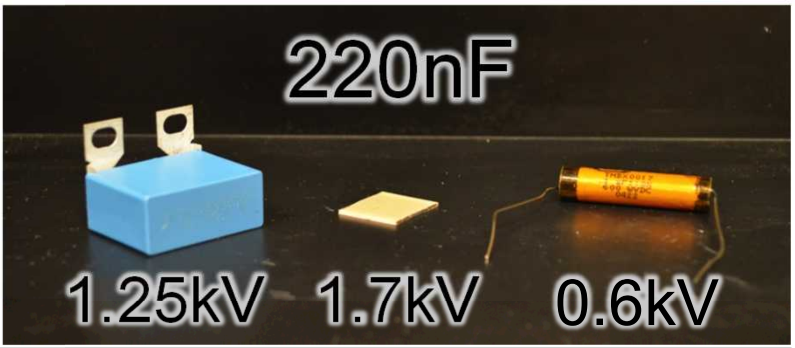
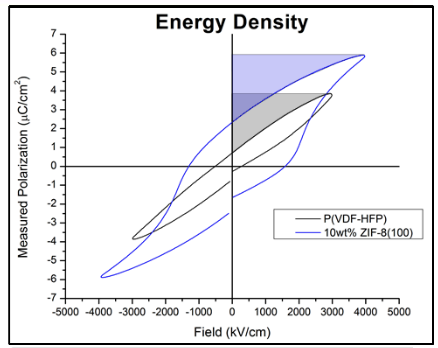
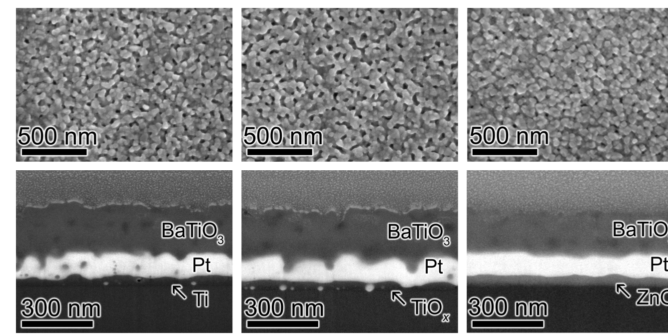
SAND2014-19247PE

Exceptional service in the national interest

Sandia National Laboratories







Dielectrics Research at Sandia

Leah Appelhans, Jon Ihlefeld, Harlan Brown-Shaklee

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Dielectrics Research at Sandia

(contributors to presented work)

Polymers

Ben Anderson*
Leah Appelhans
Kirsten Cicotte
Michele Denton
Brent Dial
Shawn Dirk
Cy Fujimoto
Trey Piñon

Inorganics

Mia Blea
John Borchardt
Geoff Brennecka‡
Harlan Brown-Shaklee
Jon Ihlefeld
Paul Kotula
Bonnie McKenzie
Michael Rye

Peter Lam (NCSU)
Jon-Paul Maria (NCSU)
Christopher Shelton (NCSU)

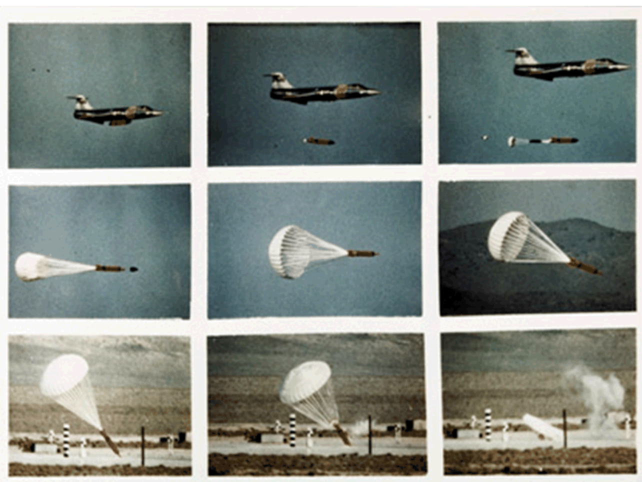
* *Now at 3-M*

‡ *Now at Colorado School of Mines*

Dielectrics Research at Sandia Then

Sandia historically focused on:

RELIABILITY of high consequence devices in EXTREME/UNIQUE environments



Shock Tolerant Electronics (1958)

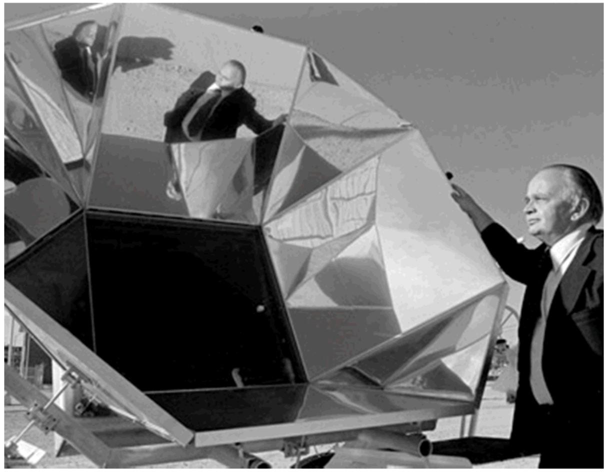
Clean Room Processing (1959-present)
US Patent #3,158,457

Arming, Fuzing, and Firing (1962)

Dielectrics Research at Sandia Then

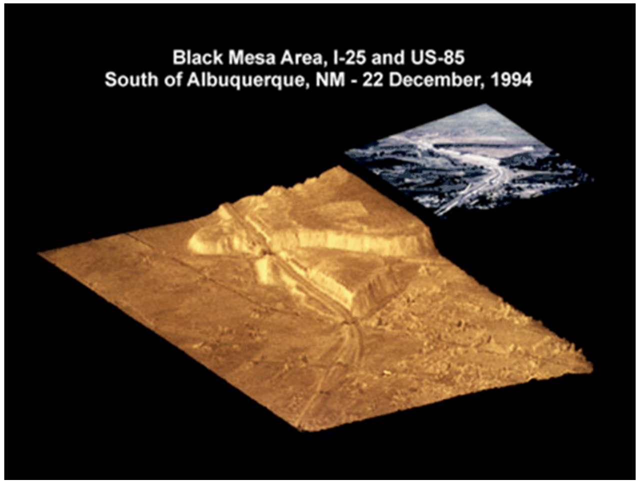
Sandia historically focused on:

RELIABILITY of high consequence devices in EXTREME/UNIQUE environments



Energy Research Initiated (1971)

Osbourn's Strained-Layer Superlattices Theory (1985)



Sandia-Advanced Synthetic Aperture Radar (1991)

Dielectrics Research at Sandia Now

Sandia still focuses on RELIABILITY and EXTREME/UNIQUE environments as well as ENABALING TECHNOLOGIES

- Radiation tolerance
- Shock/vibe and mechanical properties
- Temperature variation/extremes
- Performance reliability for >20 years
- Material compatibility

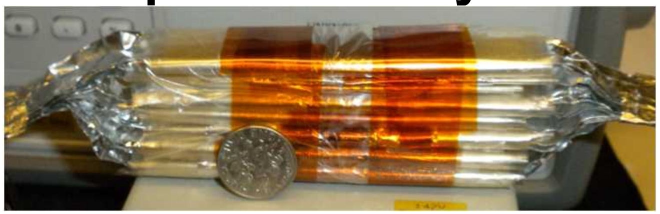
1. Develop new materials
2. Investigate commercial materials
3. Understand degradation and aging

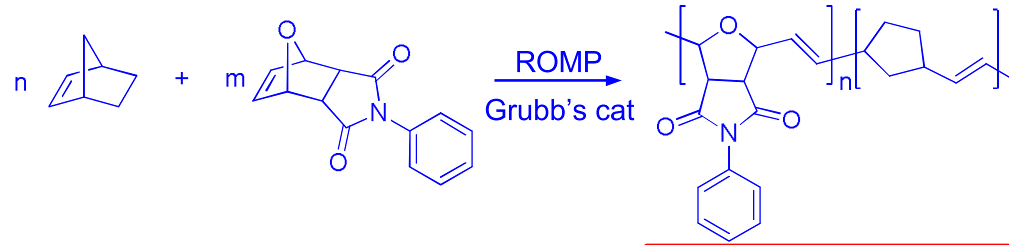
Pulse forming networks, radar, sensors, filters, metamaterials

Polymers - New Materials - SPOW

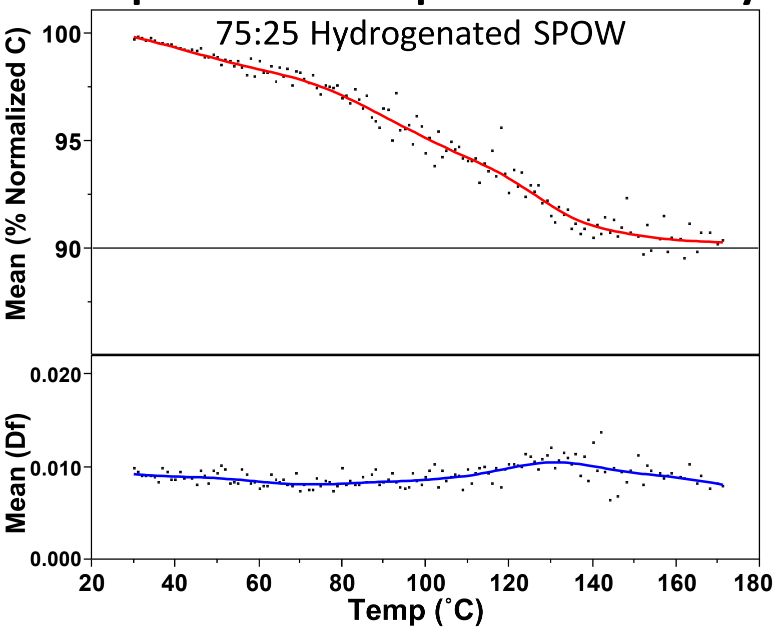
Shawn Dirk, Kirsten Cicotte, Michele Denton, Leah Appelhans, Cy Fujimoto

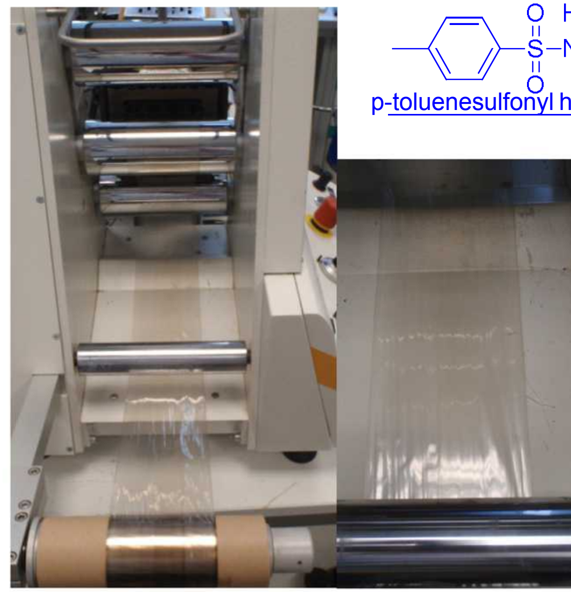
High Temperature Polymer Dielectrics

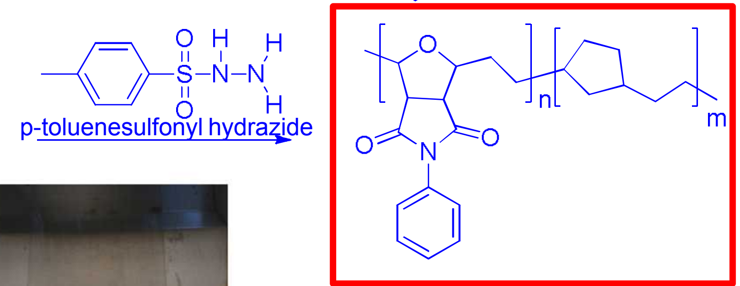




Capacitance Temperature Stability







BOPP:
E_d = ~4 J/cm^3
T_{max}= 105 °C

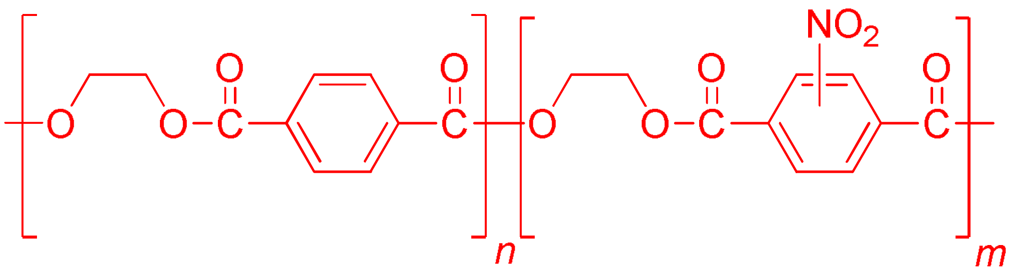
κ = 3.25 **breakdown strength** = 3270 kV/cm
theoretical energy density = 1.53 J/cm^3
T stability ≈ 150 °C **Tg** = 175 °C

Challenges: Increase breakdown strength and film quality (synthesis, microstructure control, orientation)

Dirk, S.M.; Wheeler, D.R. "Norbornylene based polymer systems for dielectric applications" US Patent # 8,223,472 July 17, 2012

Polymers – New Materials – NO_2-PET

Shawn Dirk, Brent Dial, Trey Piñon, Ben Anderson, Leah Appelhans



%PET : $\%NO_2$-PET	T_m (°C)	ΔH (J/g)	approx. % crystallinity
100:0	247	59	42
97:3	226	47	34
90:10	197	32	23
85:15	183	28	20

- T_m decreases significantly (from ~250 ˚C for PET, to ~180 ˚C for 15% nitrated PET)
- % crystallinity decreases as % nitration increases
- Modulus and yield stress/strain do not change significantly with % nitration
- Breakdown strength increases slightly (small sample size)
- Dissipation factor increases, especially at lower frequencies

%PET: $\%NO_2$-PET	Modulus (MPa)	Yield Strain at 0.5% offset (%)	Yield Stress at 0.5% offset (MPa)
100:0	2238	2.6	46.2
95:5	1956	2.9	46.3
90:10	1997	2.7	43.5
85:15	1868	2.5	37.8

Explore biaxial orientation of films to improve mech/elec properties

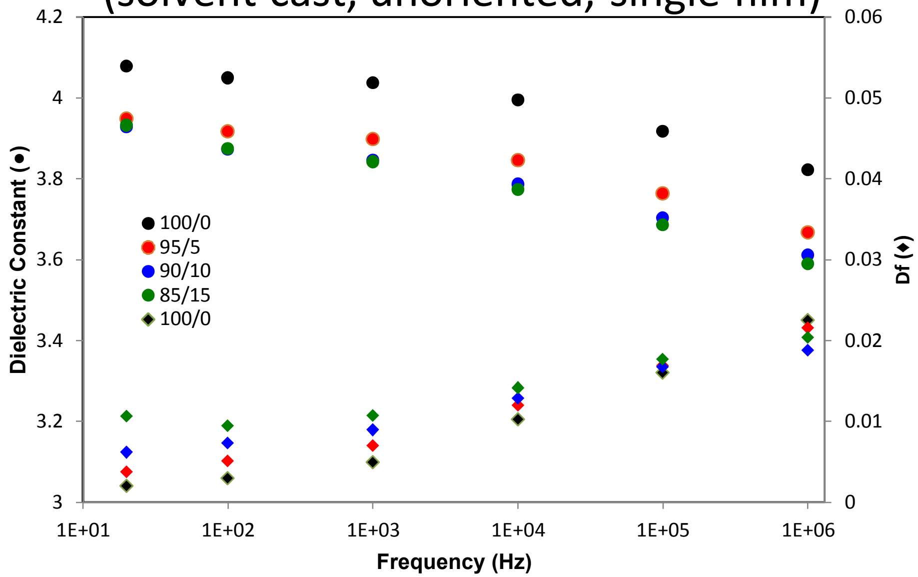
D. P. R. Kint, et al. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3761- 3770.

Polymers – New Materials – NO_2-PET

Shawn Dirk, Brent Dial, Trey Piñon, Ben Anderson, Leah Appelhans

κ/Df

(solvent cast, unoriented, single film)

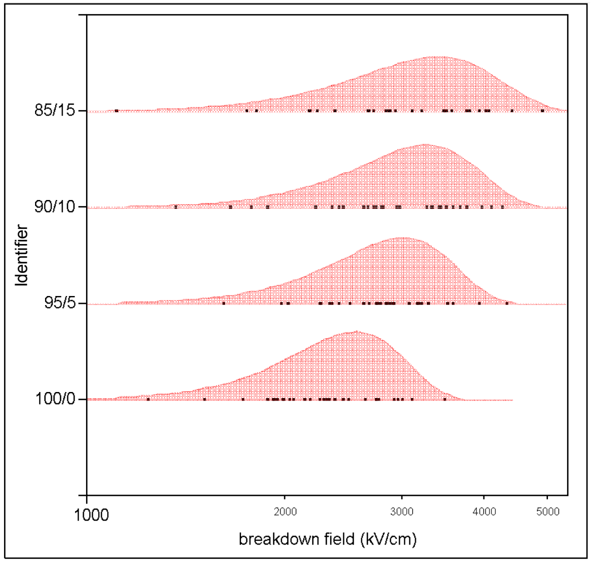


average of three films

%PET: %NO_2-PET	κ (1kHz/10kHz)	Df (1kHz/10kHz)
100:0	3.92/3.87	0.0049/0.0103
95:5	3.95/3.89	0.0072/0.0121
90:10	3.81/3.71	0.0114/0.0141
85:15	3.84/3.77	0.0107/0.0142

Breakdown Strength

(solvent cast, unoriented, single film)



average of three films

%PET : %NO_2-PET	Weibull α (kV/cm)	Weibull β
100:0	2552	5.0
95:5	3016	4.9
90:10	3264	4.7
85:15	3403	4.1

Polymers – New Materials – Composites

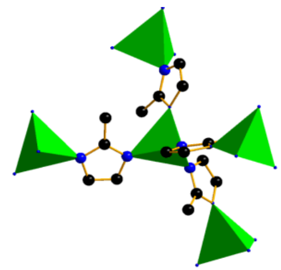
Sandia National Laboratories

MOF-Polymer Composites for Dielectrics

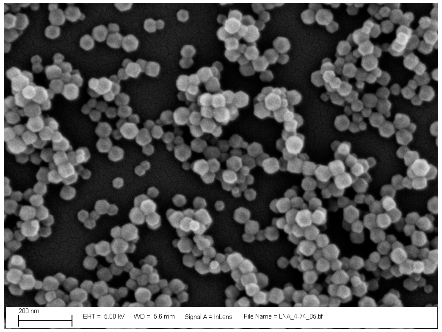
Leah Appelhans

ZIF-8/PVDF-HFP Composites

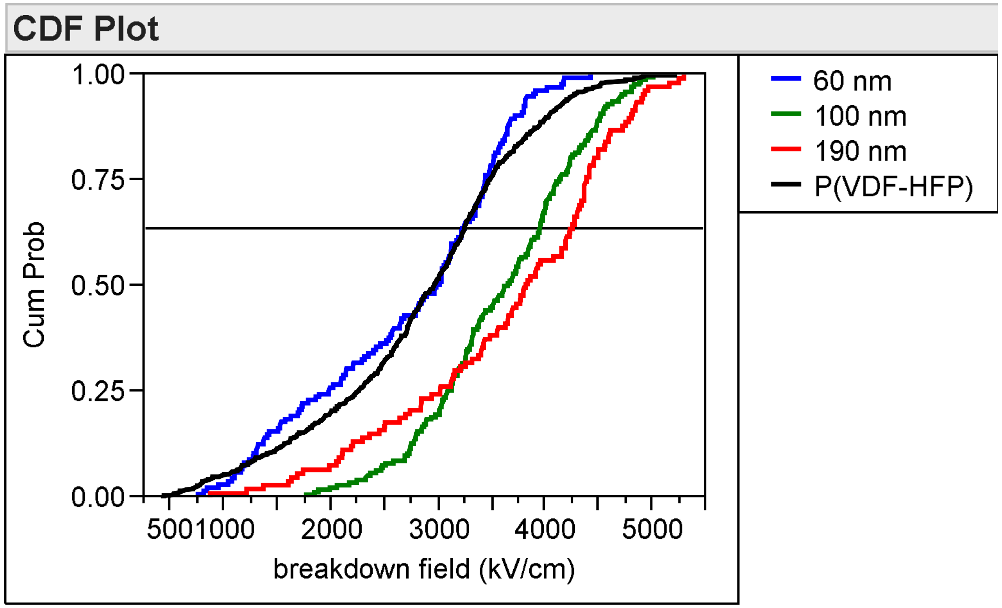
Permittivity of composites decreases due to low-κ filler, but breakdown strength shows particle-size dependent increase resulting in an overall increase in energy density.

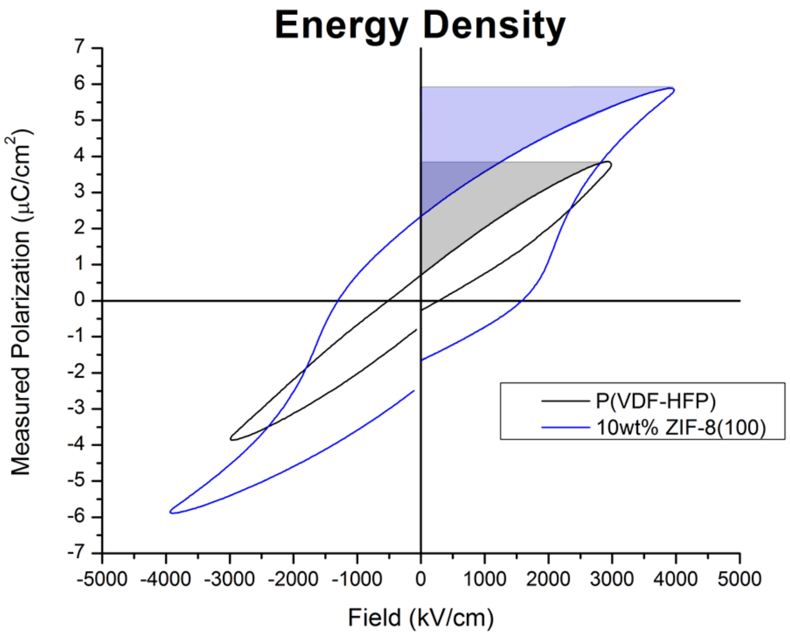


ZIF-8



Breakdown Strength





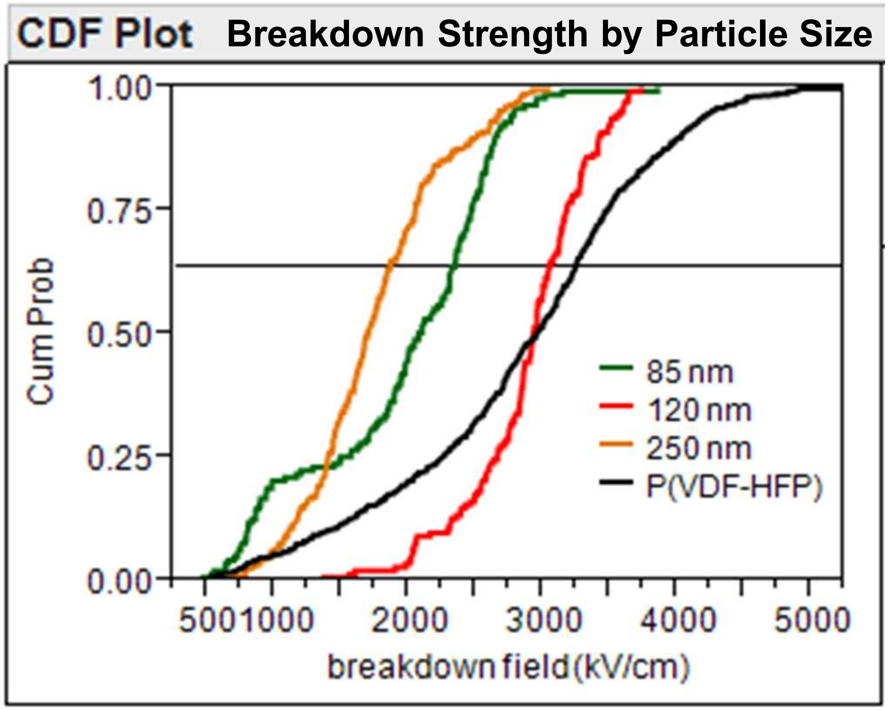
45% increase in E_d for composite

Polymers – New Materials – Composites

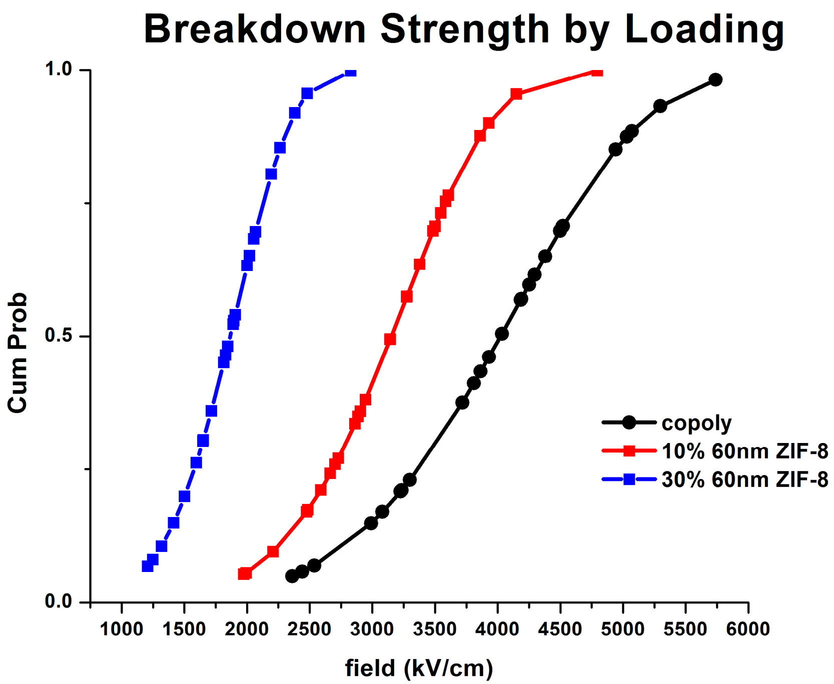
Sandia National Laboratories

Leah Appelhans

BaTar/PVDF-HFP Composites



ZIF-8/SPOW Composites

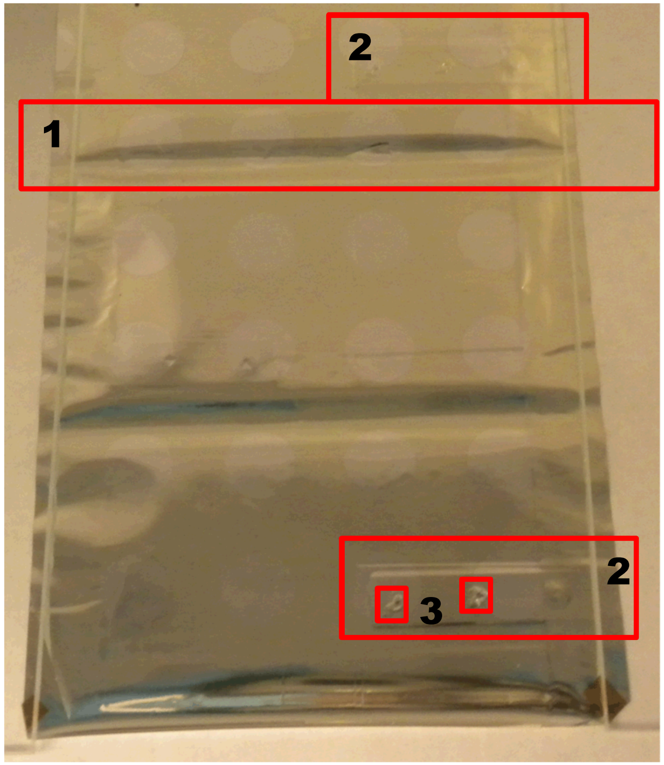


What is the origin of the particle size effect and how does it relate to mechanism?
What is the origin of increased breakdown strength?
Are breakdown *mechanisms* changed or only breakdown *strengths*, and how?
Are effects general or specific to one polymer/filler composite or family?
What/how can we learn from composites to *design* better materials?

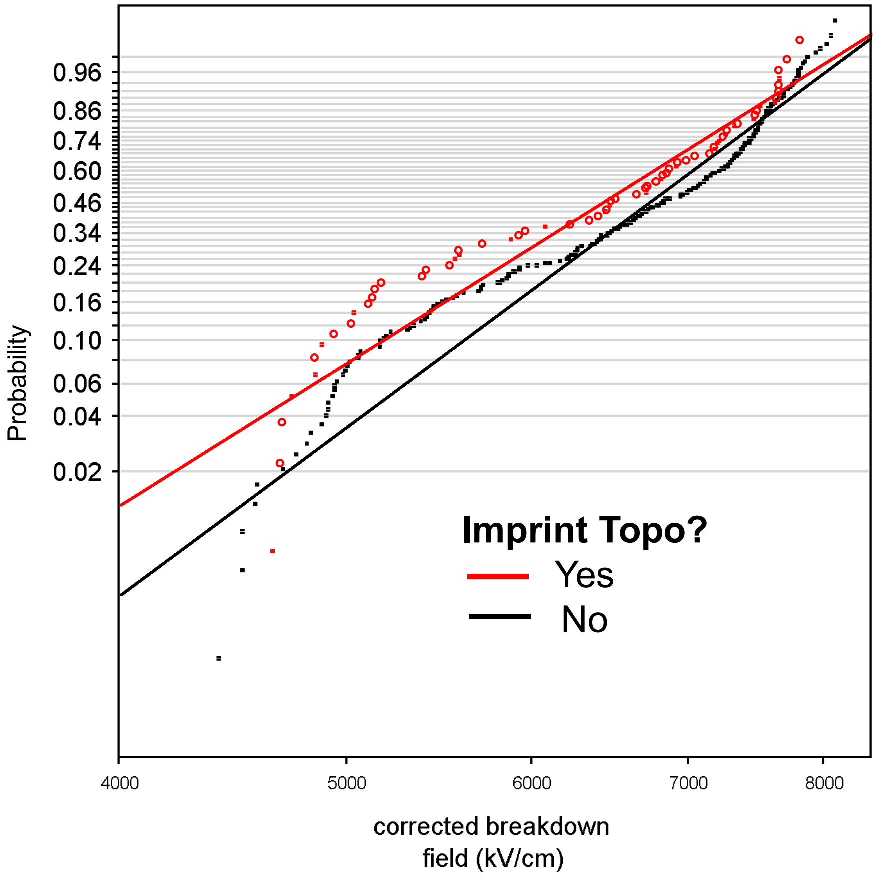
Polymers – Understanding Breakdown

Topography

Leah Appelhans



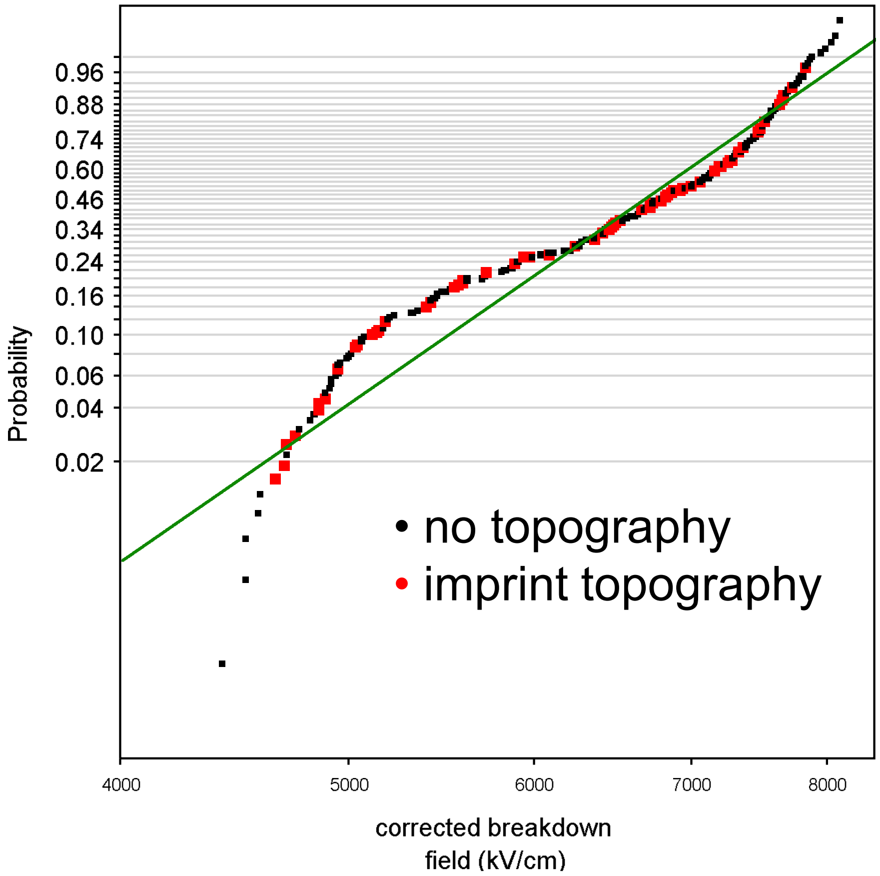
1) radius of curvature
2) lead imprint
3) lead imprint point

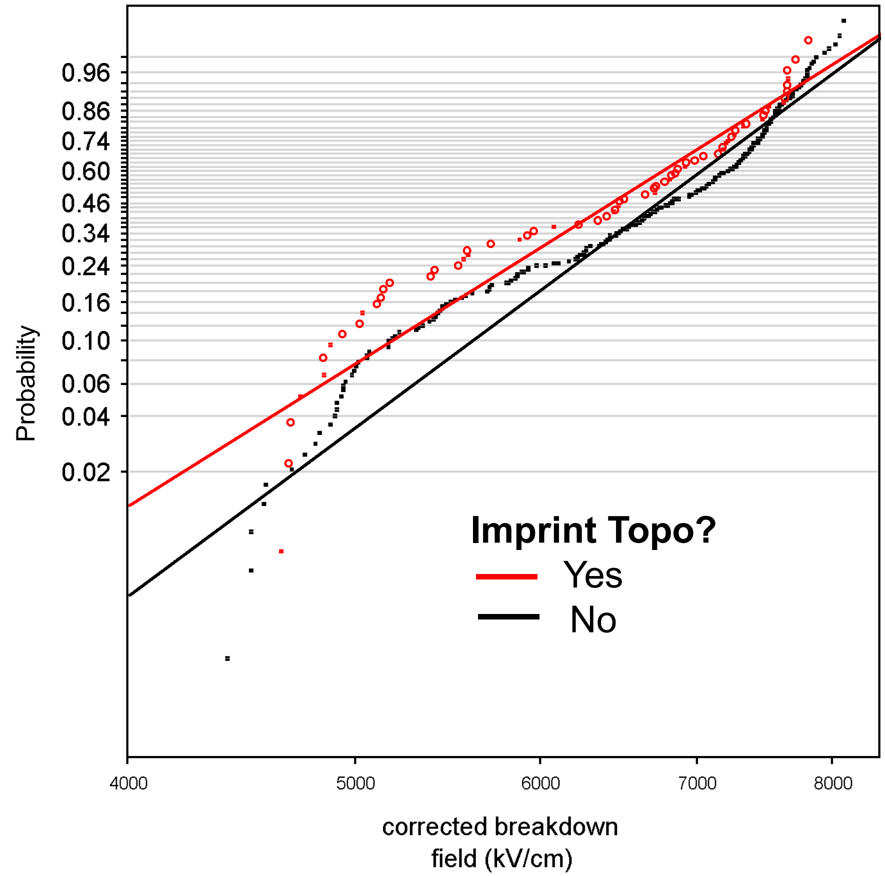


Polymers – Understanding Breakdown

Topography

Leah Appelhans



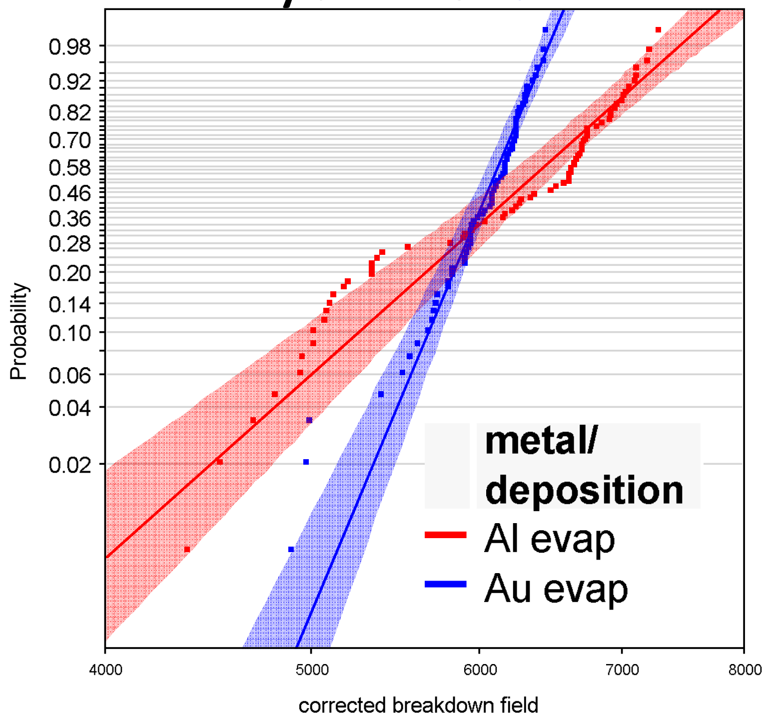


Polymers – Understanding Breakdown

Electrode Effects

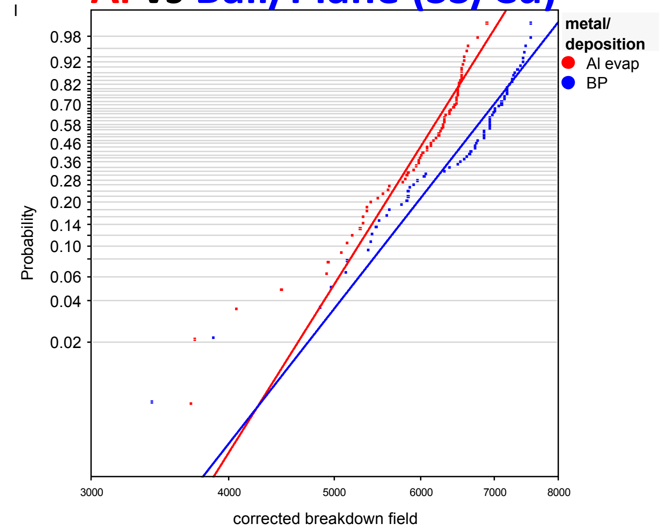
Leah Appelhans

Breakdown Strength
Mylar: Al vs Au

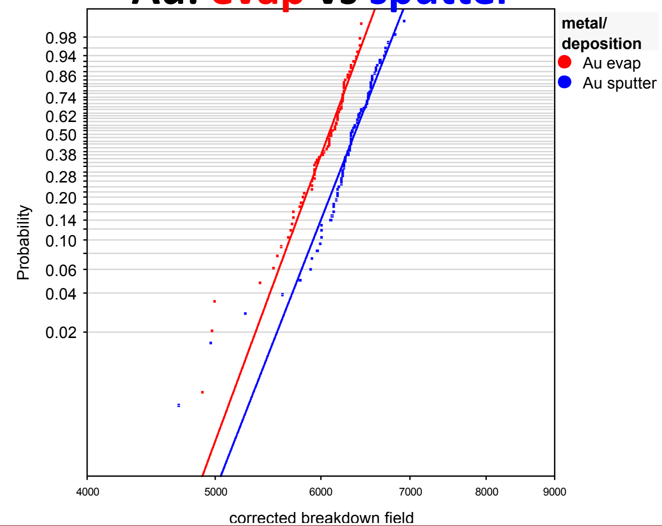


Electrode	Weibull α (kV/cm)	Weibull β
Al evap	6217	13.1
ball/plane (SS/Cu)	6833	10.5
Au evap	6146	27.2
Au sputter	6432	26.3

Al vs Ball/Plane (SS/Cu)



Au: evap vs sputter

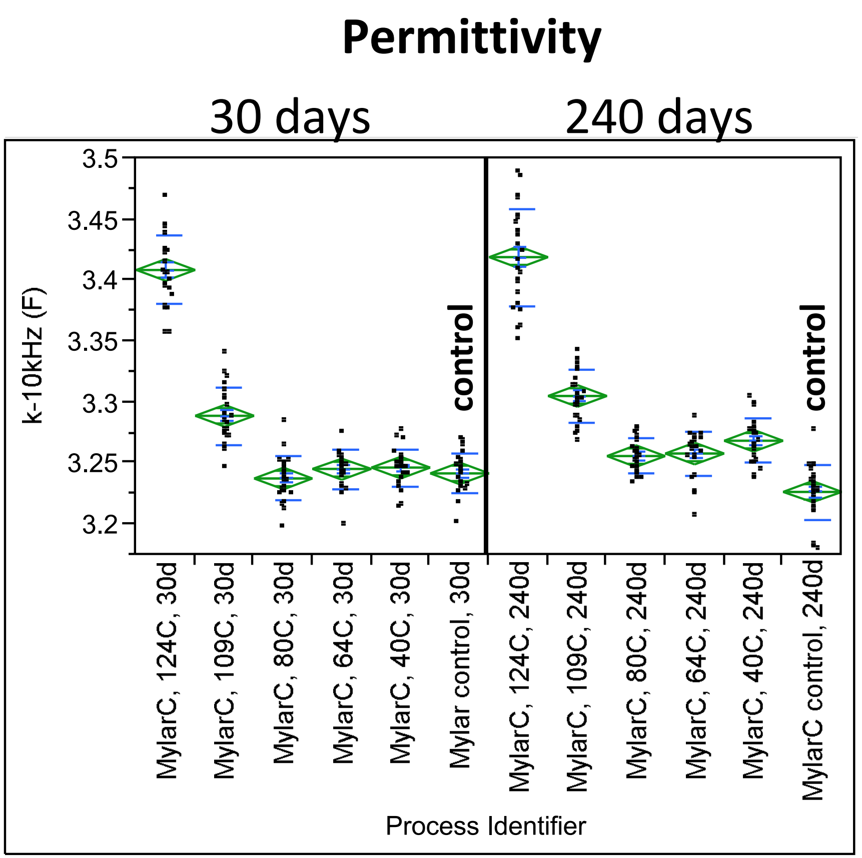


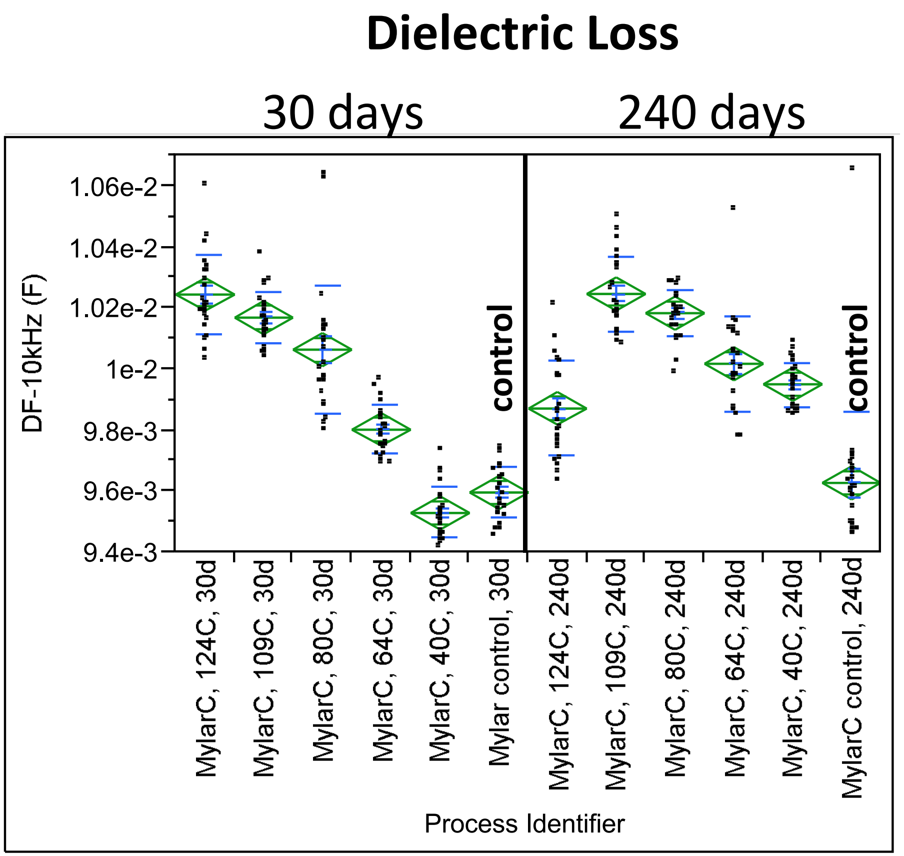
Polymers – Understanding Breakdown

Materials Reliability and Aging

Leah Appelhans

Mylar™ C, ½ mil





Polymers – Understanding Breakdown

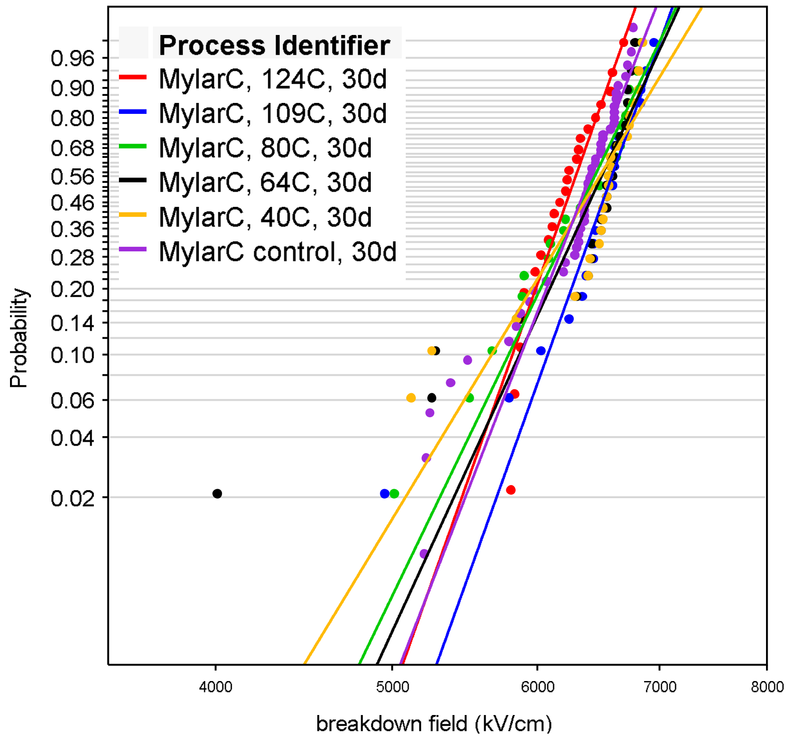
Materials Reliability and Aging

Leah Appelhans

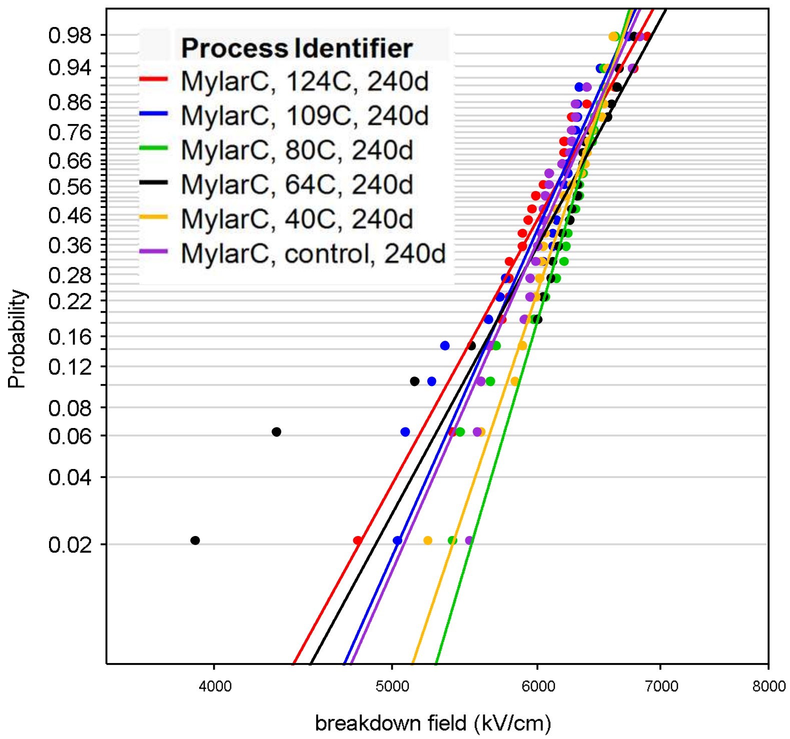
Mylar™ C, ½ mil

Dielectric Breakdown Strength

30 days



240 days

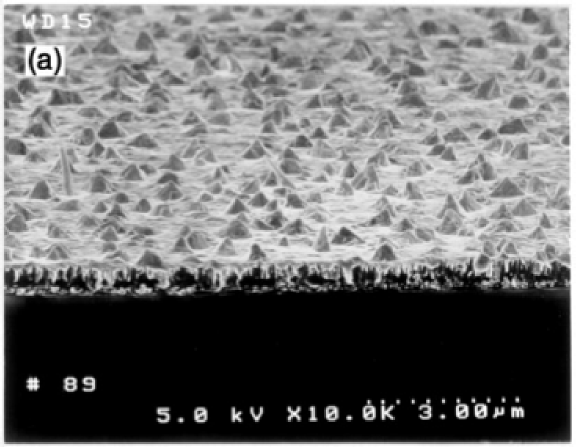


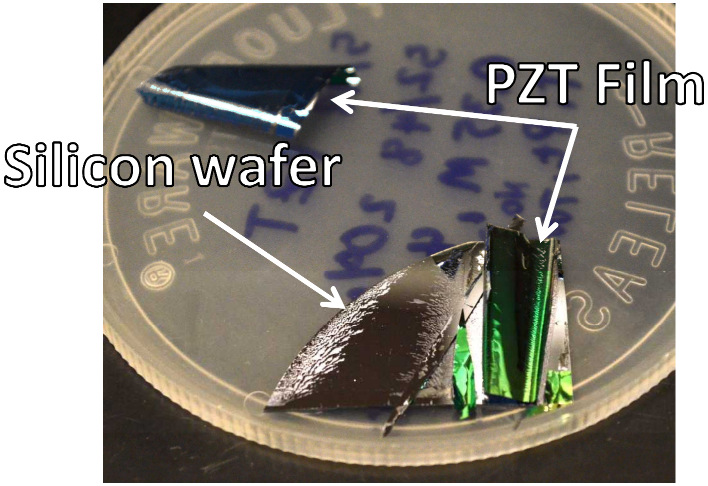
Ceramics – Materials Optimization

Jon Ihlefeld

Solution Chemistry, Substrate, and Processing Effects on the Chemical Heterogeneity in PZT Films

Pt/Ti remains state of the art in platinized silicon:





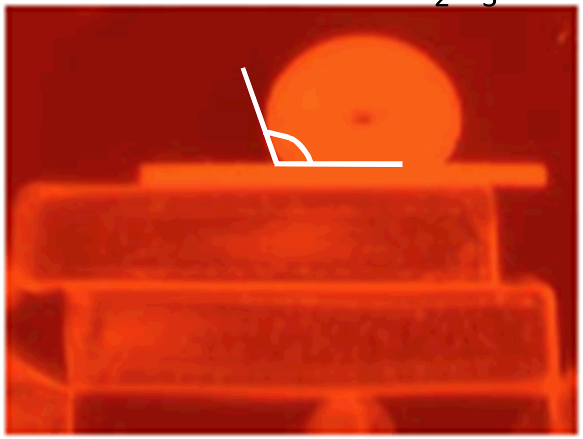
- Titanium ‘adhesion’ layers by far the most common
  - Adhesion of Pt/ZrO_2 and Pt/TiO_2 not as good as Pt/Ti
- Titanium expands upon oxidation causing hillocks
- Adhesion layer still fails with large temperature swings (>700°)
- ***>20 years of research and small improvements made***
- ***There must be a better solution!***

Al-Shareef, *et al.*, *J. Mat. Research*, **12** (2), 347-354 (1997)

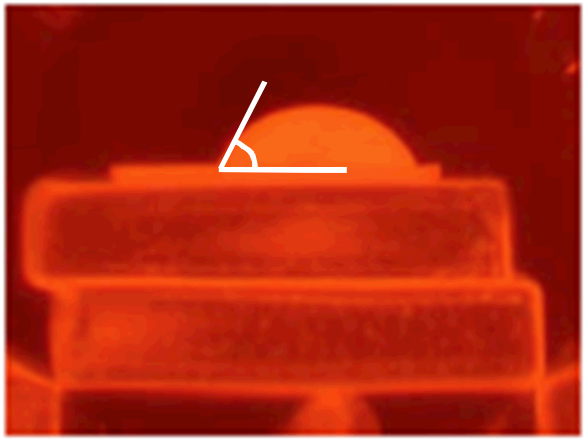
Metal Wetting and Adhesion

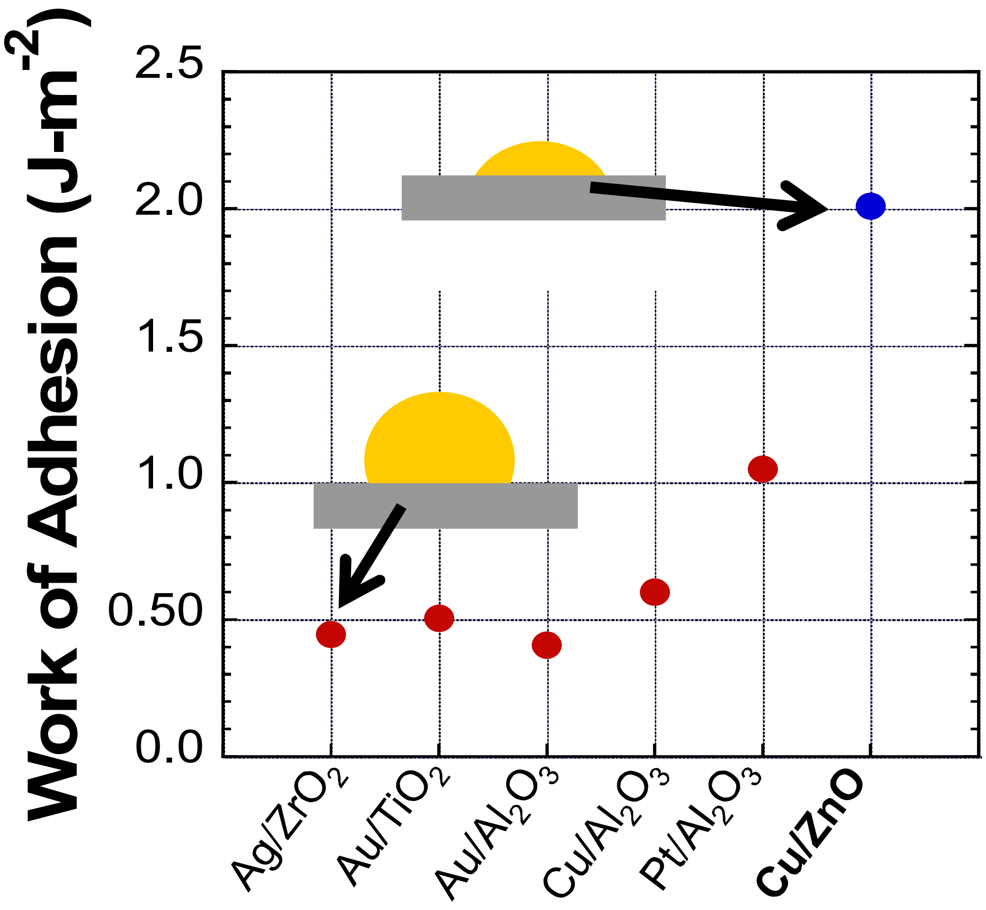
Jon Ihlefeld

Molten Cu on Al_2O_3



Molten Cu on ZnO



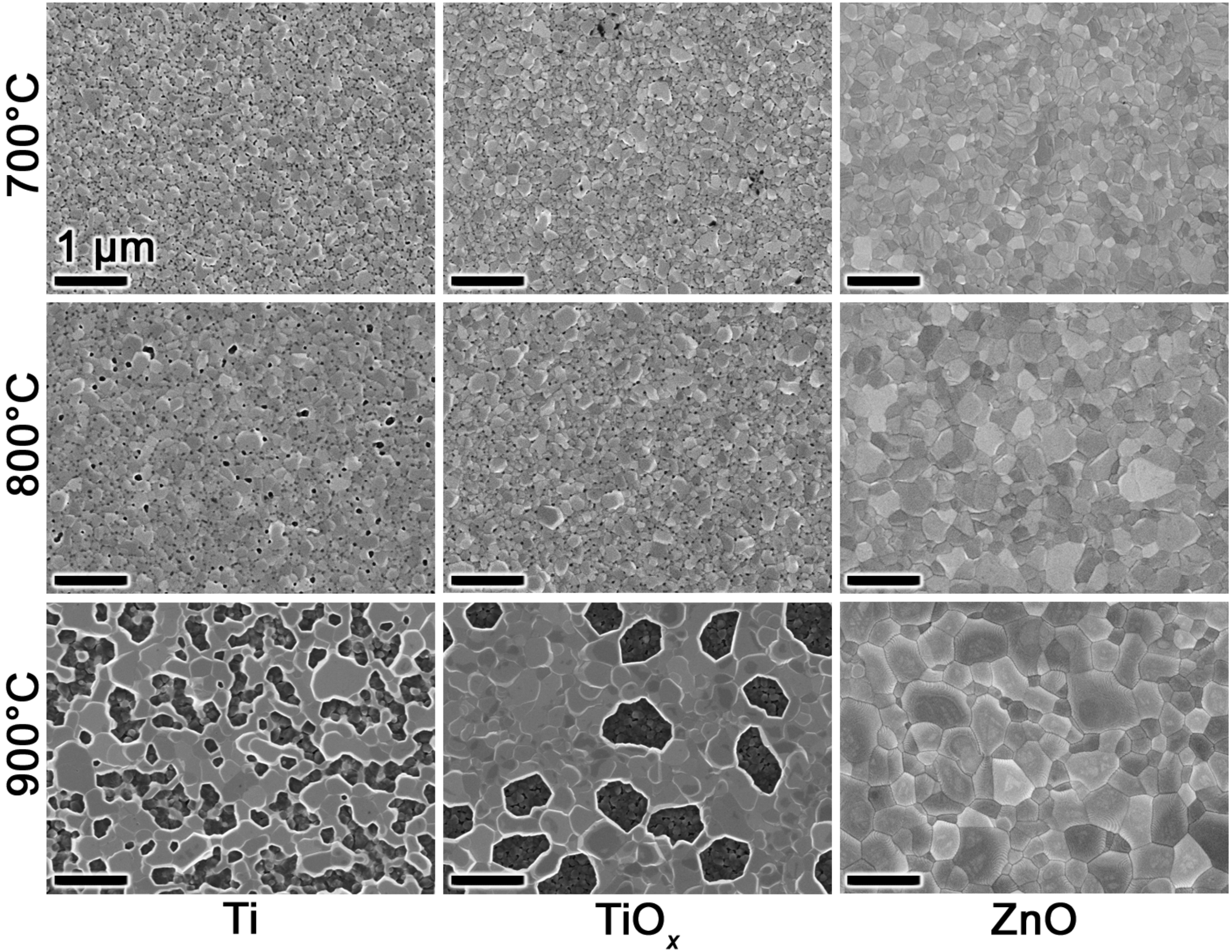


Can we use lessons learned from wetting experiments to guide selection of improved adhesion layers?

Laughlin, B. Ph.D. Dissertation, NCSU 2006

Electrode Temperature Stability

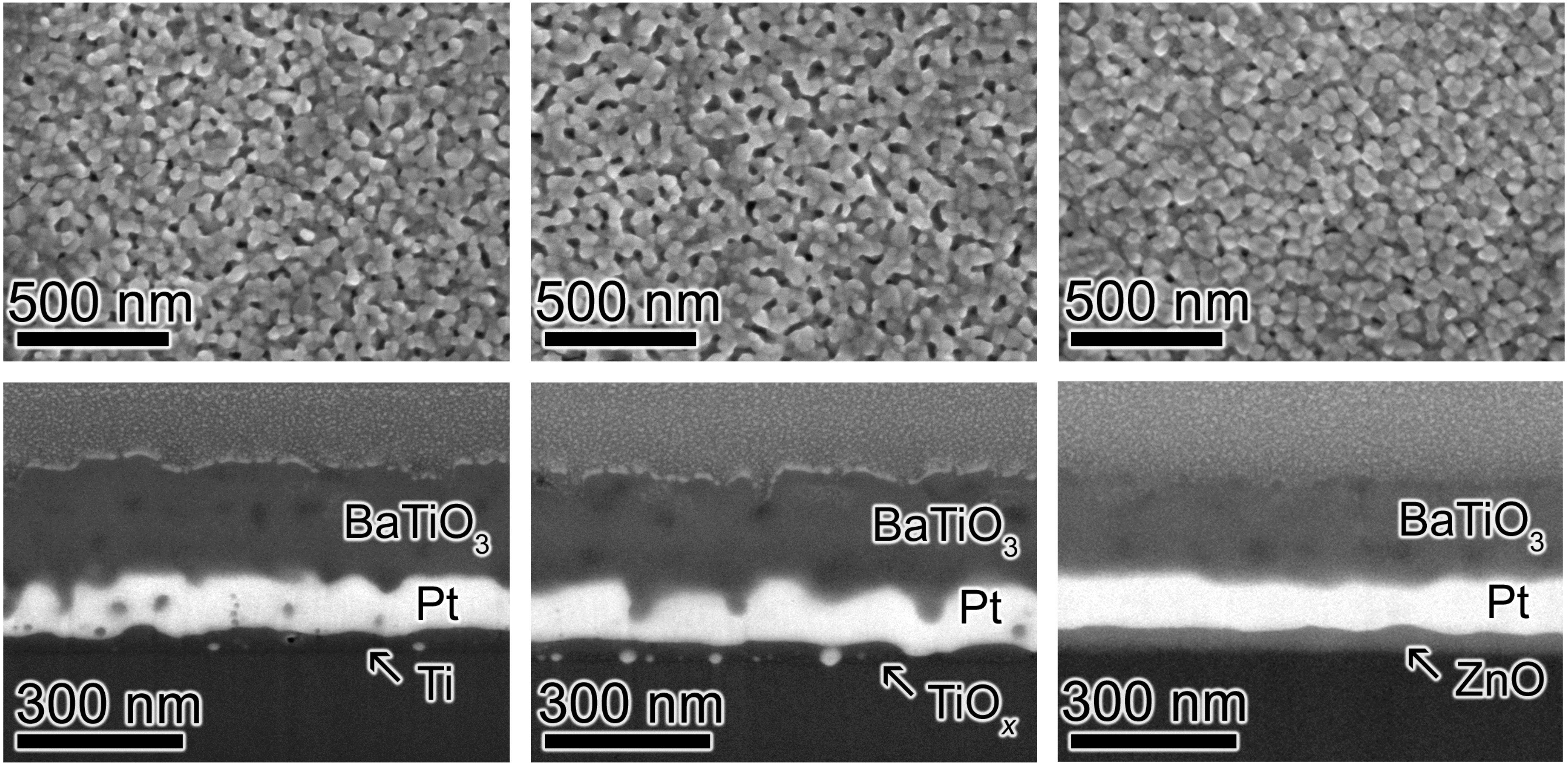
Jon Ihlefeld



C.T. Shelton and J.F. Ihlefeld *et. al.*, *Adv. Funct. Mater*. **22**, 2295-2302 (2012)

Topography and microstructure

Jon Ihlefeld

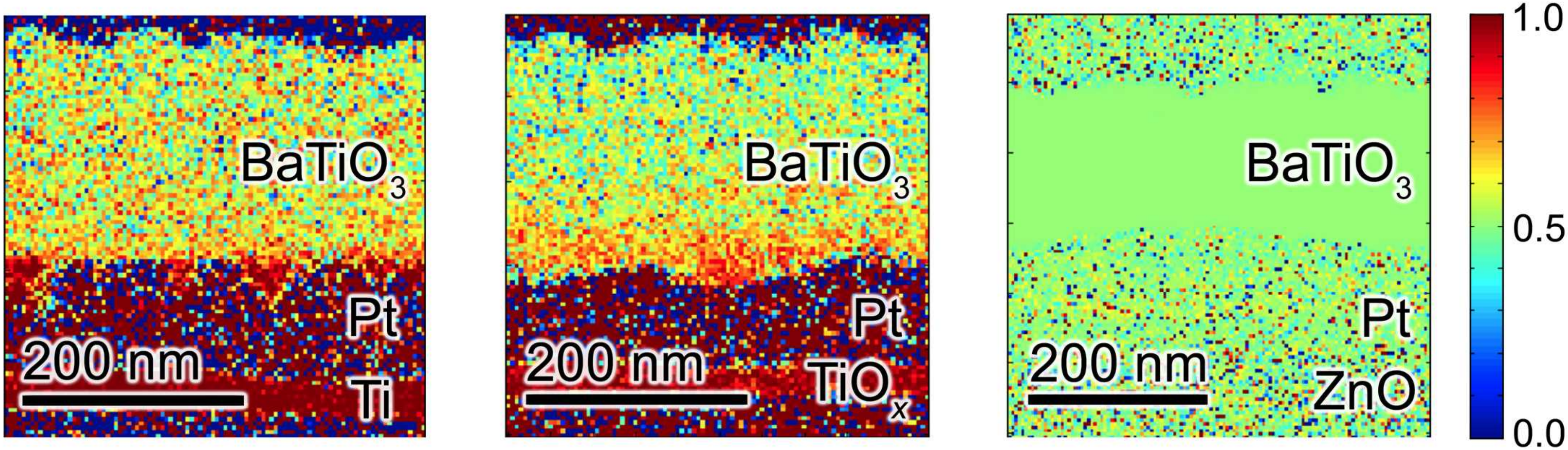


C.T. Shelton and J.F. Ihlefeld *et. al.*, Adv. Funct. Mater. **22** 2295 (2012)

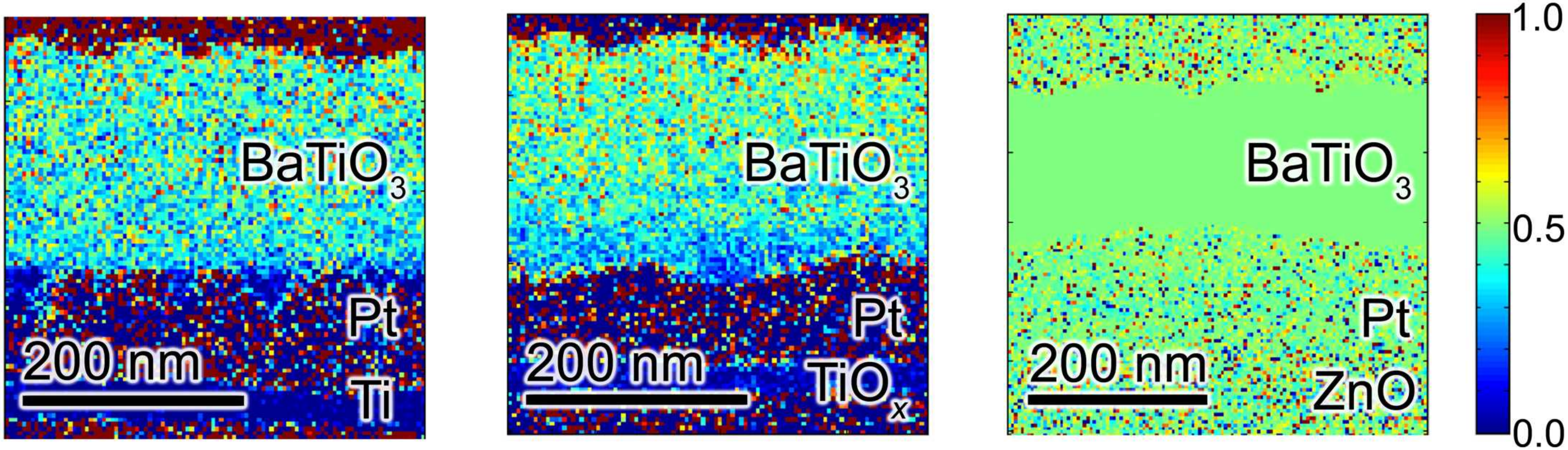
$BaTiO_3$ Compositional Analysis: No Gradient for Pt/ZnO Film

Jon Ihlefeld

Titanium Distribution



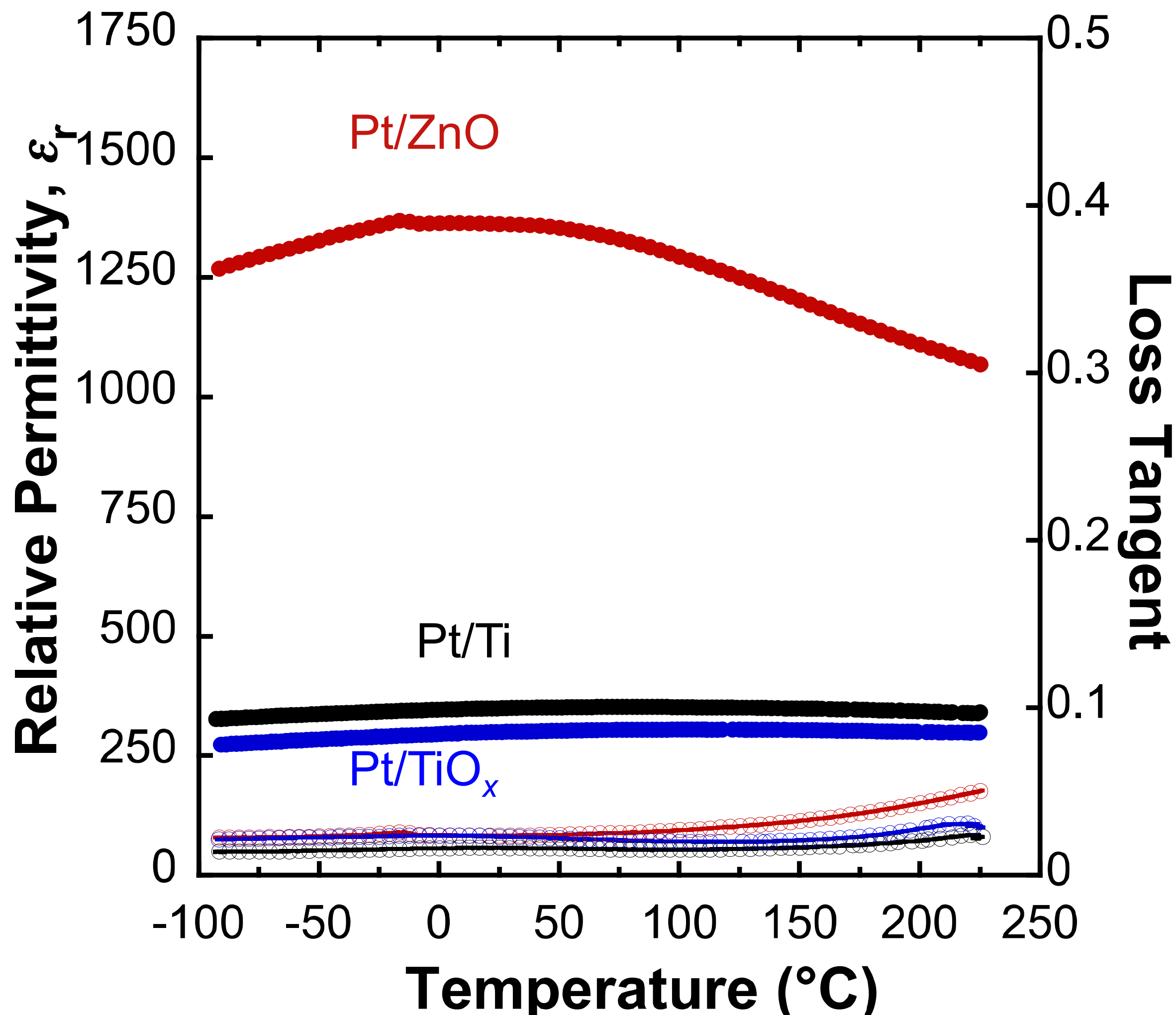
Barium Distribution



$BaTiO_3$ Dielectric Properties: Significant Enhancement on Pt/ZnO

Sandia National Laboratories
Jon Ihlefeld

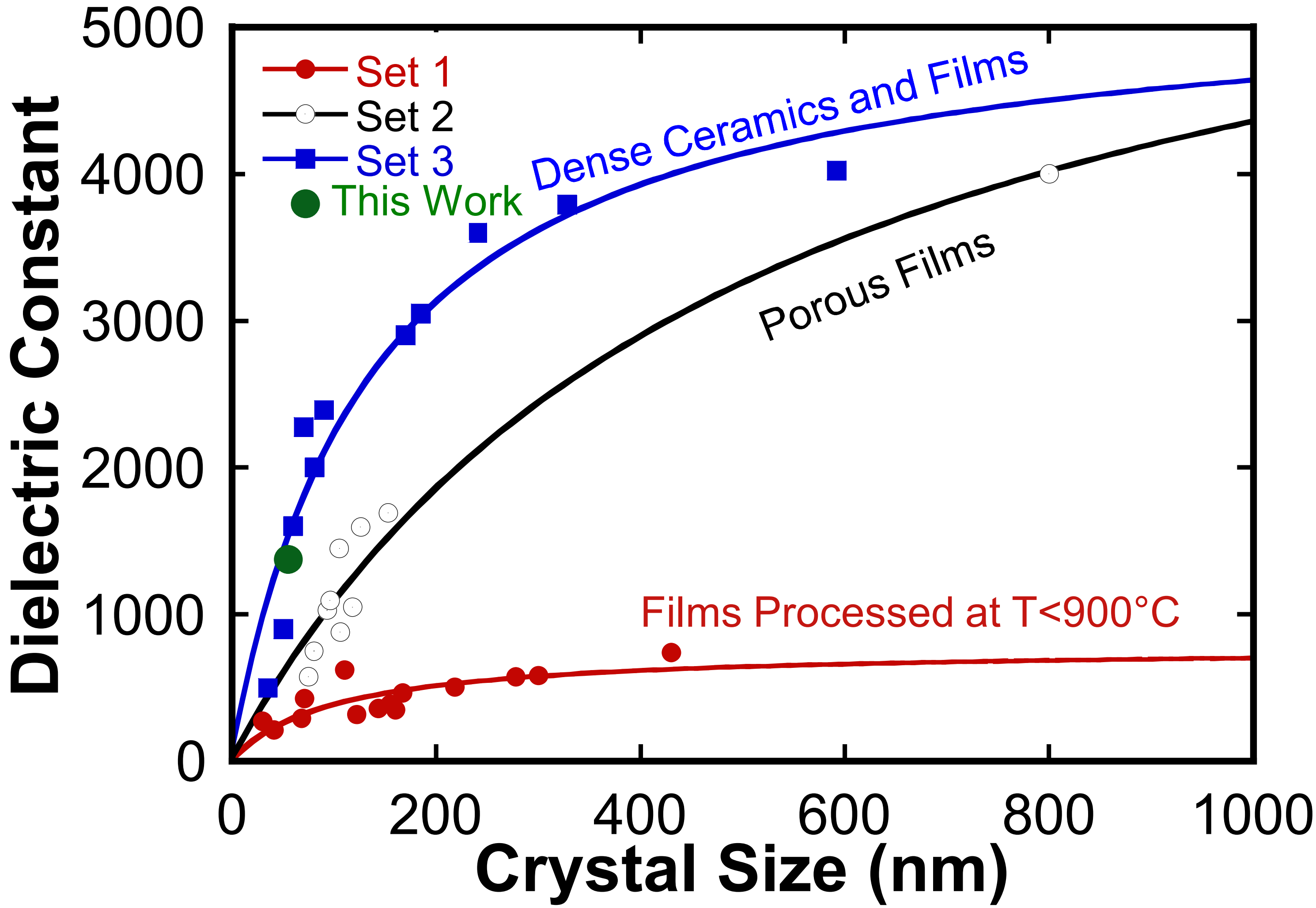
- Ti- and TiO_x-buffered films actually survived
- $BaTiO_3$ on Pt/ZnO substantially outperforms other substrates
- Microstructure nearly identical: Why such a disparity?
- What about other Ferroelectrics?



C.T. Shelton and J.F. Ihlefeld *et. al.*, Adv. Funct. Mater. **22** 2295 (2012)

$BaTiO_3$ Scaling Effects

Jon Ihlefeld



First known $BaTiO_3$ film with bulk properties on Si

Plot adapted from Aygün *et. al. J. Appl. Phys.* (2011)

Ceramics – Relaxor Capacitors

Harlan Brown-Shaklee

Reliable high capacitance multilayer capacitors are required for grid surety

1. Develop MLCCs based on the $Bi(Zn_{0.5}Ti_{0.5})O_3$ –$BaTiO_3$ system that exhibit favorable voltage tuning behavior

2. Study the dielectric relaxation in frequency *and* time domains

   -Does a fast discharge pulse release the energy stored by a slow charge?

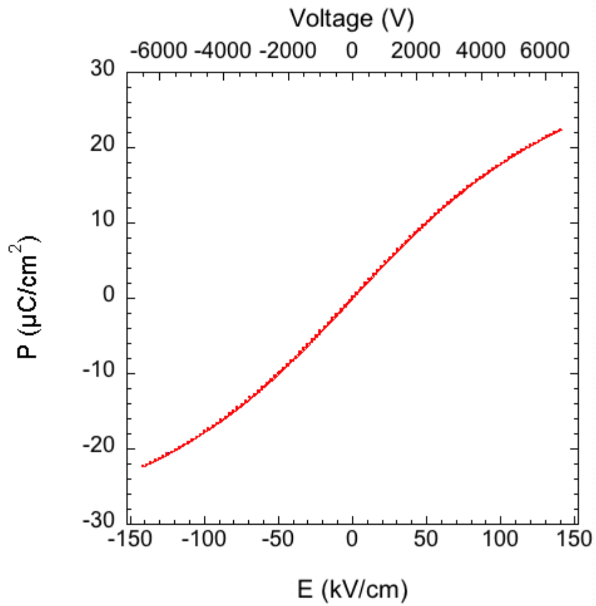
   a) Low piezo response

   b) Forward Fourier transform reveals dominant frequency components from a time domain signal

   c) Superposition does not hold for circuits containing non-linear capacitive elements

Energy densities of >1.3 J/cc have been demonstrated

Sandia National Laboratories
Harlan Brown-Shaklee



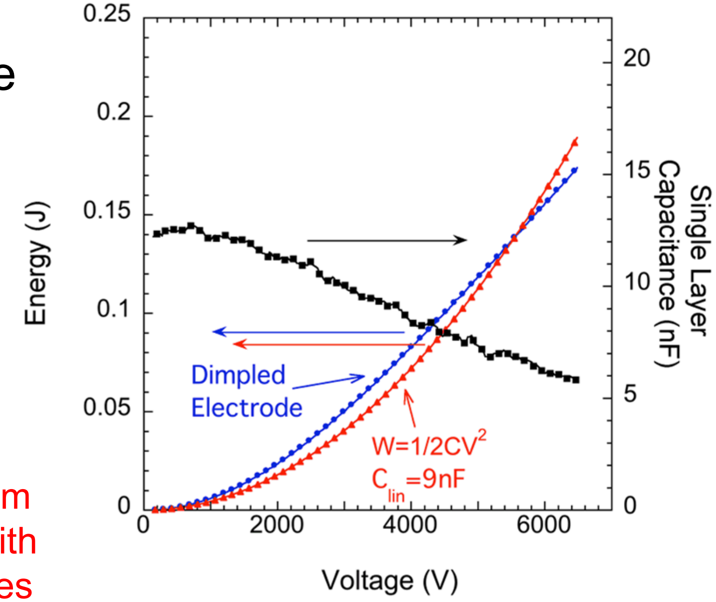
Dimpled Electrode

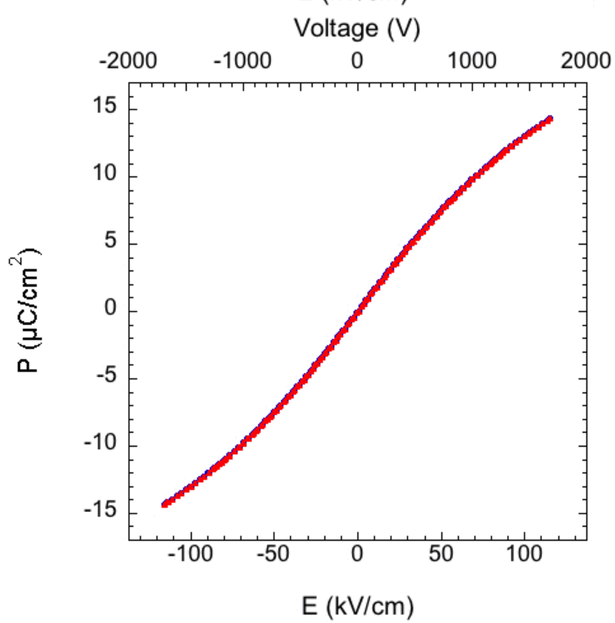
t=460μm
A=2.77cm²
v=0.127cm³

$E/v_{100kv/cm}$=0.82 J/cm³

$E/v_{140kv/cm}$=1.35 J/cm³

Breakdown >230 kV/cm have been achieved with smaller sample volumes

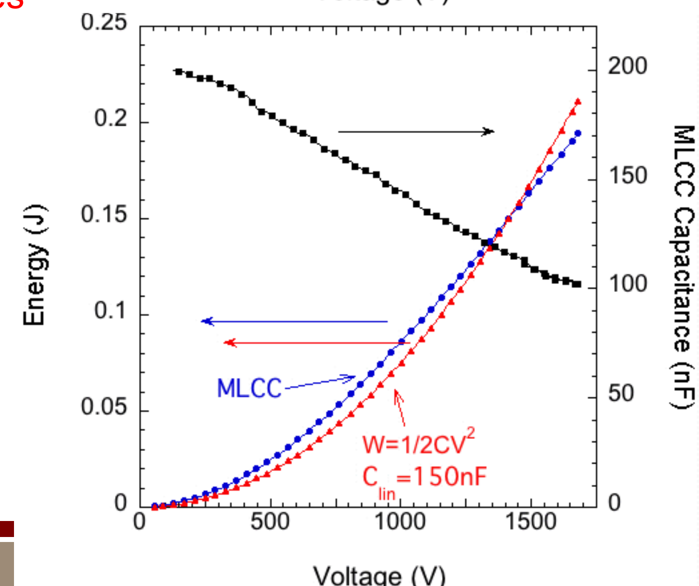




200nF MLCC

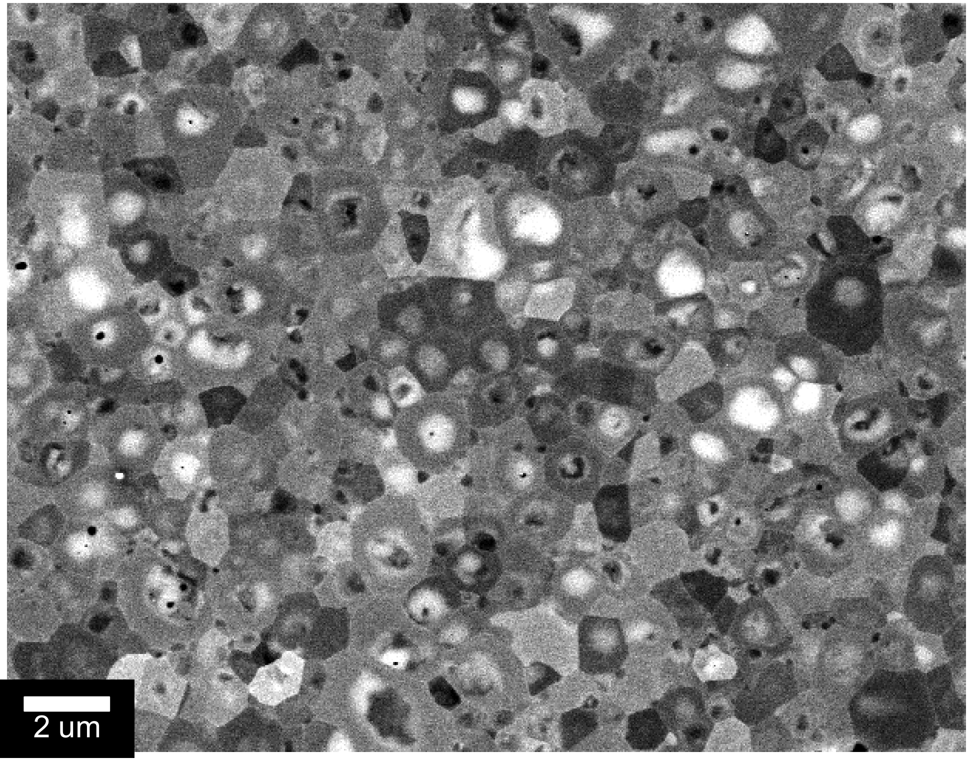
t=145μm
A=18.1cm²
v=0.262cm³

$E/v_{100kv/cm}$= 0.64J/cm³



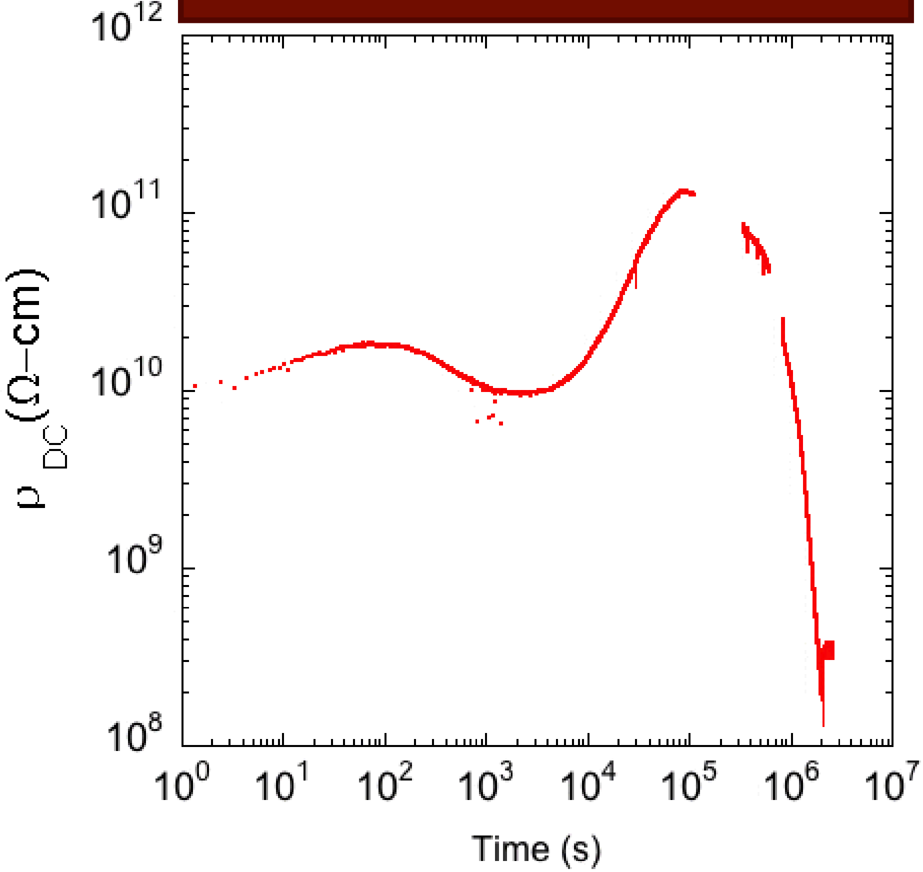
Understanding long-term reliability

Harlan Brown-Shaklee



How does the inherent microstructural non-uniformities improve the performance during aging?

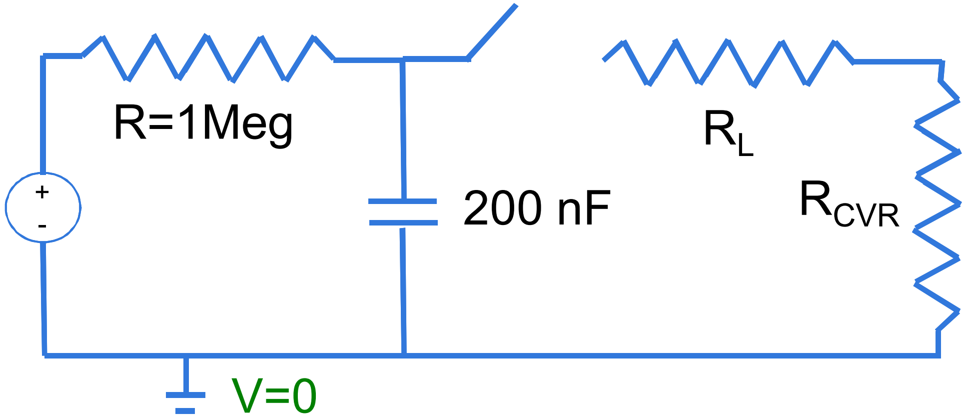
Dielectric stress in disc capacitor held constant at 250°C

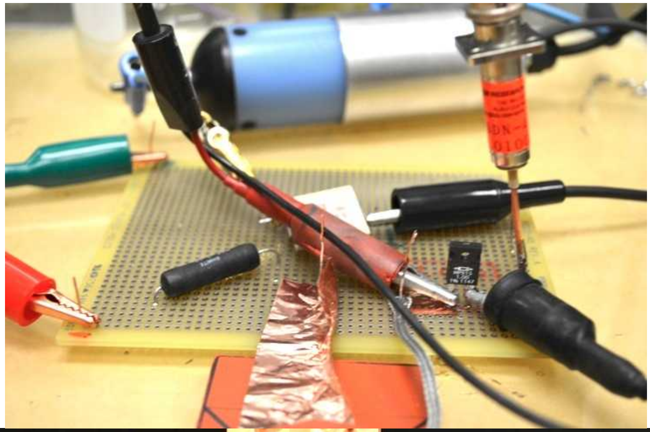


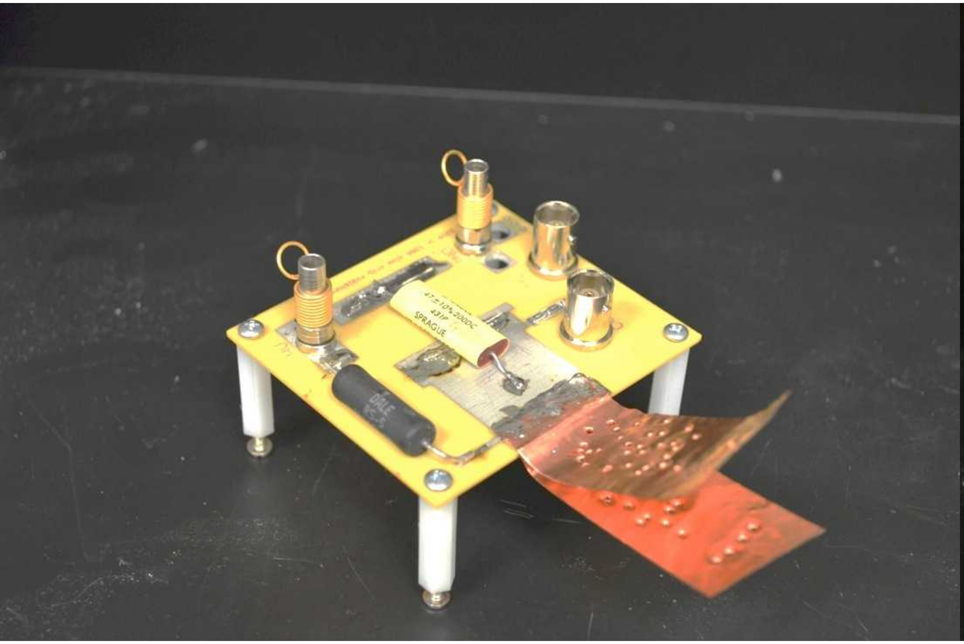
We are interested in MLCCs for power electronics and pulse discharge

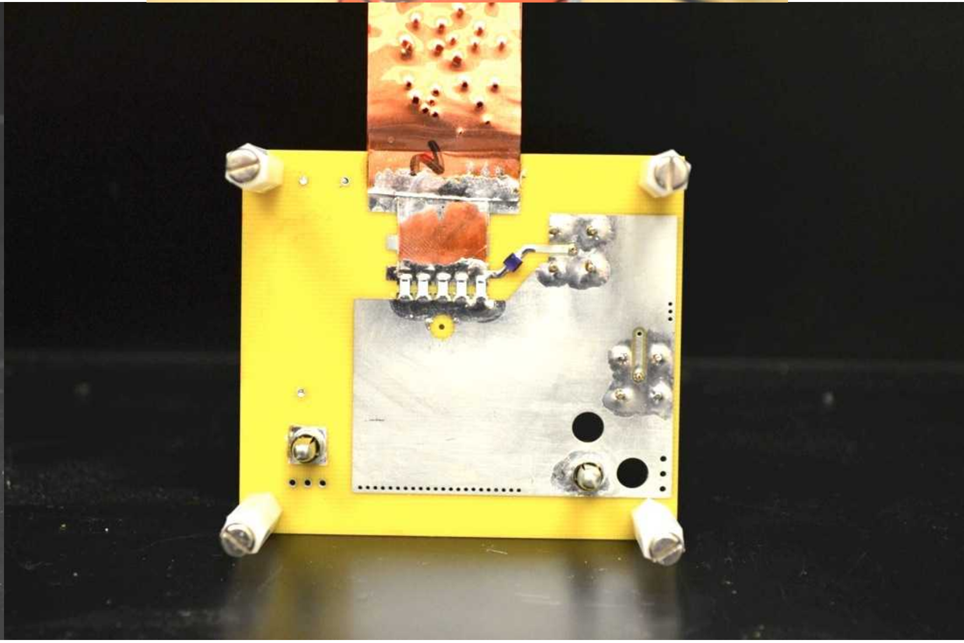
Sandia National Laboratories
Harlan Brown-Shaklee

Most measurements we make are in frequency domain but pulse discharge occurs in the time domain…



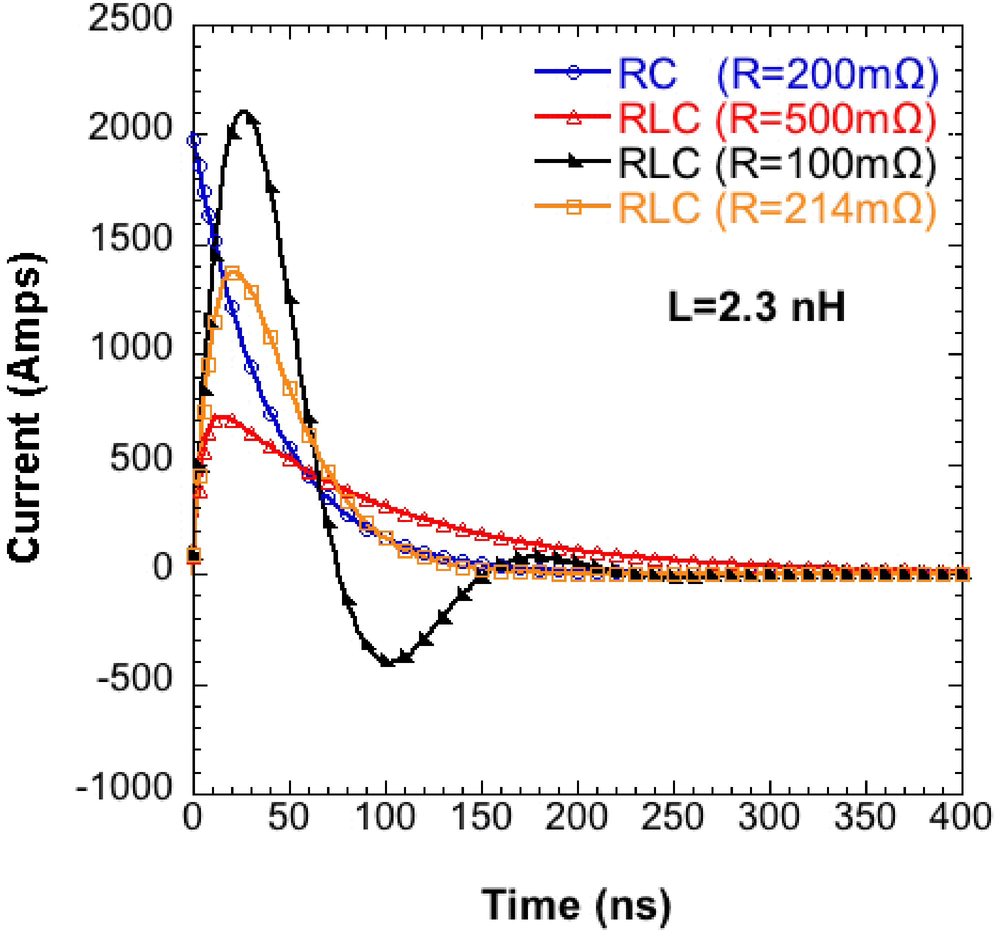






Capacitors can be charged and discharged using RC or RLC circuits

Harlan Brown-Shaklee



$$i(t)_{RC} = \frac{V_0 e^{\frac{-t}{RC}}}{R_{load}}$$

$$i(t)_{RLC-OD} = \frac{V_0}{L\omega_2} e^{\left(-\frac{Rt}{2L}\right)} \sinh(\omega_2 t)$$

$$i(t)_{RLC-UD} = \frac{V_0}{L\omega_1} e^{\left(-\frac{Rt}{2L}\right)} \sin(\omega_1 t)$$

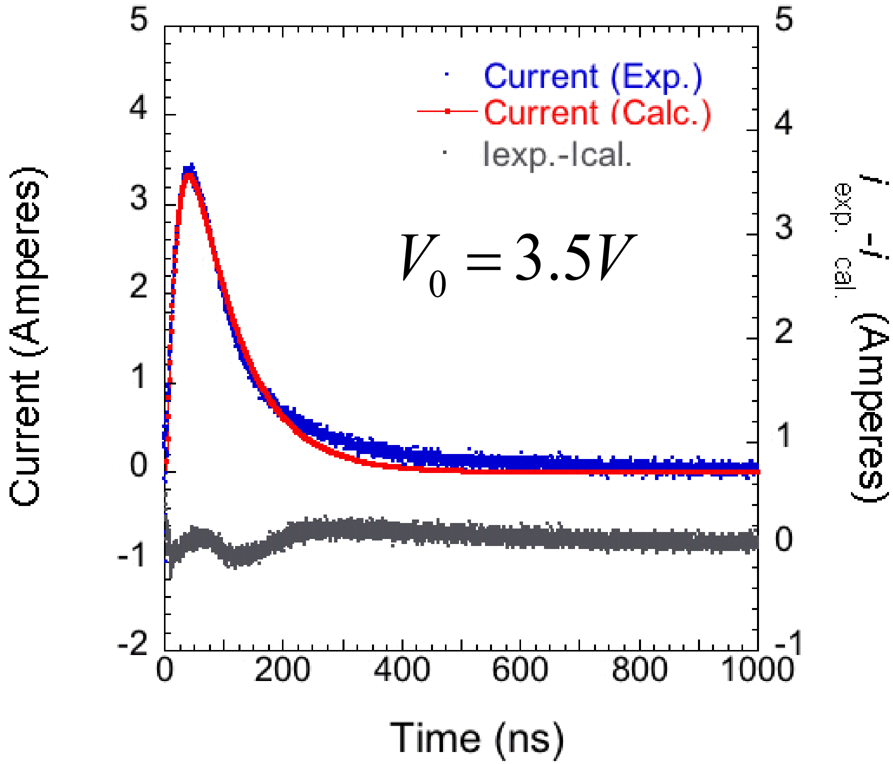
$$i(t)_{RLC-CD} = \frac{V_0 t}{L} e^{-\omega_0 t}$$

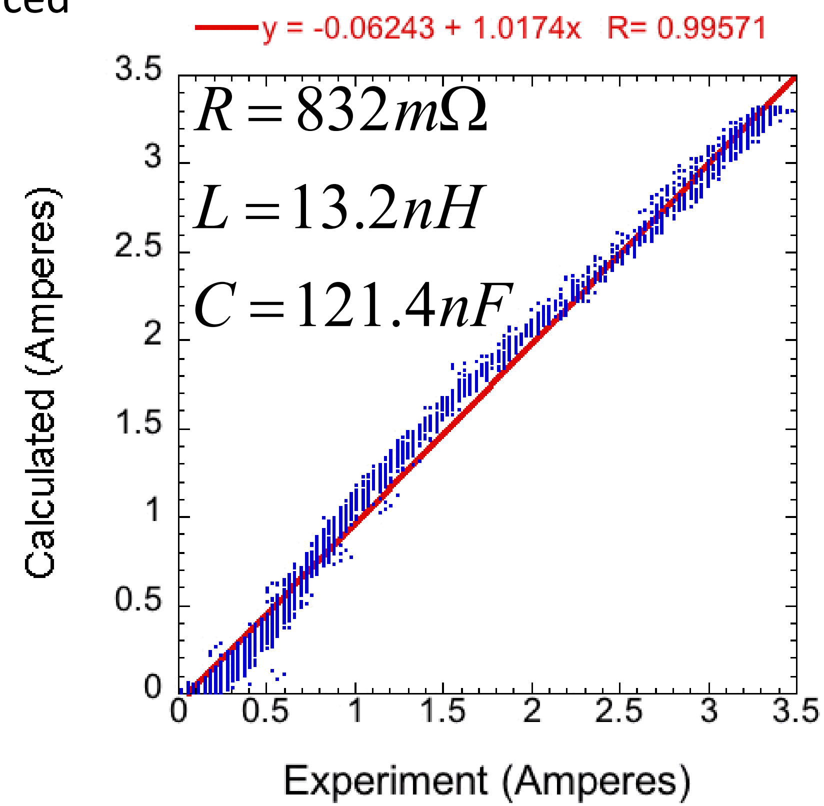
For high C and fast discharge, one encounters circuit inductance which requires better circuit design

Testing relaxor MLCC's for pulse discharge

Harlan Brown-Shaklee

Characteristic underdamped waveform was produced



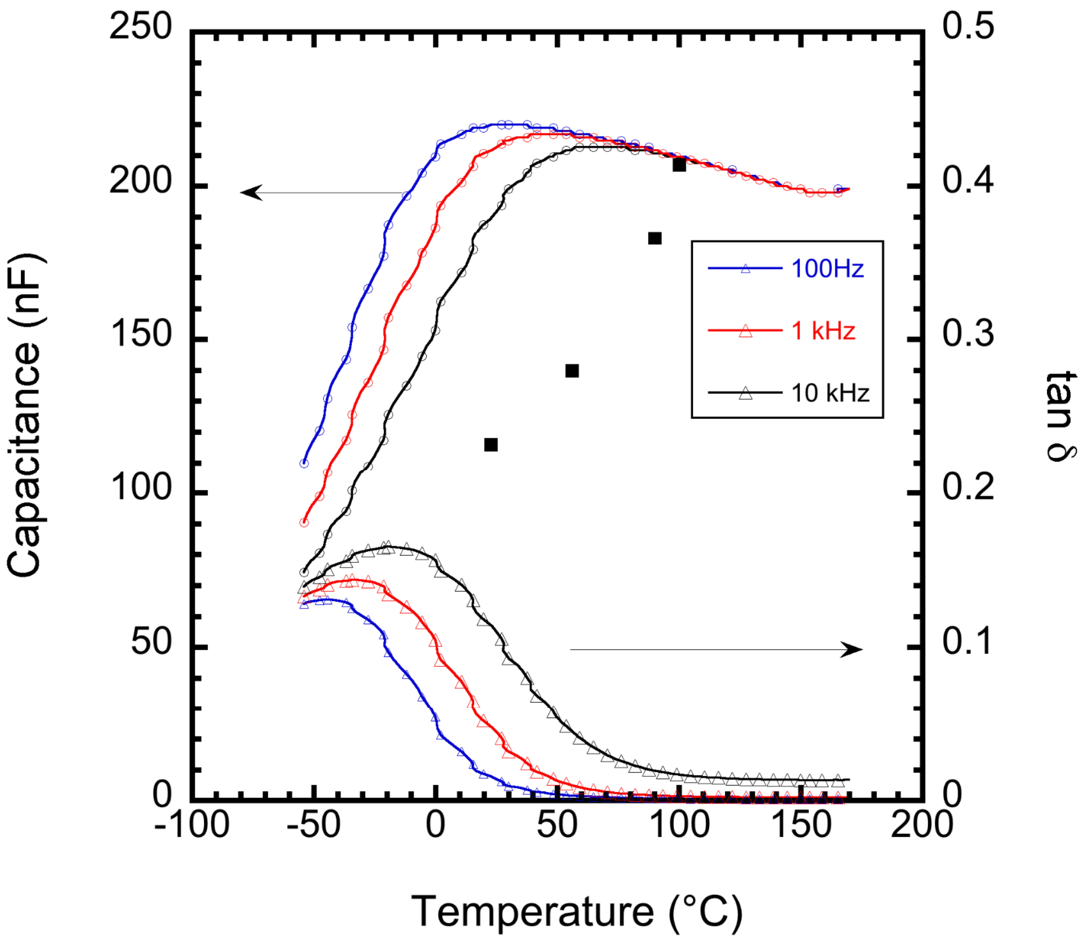


The circuit with the ceramic MLCC has lower inductance (form factor) but higher resistance than the polymer capacitor

The calculated capacitance is ~50% of what was measured at 100Hz

Dielectric relaxation was also shown at elevated temperatures

Frequency Domain



Time Domain

Temperature (°C)	Capacitance (nF)
22.5	116
56	140
90	183
100	207

$$\omega_0 = \frac{1}{\sqrt{LC}}$$

Dielectrics Research at Sandia

- Wide Bandgap Semiconductor Devices
- Materials for Pulse Forming Networks (10^1-10^8 amp systems)
- Materials for Enhanced RF
- Metamaterials
- Sensors
- Optoelectronics
- Actuators, Resonators and Filters
- Ferroelectrics
- Multifunctional Materials

What Sandia Needs from CDP

- Understand failure (HALT) in existing materials
  - Dielectrics for WBG devices
  - Polymers and Polymer composites
  - Ferroelectrics, paraelectrics, and piezoelectrics