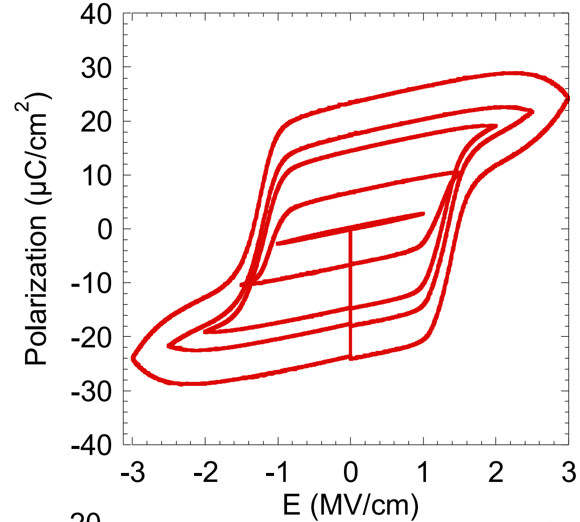


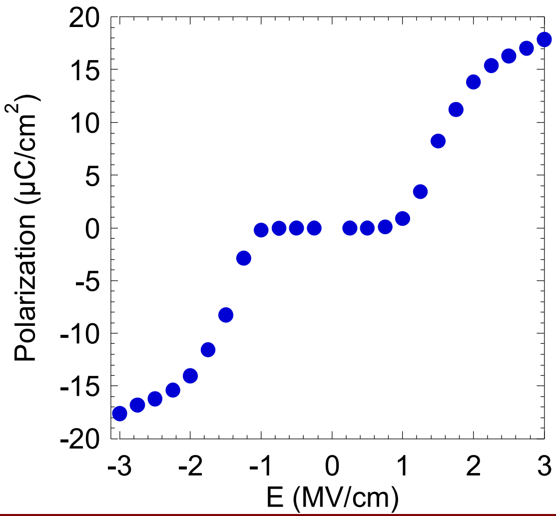
Polarization: Wake Up

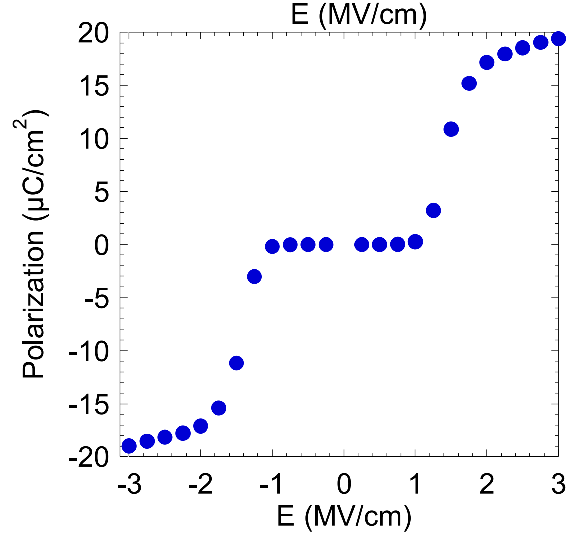
20 nm Initial | 6 V Polarization | 4 V Square Wave 10^3 cycles











S.W. Smith, et al., APL **110**, 072901 (2017) DOI:10.1063/1.4976519

Polarization: Wake Up

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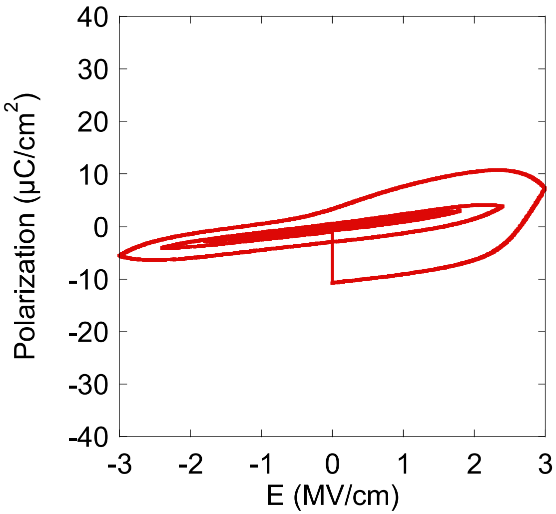
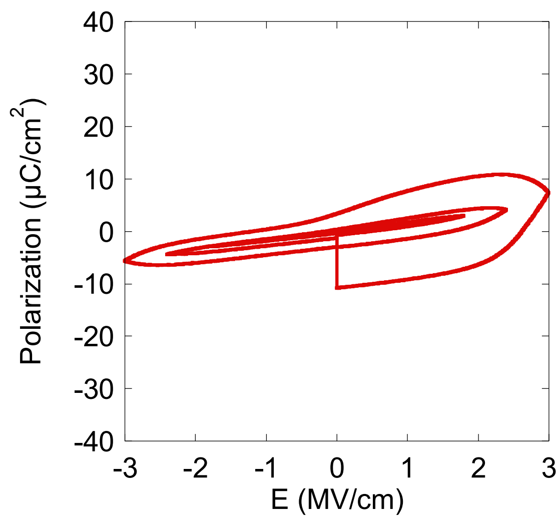
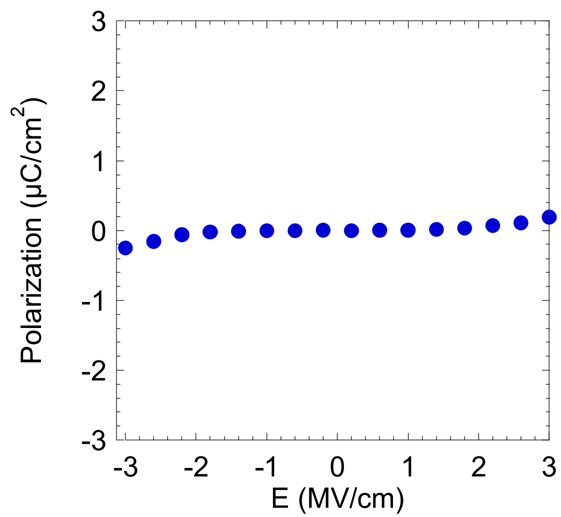
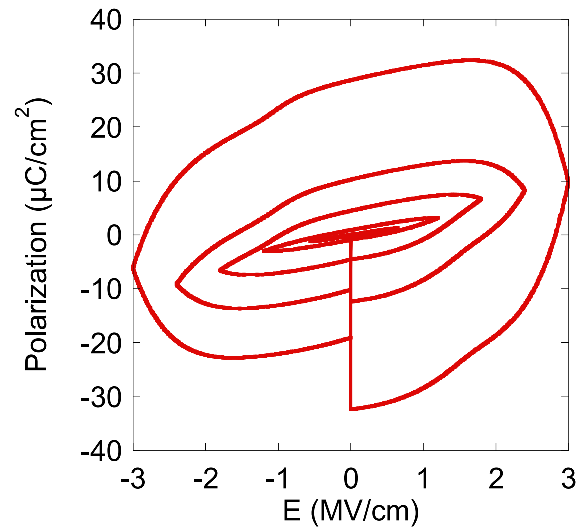
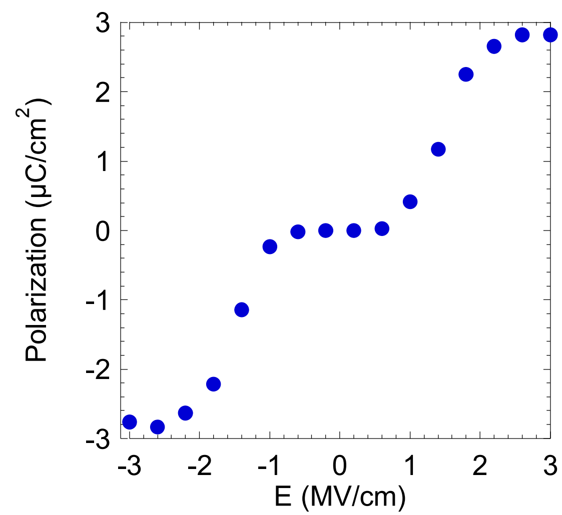
5 nm | Initial | 1.5 V Polarization | 1.5 V Square Wave 10^5 cycles



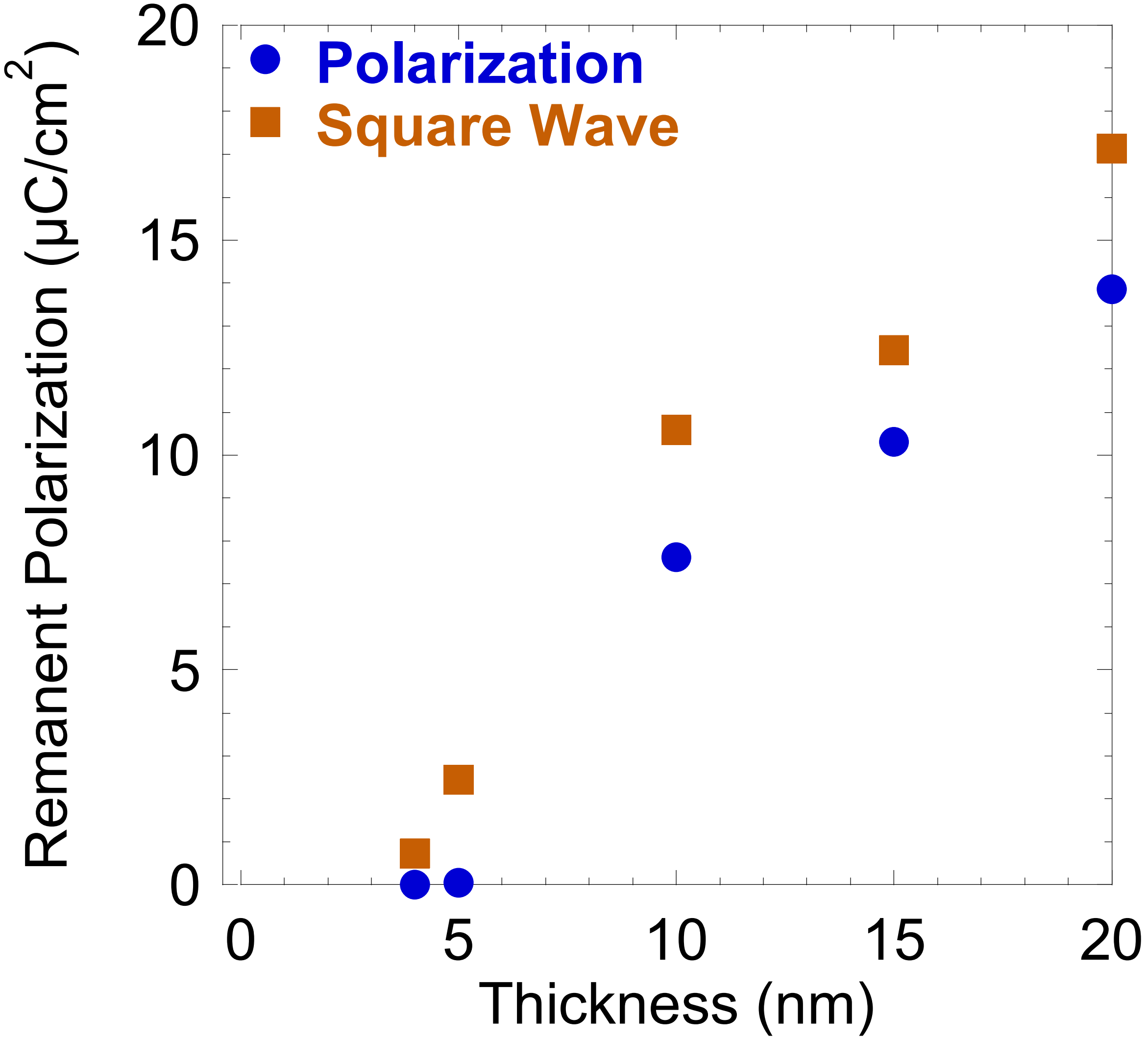






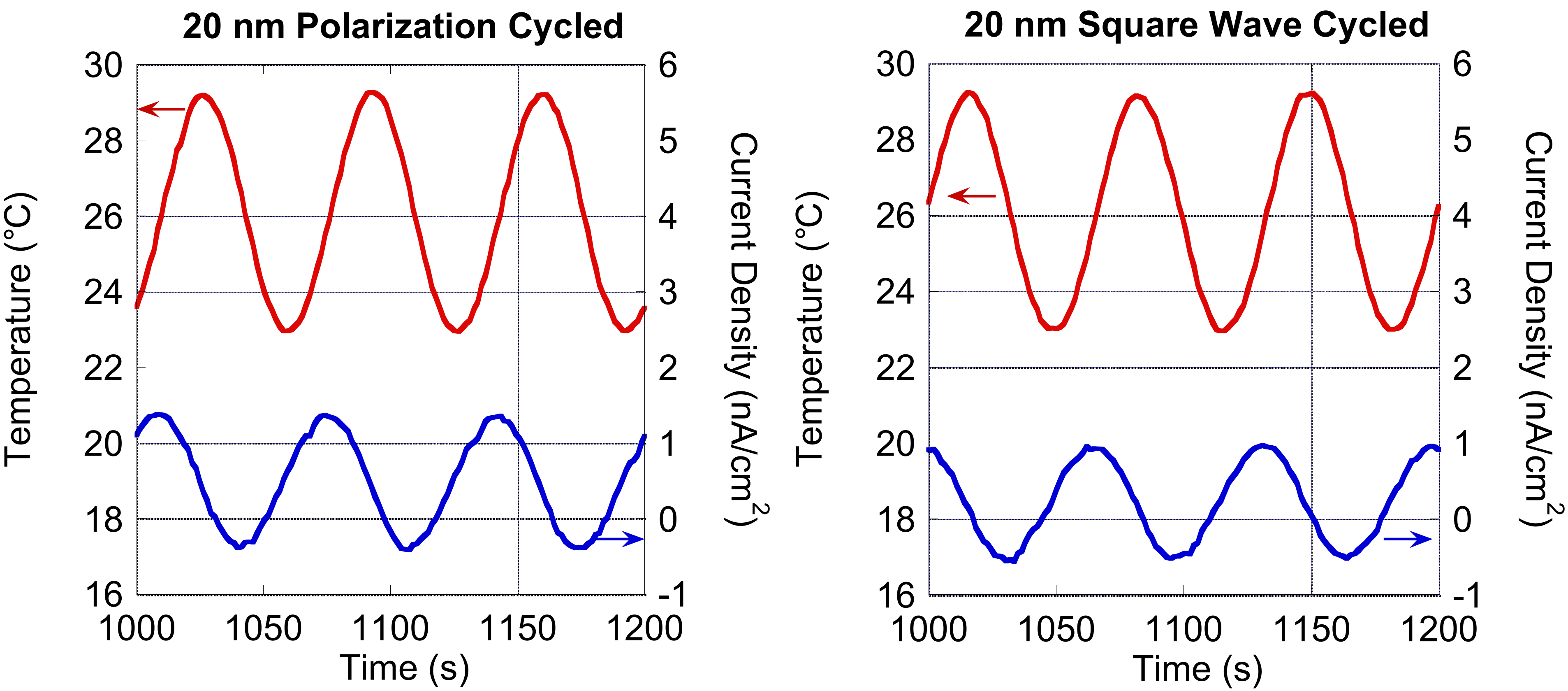


Polarization Trend

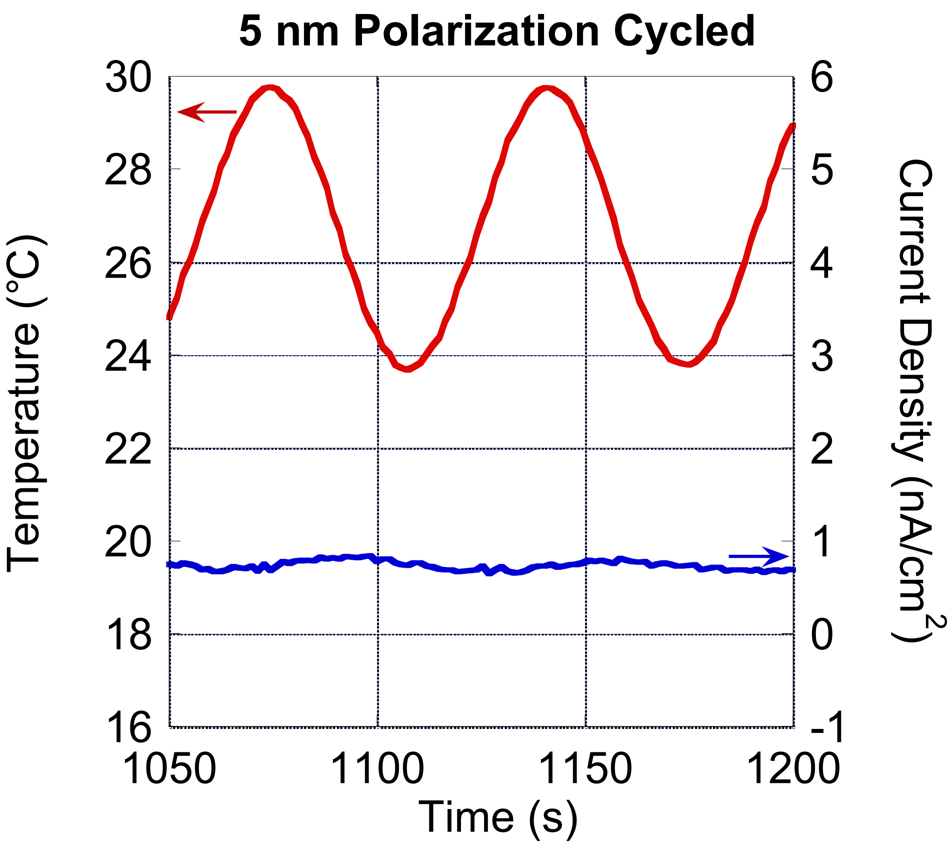


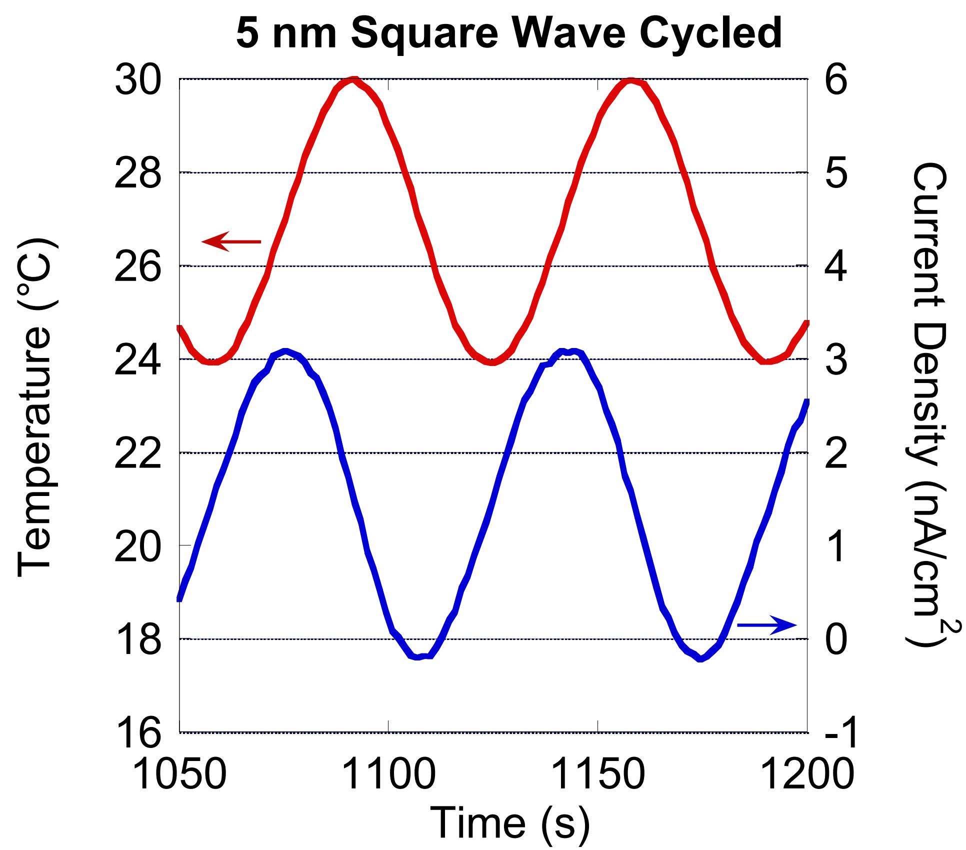
- Remanent polarization decreases with decreased thickness.
- Square waveform cycling increases remanent polarization.

Pyroelectric Measurement Data

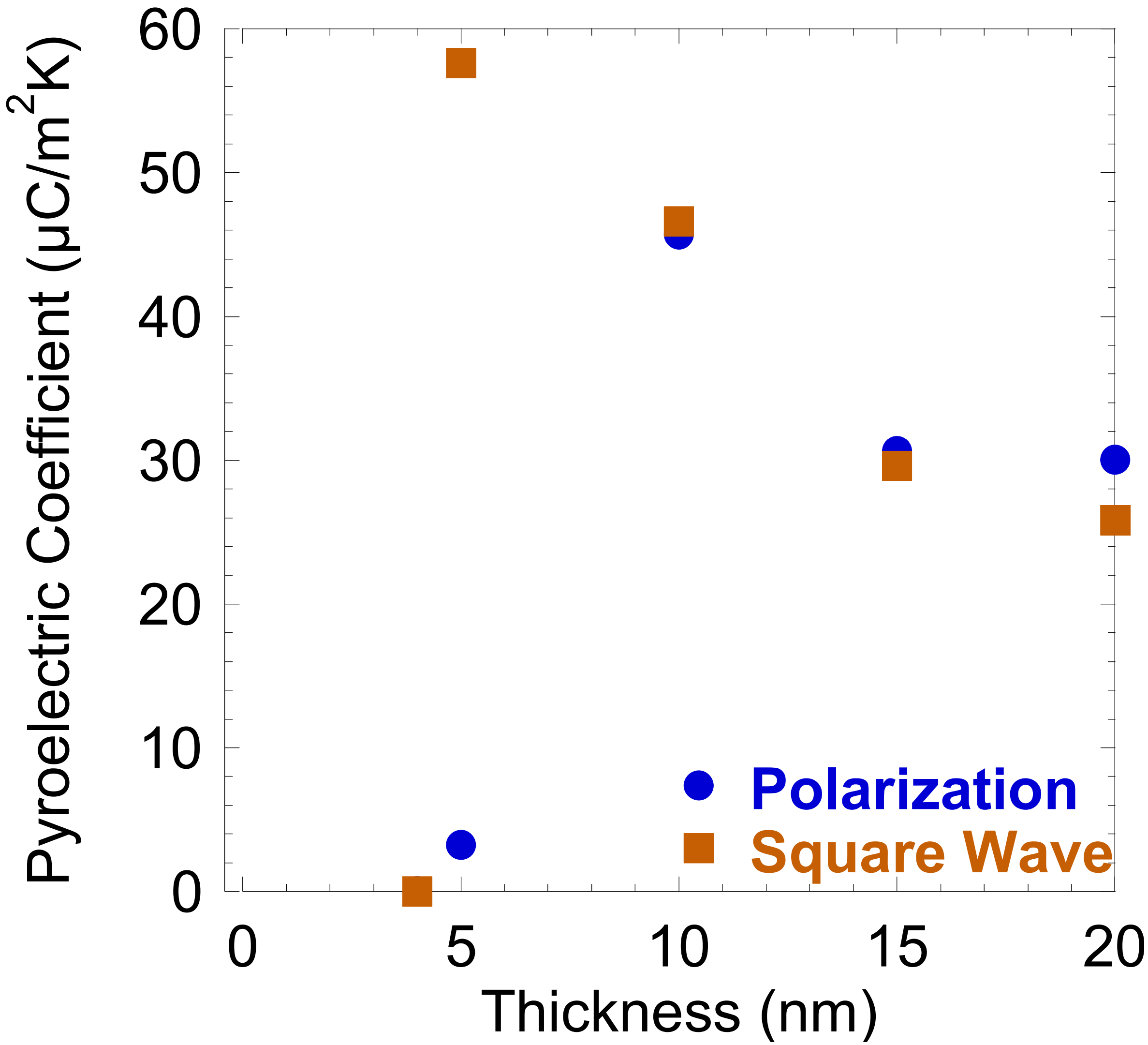


Pyroelectric Measurement Data



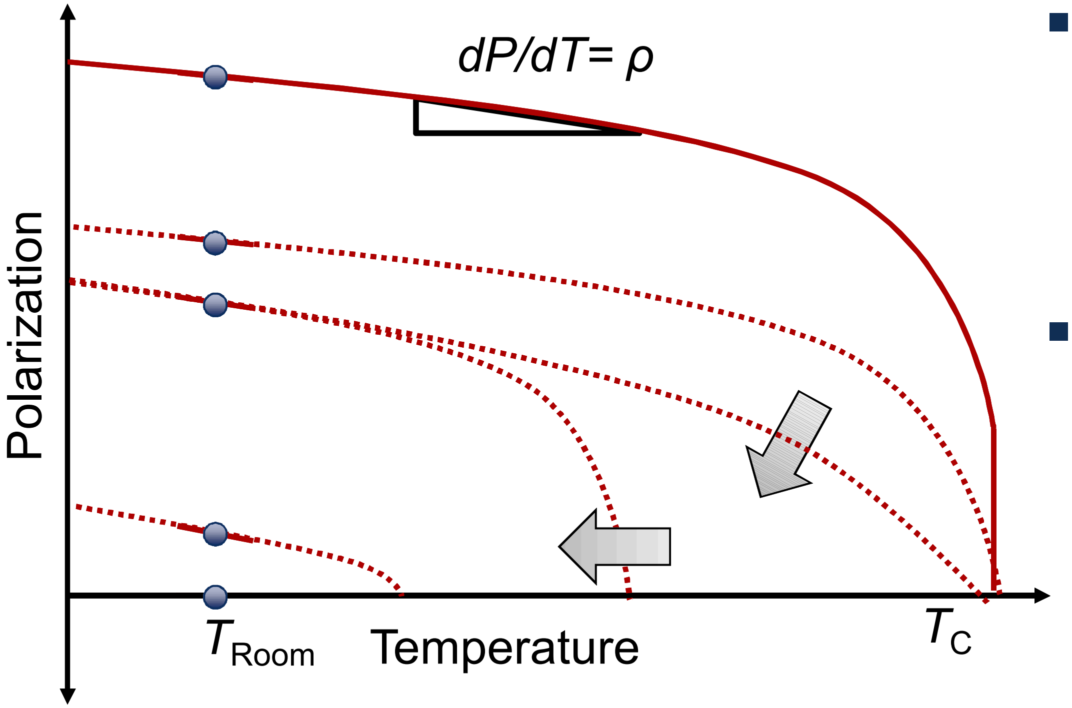


Pyroelectric Coefficient



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

Pyroelectric Coefficient & Polarization



- As thickness decreases:
  - Polarization decreases.
  - Pyroelectric coefficient increases.
- Polarization vs. temperature curve response:
  - T_C decreases.
  - Phase transition becomes more gradual.

Conclusions

- ALD (Hf, Zr)O_2 displays switchable polarization and pyroelectric response down to 5 nm.
  - Polarization decreases with decreased thickness.
  - Pyroelectric response increased with decreased thickness.
- Pyroelectric measurements provide insight into stability of ferroelectric orthorhombic phase: Curie temperature and transition.