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Pyroelectric Response in $Hf_{1-x}Zr_xO_2$ Thin Films

Sean W. Smith, Andrew Kitahara, Michael D. Henry, Michael T. Brumbach, Mark A. Rodriguez, and Jon F. Ihlefeld

Sandia National Laboratories

Albuquerque, NM USA

Ssmith5@sandia.gov

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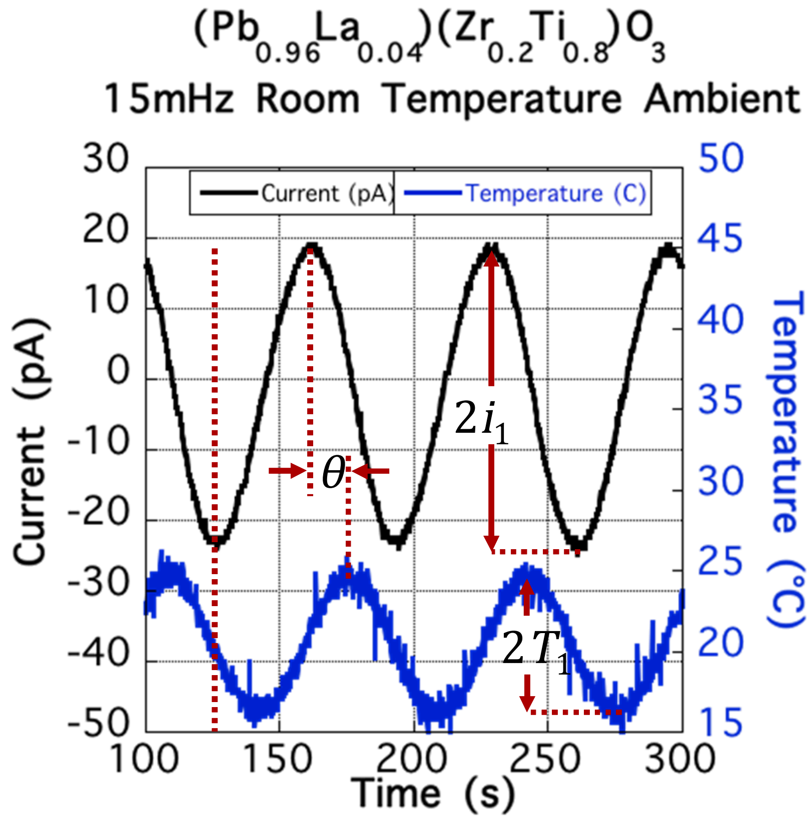
Doped HfO_2 Pyroelectric Response

- Ferroelectric with permanent polarization must have a pyroelectric response
- Park *et al*. Nano Energy 2014
  - $Hf_{1-X}Zr_XO_2$ ($0.7 \leq X \leq 0.9$)
  - Measured Polarization-Electric field hysteresis curves at various Temperatures
- Hoffman *et al.* Nano Energy 2015
  - Si:HfO_2
  - Measured pyroelectric coefficient due to orthorhombic to tetragonal phase change
  - Pyroelectric current measured while sample temperature increased
- These methods can be influenced by extrinsic artifacts such as leakage current.

Pyroelectric Measurements

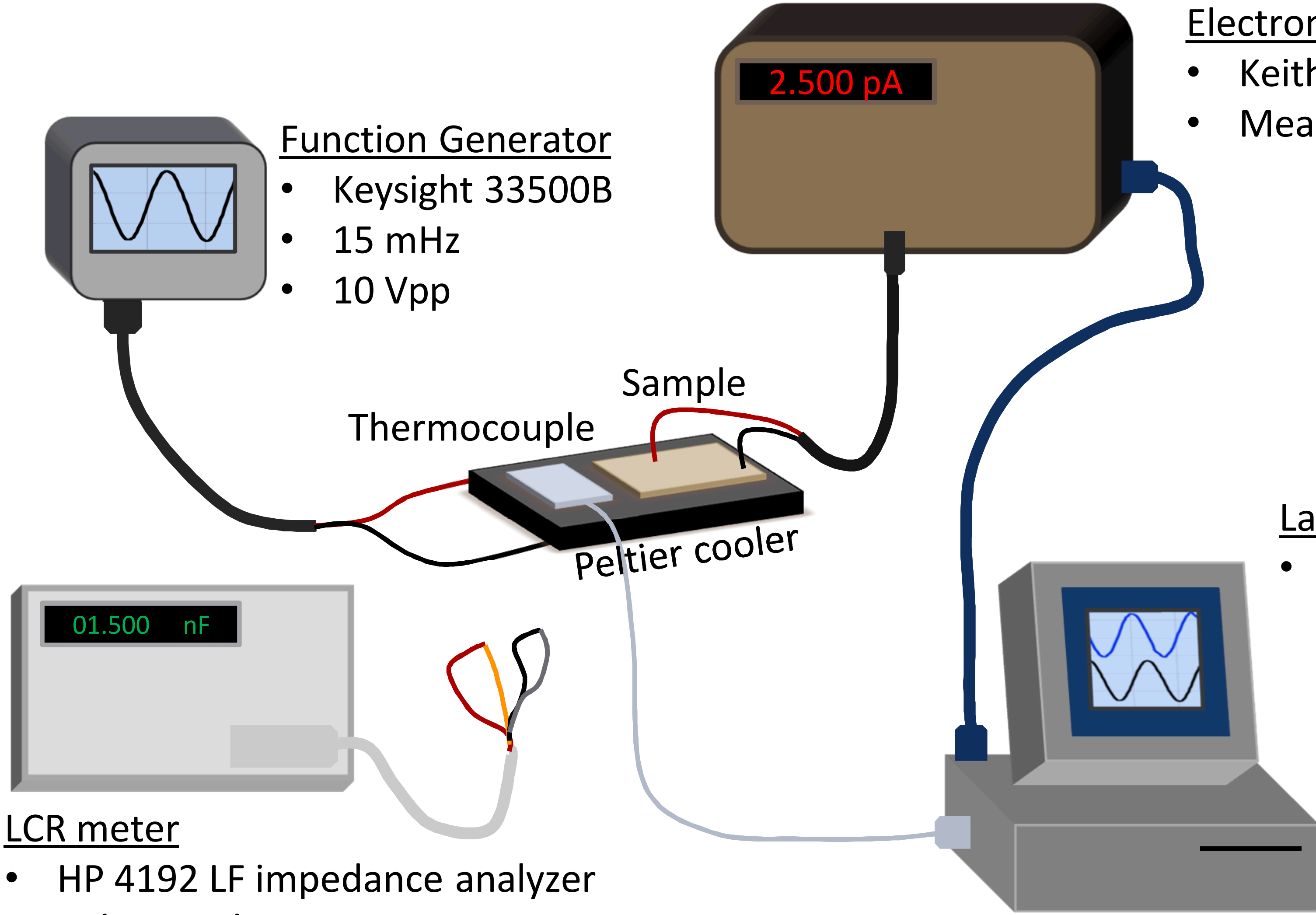
- Static
  - Charge compensation by leakage current
- Indirect
  - Incomplete switching or fatigue
- Dynamic
  - Linear temperature – (Byer-Roundy)
    - Difficult to separate pyroelectric and other thermally induced currents
  - Oscillating temperature
    - Peltier device small sinusoidal temperature waveform
    - Pyroelectric current is 90° out of phase with temperature waveform



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

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

Pyroelectric Setup



Electrometer
- Keithley 6512
- Measures current

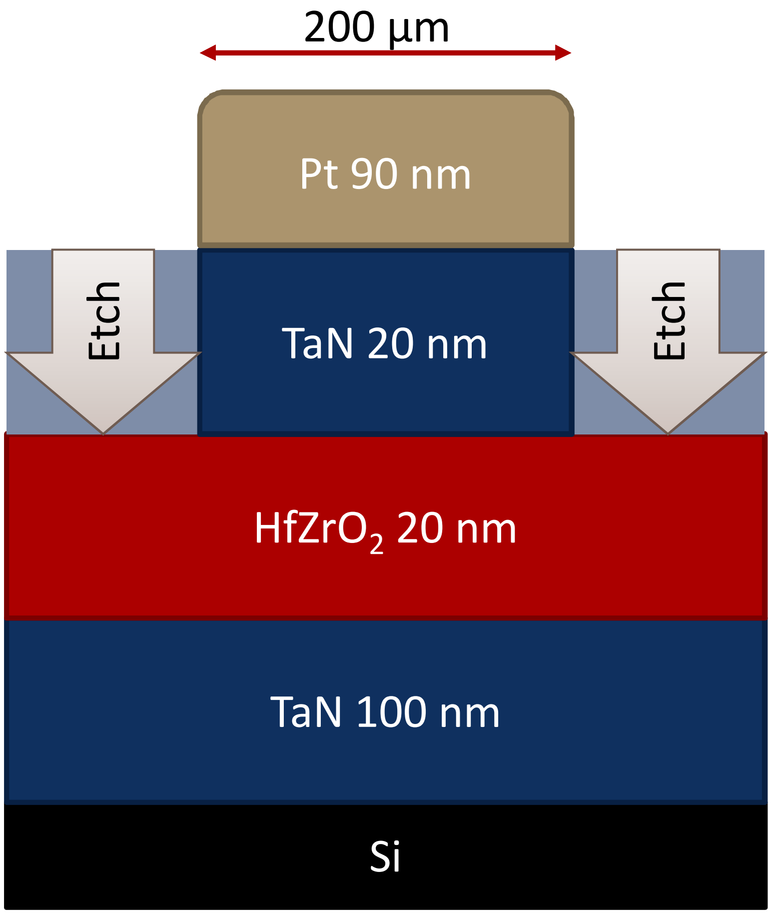
Function Generator
- Keysight 33500B
- 15 mHz
- 10 Vpp

Labview
- Collects current and temperature measurement

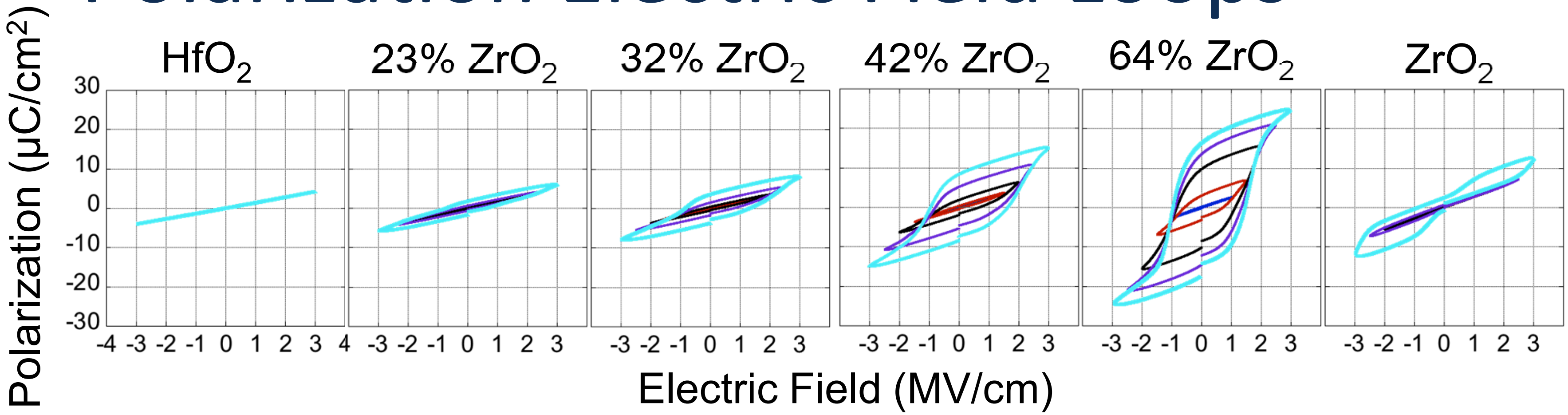
LCR meter
- HP 4192 LF impedance analyzer
- Pole sample 4V
- Check capacitance and loss tangent at 1 kHz

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
  - Cycle ratio to control composition
- RF sputter blanket TaN cap
- 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

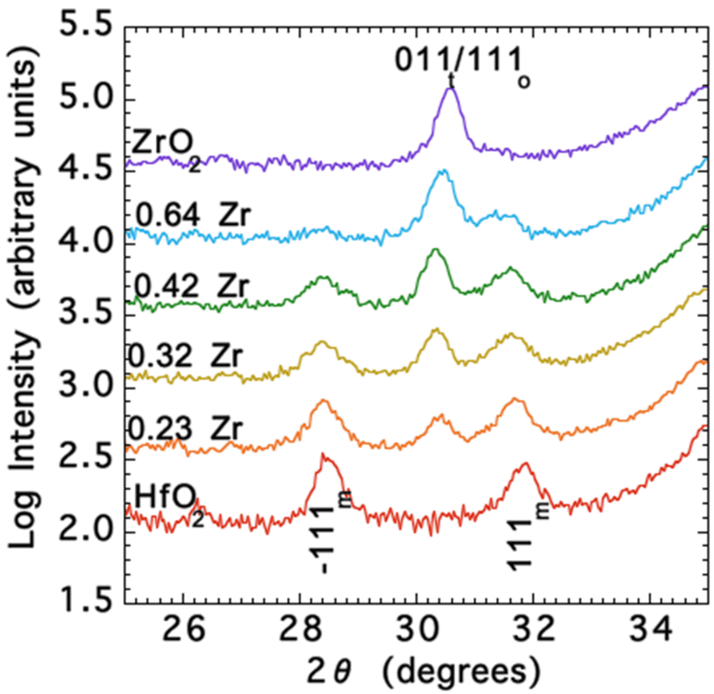


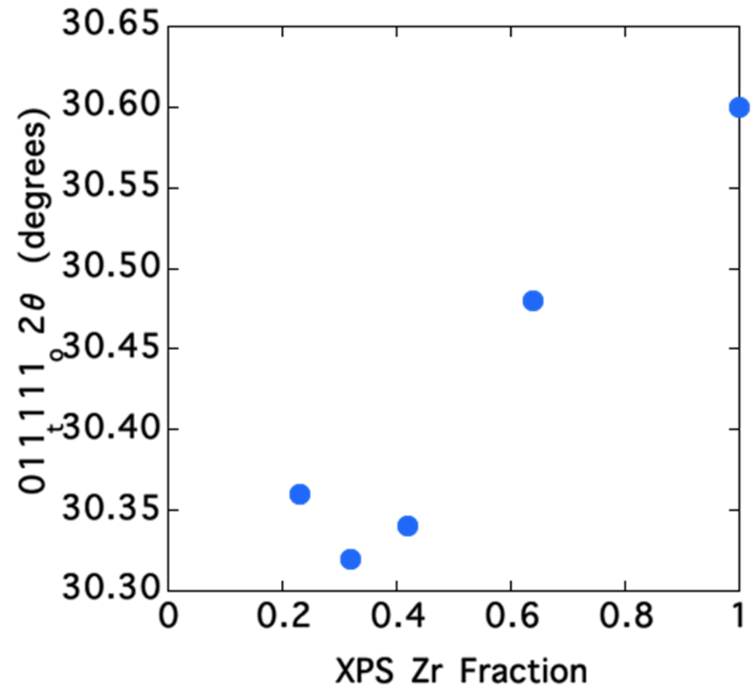
Polarization Electric Field Loops



- Composition, measured by XPS, is HfO_2 rich as expected with larger HfO_2 growth per cycle.
- Trend similar to literature.
  - Antiferroelectric consistent with ZrO_2
- Remanent polarization does not saturate due to leakage current

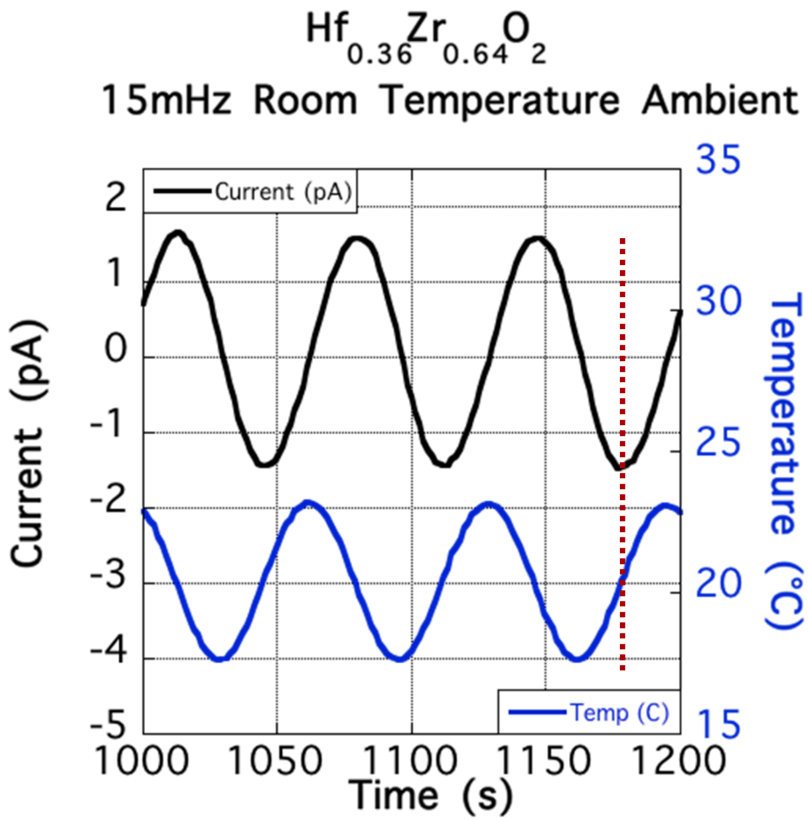
Phase Assemblage



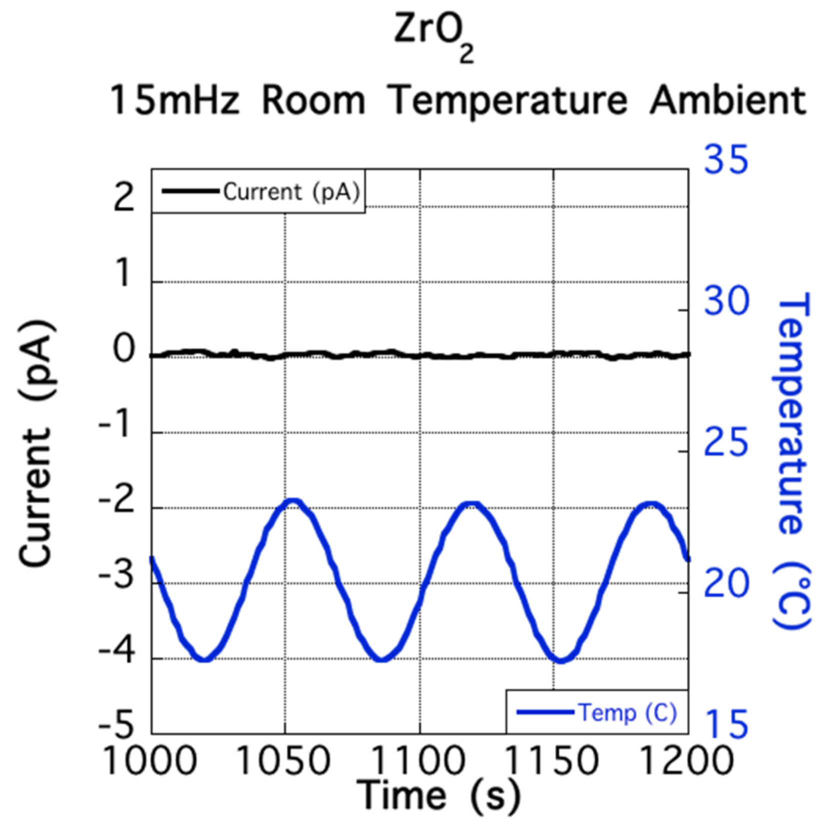


- Monoclinic peaks decrease and Orthorhombic/Tetragonal increase with increased Zr content
- 011t/111o peak shifts to higher angles with increased Zr content
- Orthorhombic/tetragonal intensity correlates with polarization response

Pyroelectric Waveforms

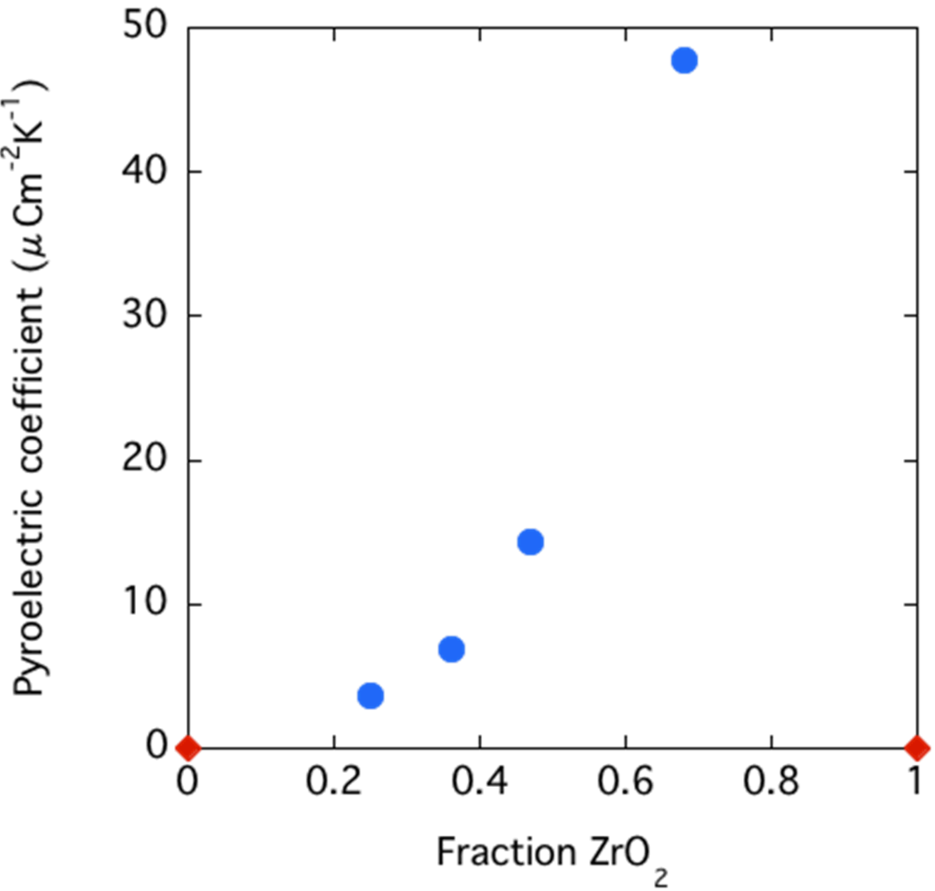


Pyroelectric current measurement for $Hf_{0.36}Zr_{0.64}O_2$ film.



Pyroelectric current measurement for ZrO_2 film.

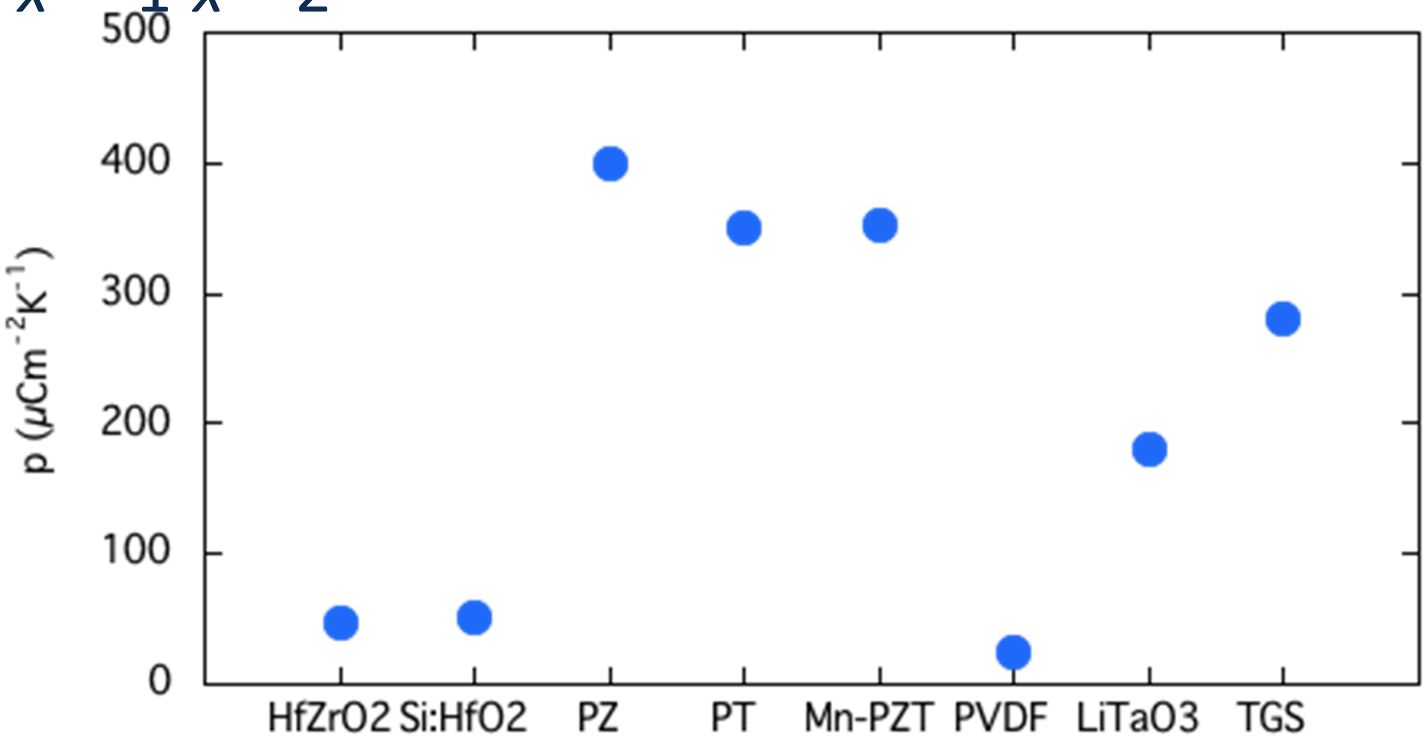
Pyroelectric Coefficients



Room temperature pyroelectric coefficient for $Hf_{1-x}Zr_xO_2$ films as a function of Zr content.

- Pure HfO_2 and ZrO_2: no pyroelectric response
- Increasing pyroelectric coefficient with Zr content
  - Maximum: 48 $\mu Cm^{-2}K^{-1}$ at 68% ZrO_2
- Follows polarization and orthorhombic phase content trend.

$Hf_xZr_{1-x}O_2$ & Other Materials



Material	p (μCm^{-2}K^{-1})	Dielectric properties: e	Dielectric properties: tan δ	F_I 10^{-10} (mV^{-1})	F_V (m^{2}C^{-1})	F_D 10^{-6} (Pa$^{-1/2}$)	Reference
$Hf_{0.32}Zr_{0.68}O_2$	48	25	0.014	0.22	0.10*	13*	This work
5.6 mol% Si:HfO_2	52	38	0.025	0.20	0.06	7	Hoffmann 2015 Nano Energy
Mod. PZT	400	290	0.003	0.02	0.06	58	Whatmore 2004 J Electroceramics
Mod. PT	350	220	0.01	0.01	0.07	32	
Mn -PZT thin film	352	257	0.007	-	-	39	Sebald 2008 IEEE Trans.
PVDF	25	9	0.03	0.11	0.14	7	Ploss 1991 Sensors and Actuators A
$LiTaO_3$	180	47	0.005	0.56	0.14	39	
TGS	280	38	0.01	1.2	0.36	66	

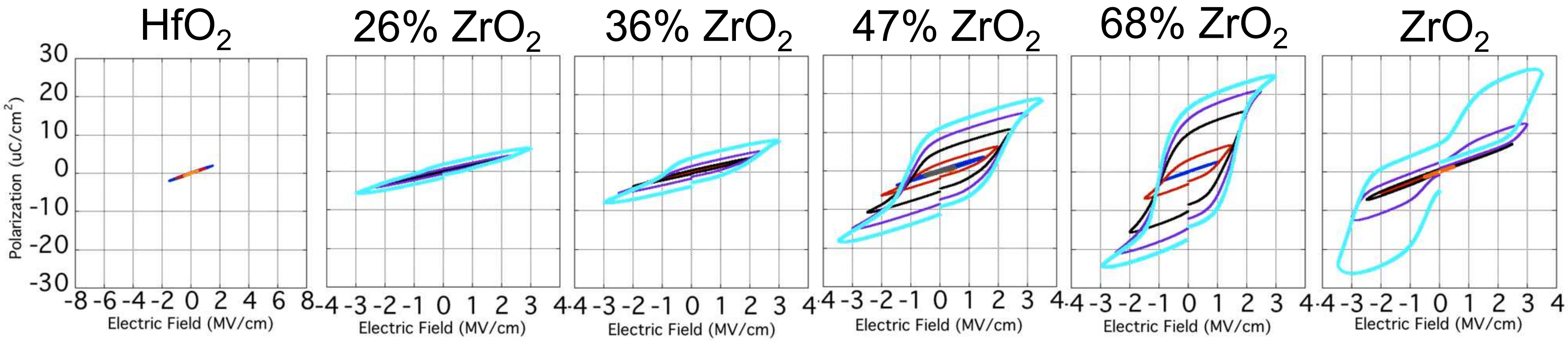
* Literature value bulk heat capacity

Conclusions

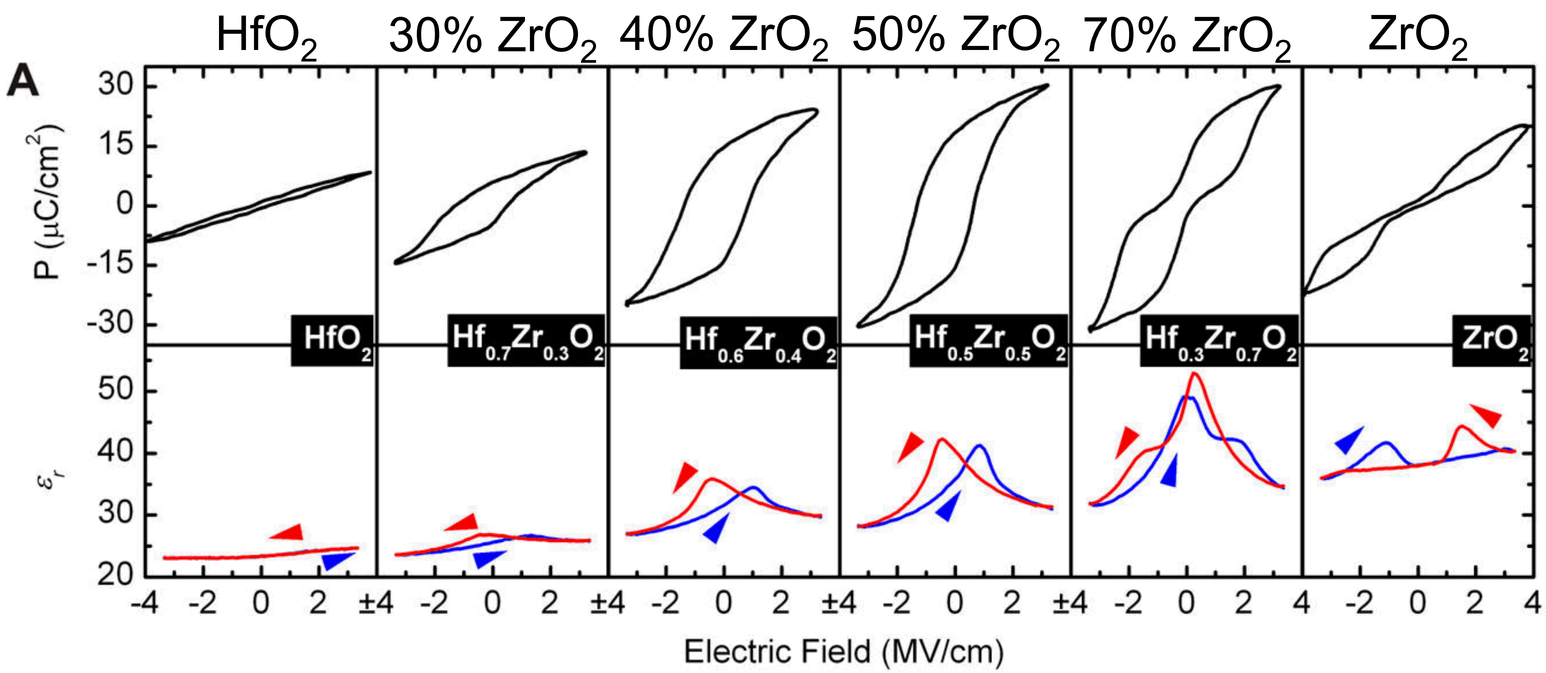
- We do observe a pyroelectric response in $Hf_{1-X}Zr_XO_2$
  - Consistent with permanent polarization
  - Consistent with ferroelectricity
- Pyroelectric response, polarization magnitude, orthrohombic/tetragonal phase fraction, are all correlated with Zr content.
- $Hf_{0.32}Zr_{0.68}O_2$ pyroelectric coefficient and IR detector figures of merit similar to PVDF and $LiTaO_3$
  - p=48 $\mu Cm^{-2}K^{-1}$
  - F_I= 0.22 mV^{-1}
  - F_V= 0.10 m^2C^{-1}
- This could be a promising material for large area IR detectors or low frequency detection.

BONUS SLIDES

Polarization electric field loops

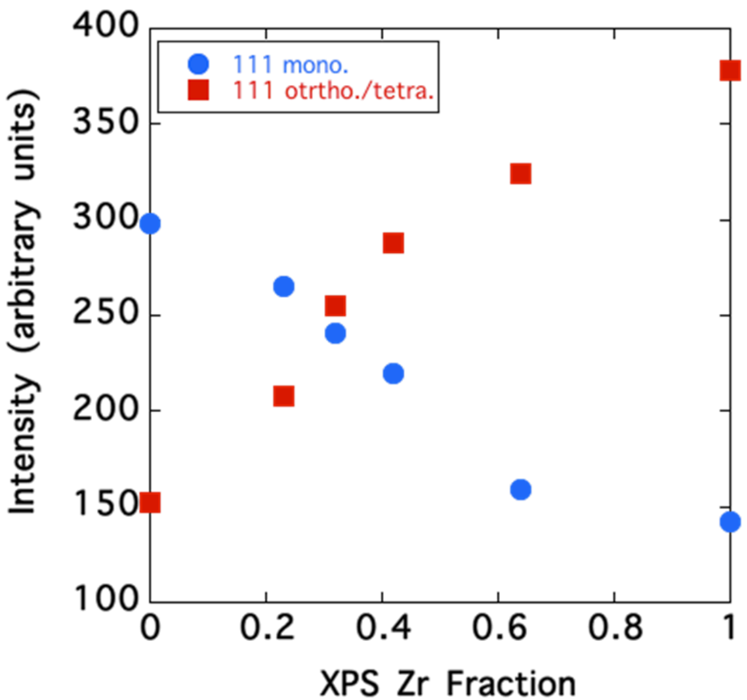


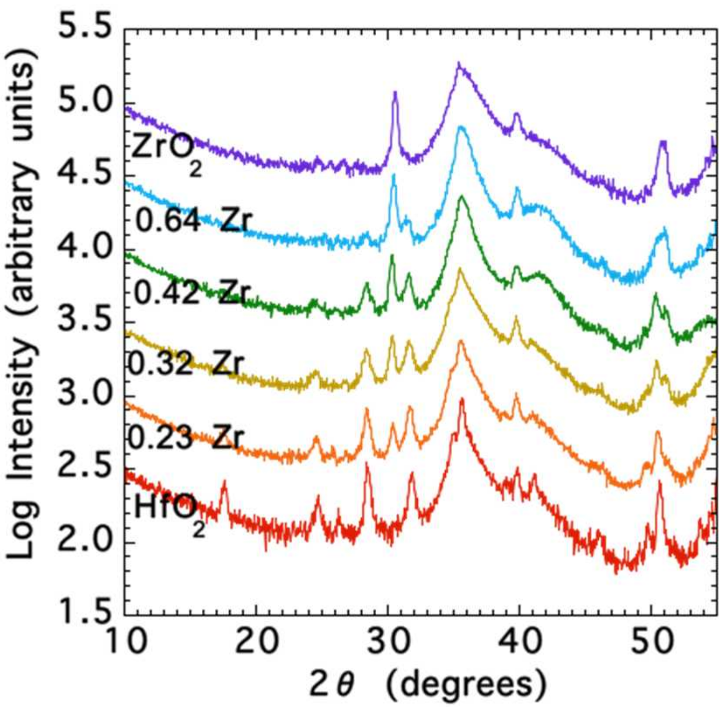
This work – 20 nm $HfZrO_2$ with TaN electrodes.



Muller 2012 Nanoletter – 9 nm $HfZrO_2$ with TiN electrodes.

X-ray results





ZrO_2 pyro waveforms zoomed in

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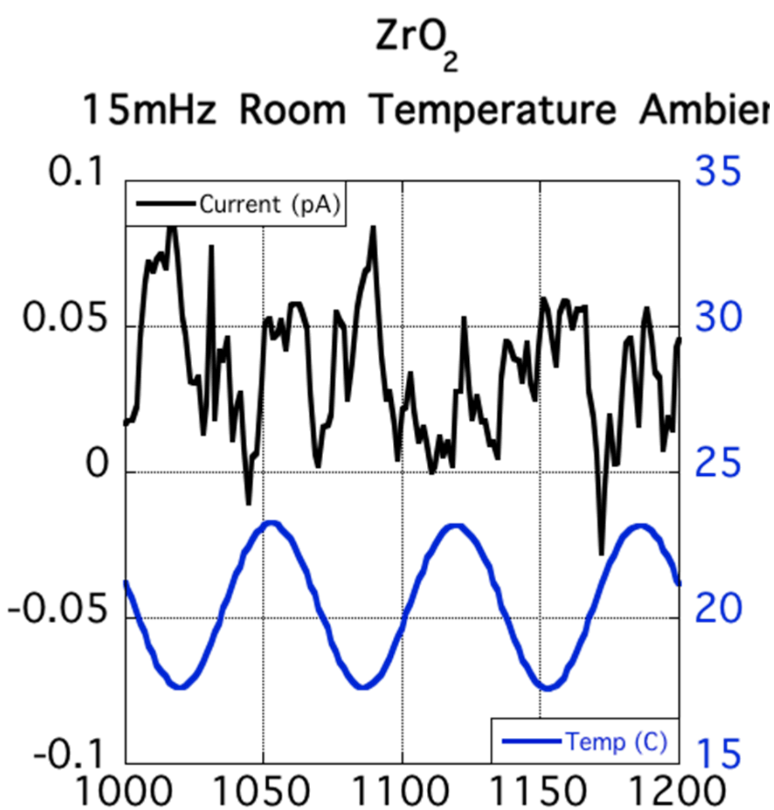

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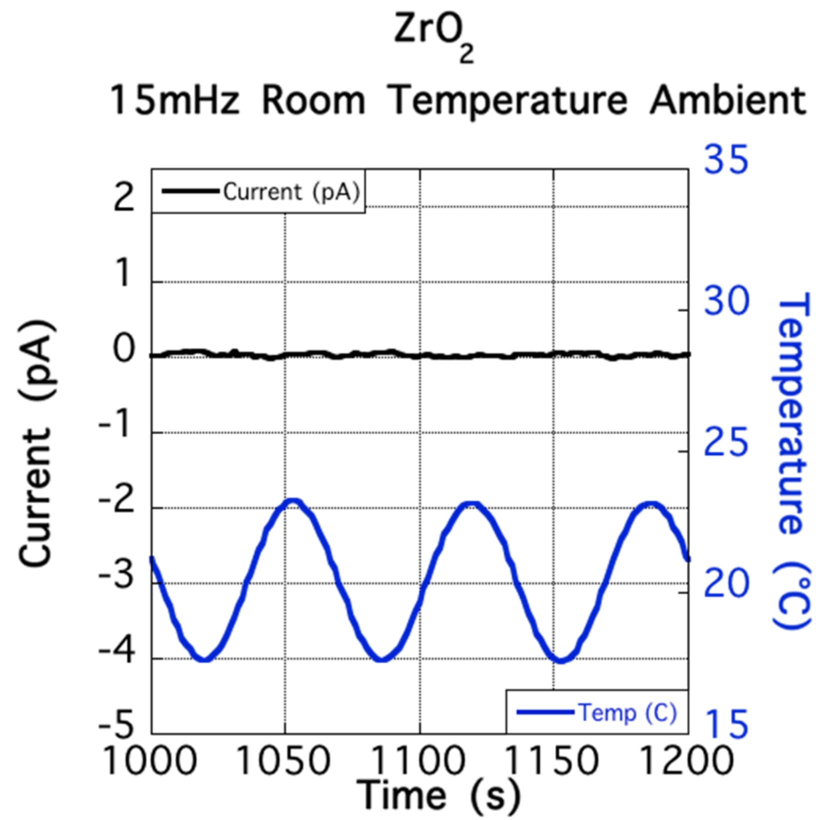

Pyroelectric current measurement for ZrO_2 film.