

Towards High Energy Density Glass Capacitors

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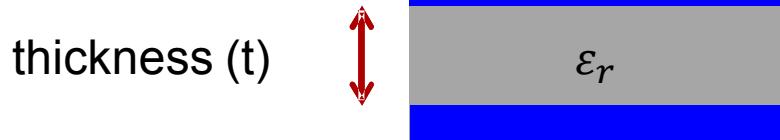
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Outline

- Linear Dielectrics as Energy Storage Devices
- Glass as a Dielectric Material
- Alkali Free Glass
 - Properties of Thinned Glass
 - Multi-layer Glass Capacitor
- Conclusions

Energy Density of Linear Dielectrics

Area (A) 

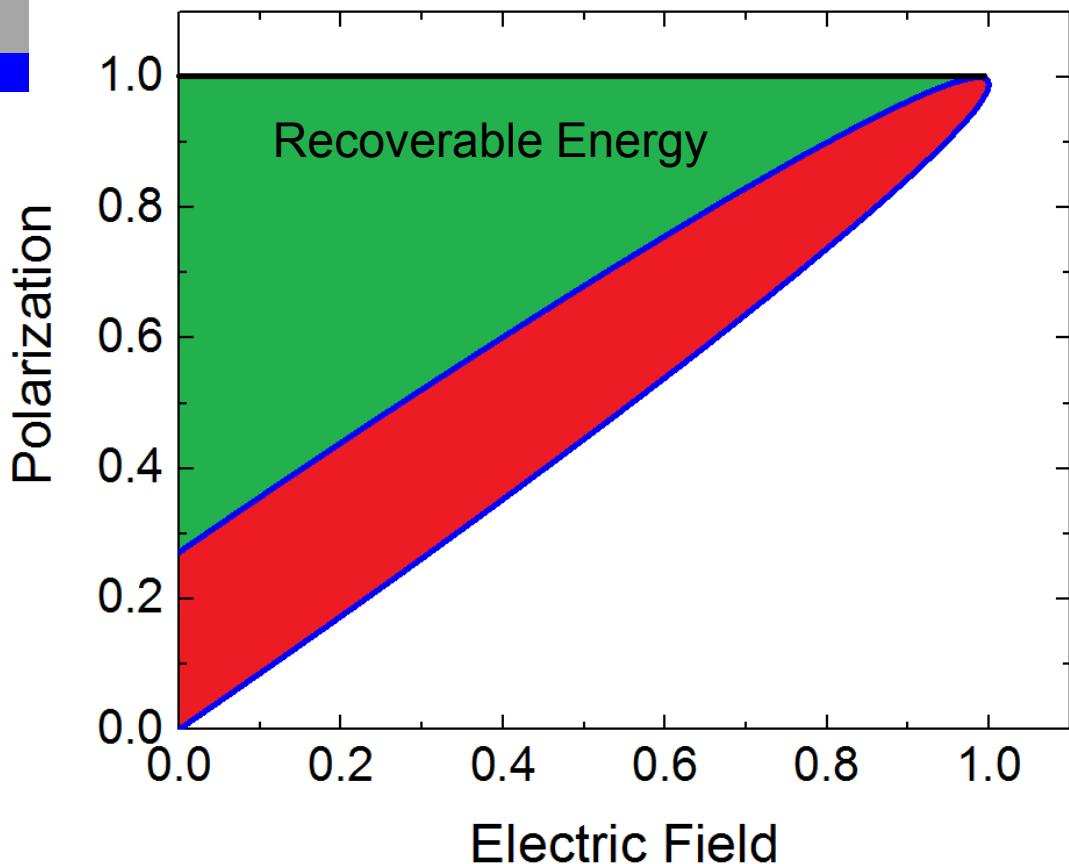


$$C = \epsilon_r \epsilon_0 \frac{A}{t}$$

$$W = \int P dE$$

$$W = \frac{1}{2} CV^2 = \frac{1}{2} \epsilon_r \epsilon_0 \frac{A}{t} V^2$$

$$U = \frac{\text{Energy}}{\text{Volume}} = \frac{1}{2} \epsilon_r \epsilon_0 E^2$$

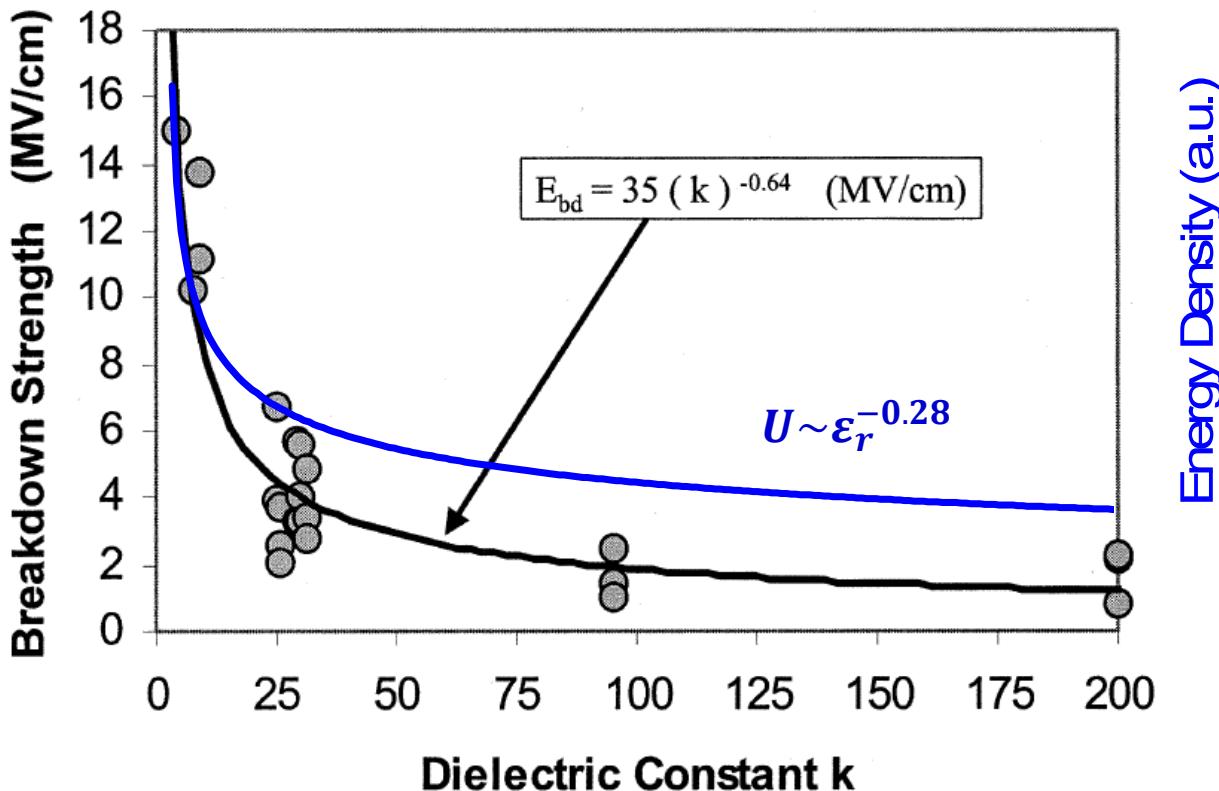


Trends in Breakdown Strength of Dielectrics

Larger gains from increasing breakdown strength

$$U = \frac{Energy}{Volume} = \frac{1}{2} \epsilon_r \epsilon_0 E^2$$

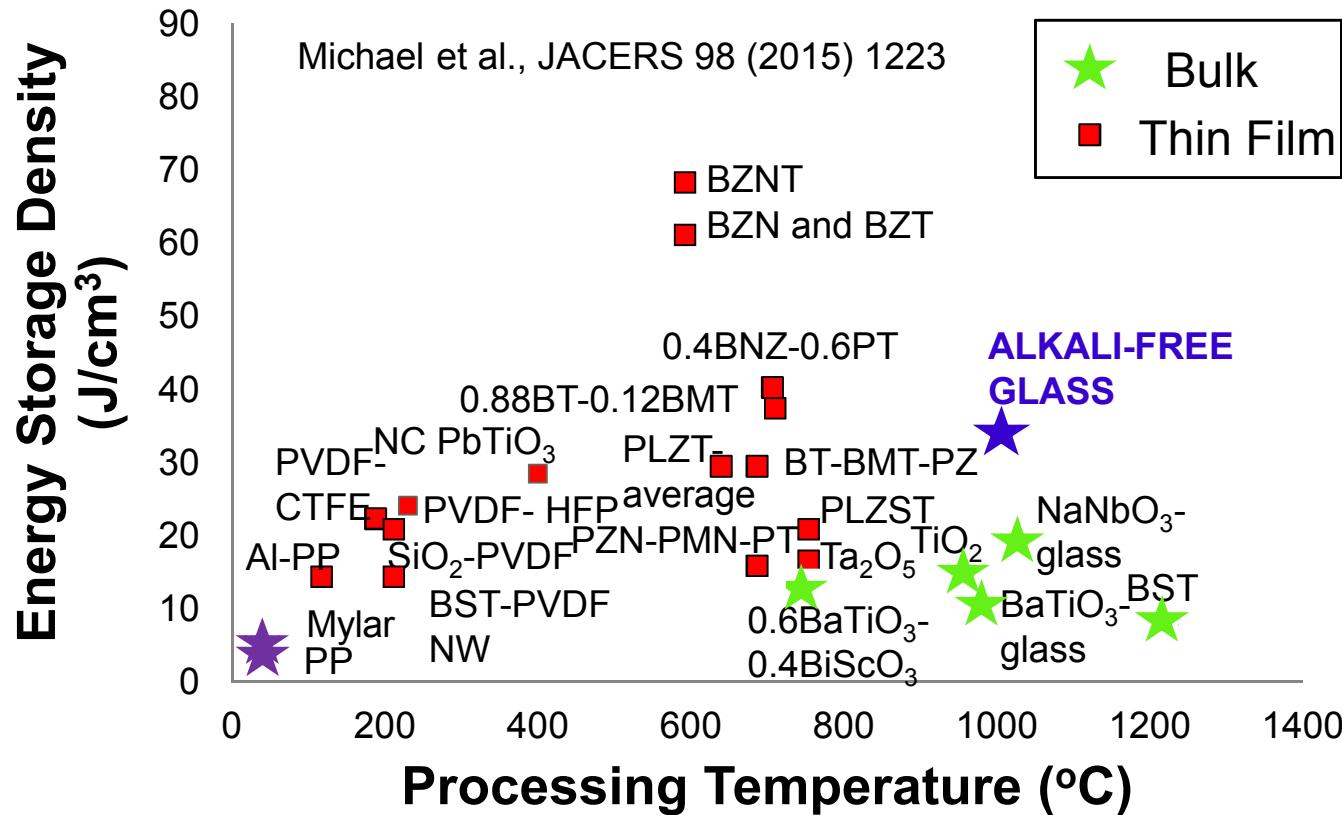
Limited value to tuning ϵ_r



McPherson et al. IEEE TED, 2003

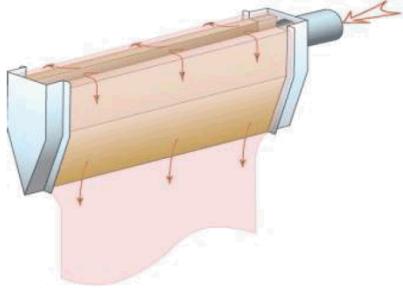
- Thermochemical modeling suggests link between polarizability and bond strength
 - Increasing permittivity in inorganic compounds will invariably lead to decrease in energy density due to drop in E_B**

Comparison of Energy Storage Materials



- Alkali-free glass competitive with many emerging materials
- May have an advantage in manufacturing
- Packaged capacitors: 0.5-5 J/cc (depending on voltage rating)
 - Can we make 1 kV, 100 nF capacitors?

Alkali-Free Glasses

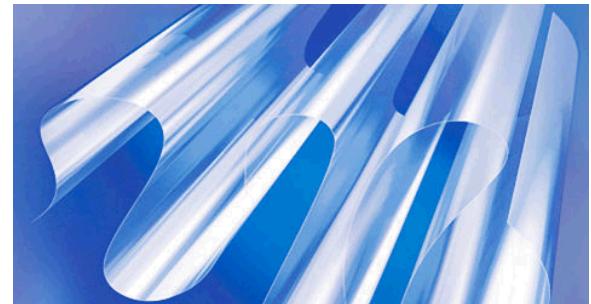


- “Overflow drawn down process”



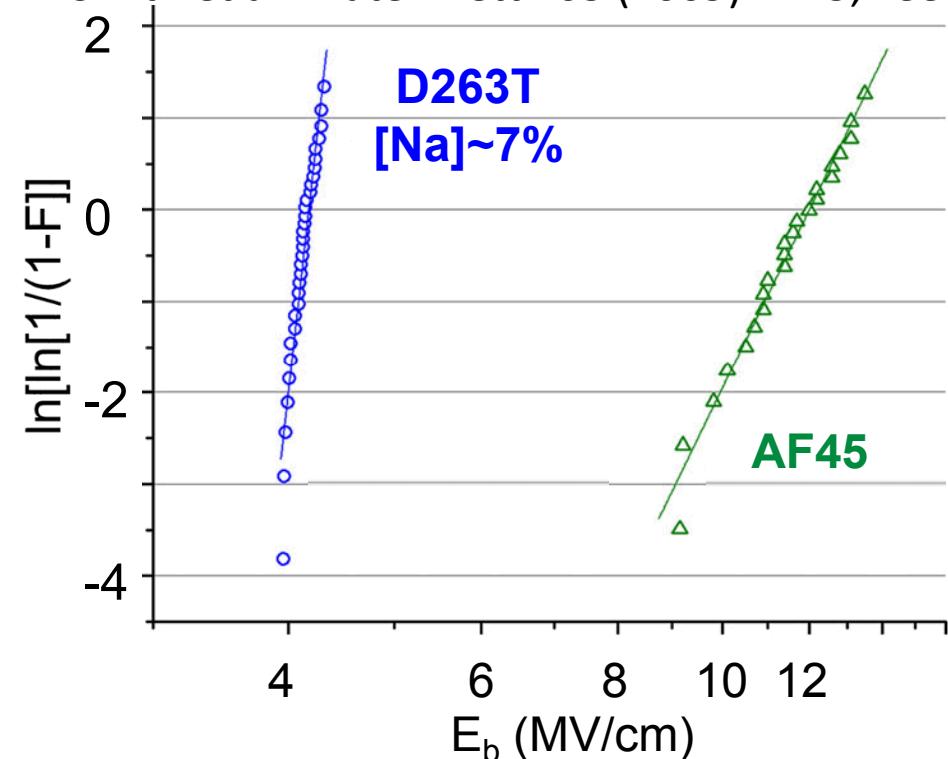
Parameter	Value
Density (g/cm ³)	2.3-2.5
Young's Modulus (GPa)	73-75
ε_r	5-6
$\tan \delta$	0.001
ρ (Ω^*cm @ 250 °C)	>10 ¹²
Strain Point	650-700 °C

- Sold by many vendors world wide
- Boro-alumino-silicate glass category
- Sold in thicknesses ~ 100 – 200 μm
- [Na] < 350 ppm (typical)

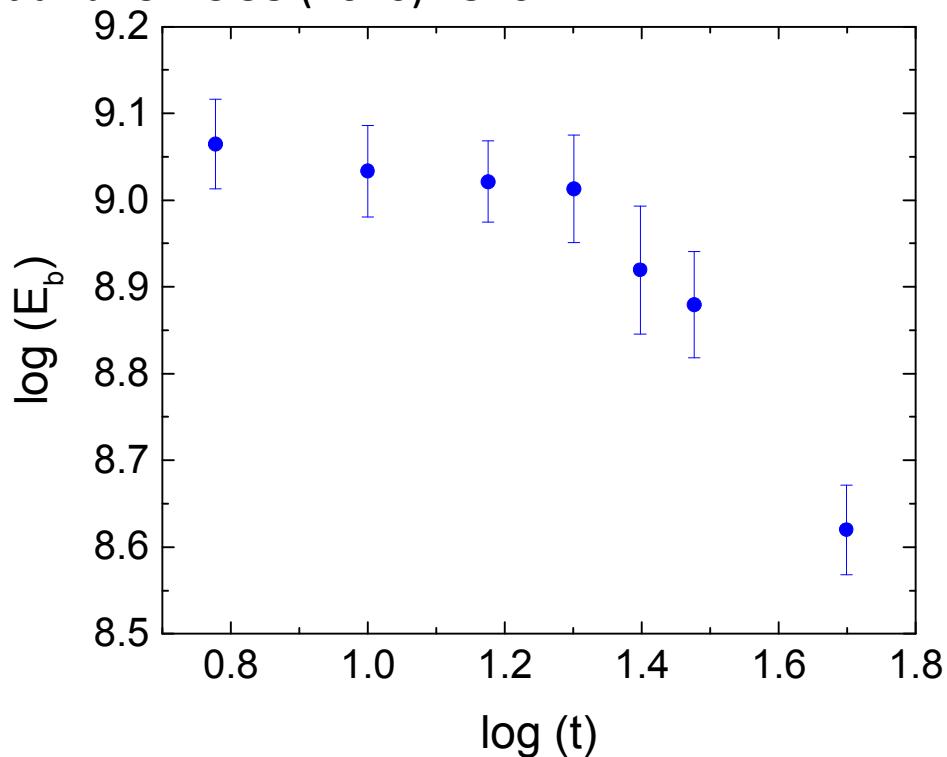


Breakdown Strength of Alkali-free Glass

- Smith et al. Mater. Lett. 63 (2009) 1245, Lee et al. JACERS 93 (2010) 2346



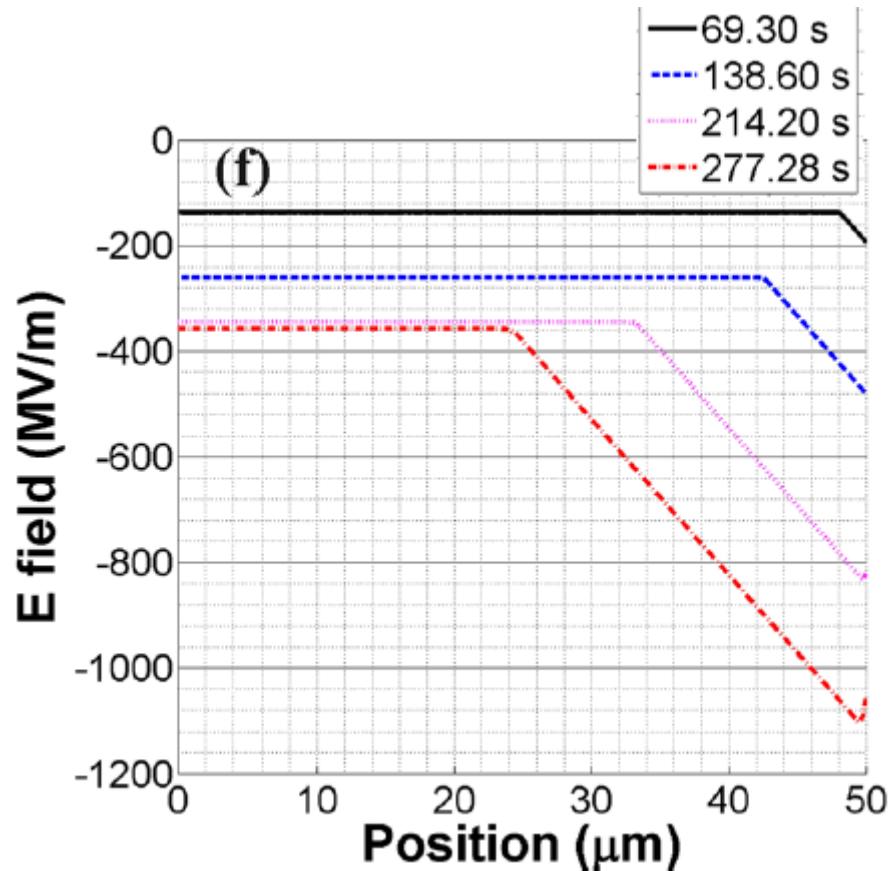
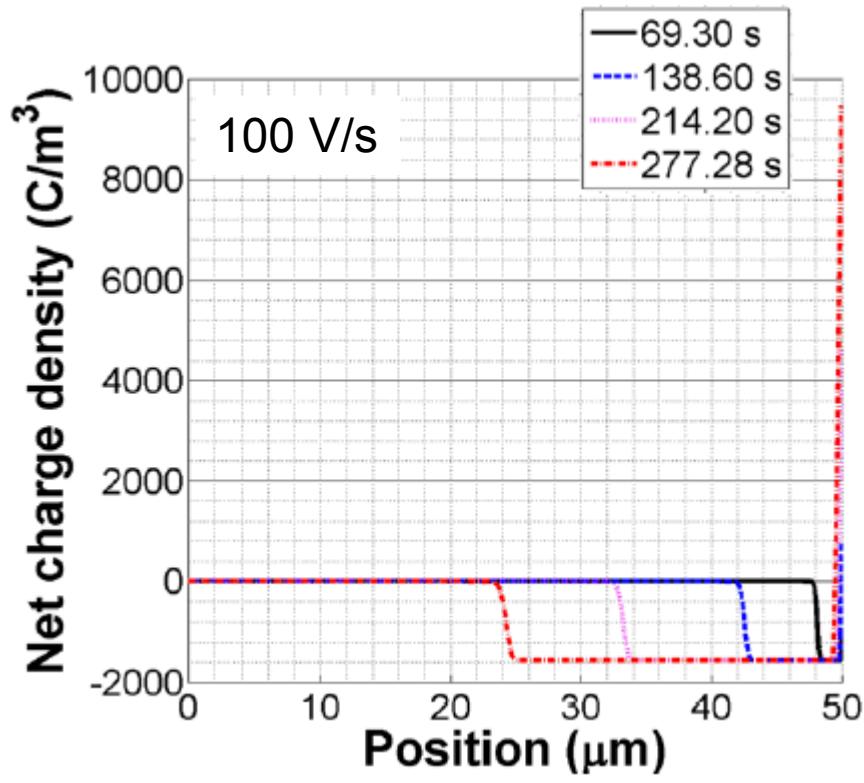
Parameter	D263T	AF45
t (μm)	30	19
E_b (MV/cm)	4.2	12
β	47.9	10.7



- Schott AF45 glass etched via sonicating in HF
- For $t < 20 \mu\text{m}$, $E_b > 10 \text{ MV/cm}$
- $U_{\text{dielectric}} \sim 35 \text{ J/cc}$

Breakdown Governed By Residual Na Content

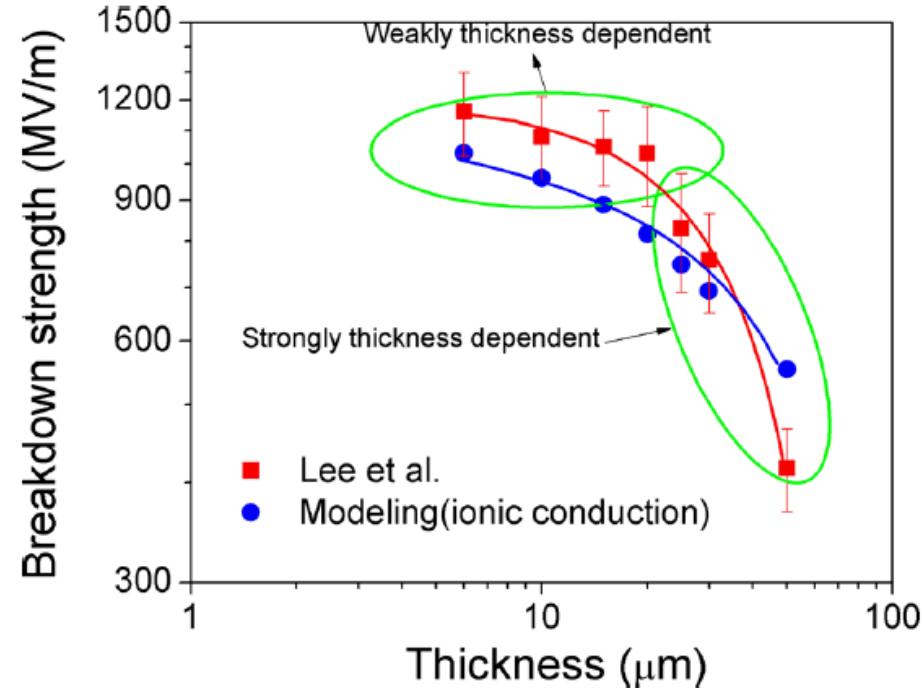
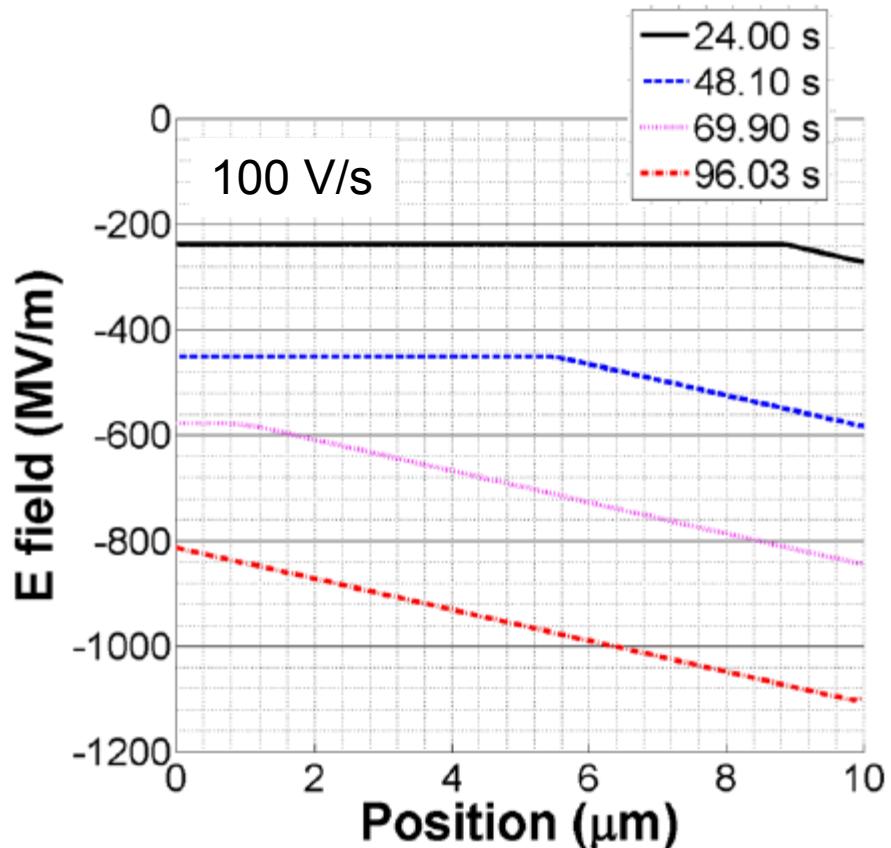
Choi et al. JAP 118 (2015) 084101



- Mobile ions (Na^+) depleted from anode, giving rise to field enhancements that can lead to breakdown

Breakdown Governed By Residual Na Content

Choi et al. JAP 118 (2015) 084101



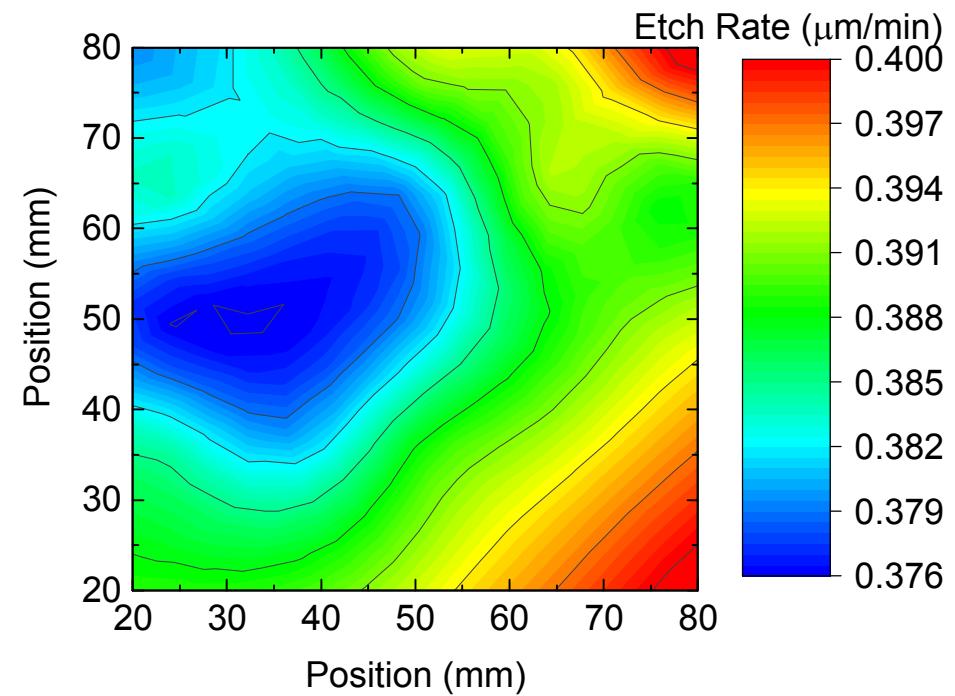
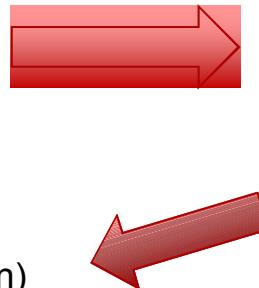
- For dielectric layers $< 20 \mu\text{m}$, depletion extends across entire layer $\Rightarrow E_B$ less thickness dependent

What do we want?

- Goal is to make high energy density capacitors in the 100-1000 nF size
 - Need thin glass!
 - $C = \frac{\epsilon_0 \epsilon_r A}{t}$
 - Breakdown field higher for $t < 20 \mu\text{m}$
 - Need a way to take hundreds of sheets of glass and connect them mechanically and electrically
 - Thin glass is NOT very robust.
 - Targeting temperature range of -55 to +65 °C
 - We really need thin glass

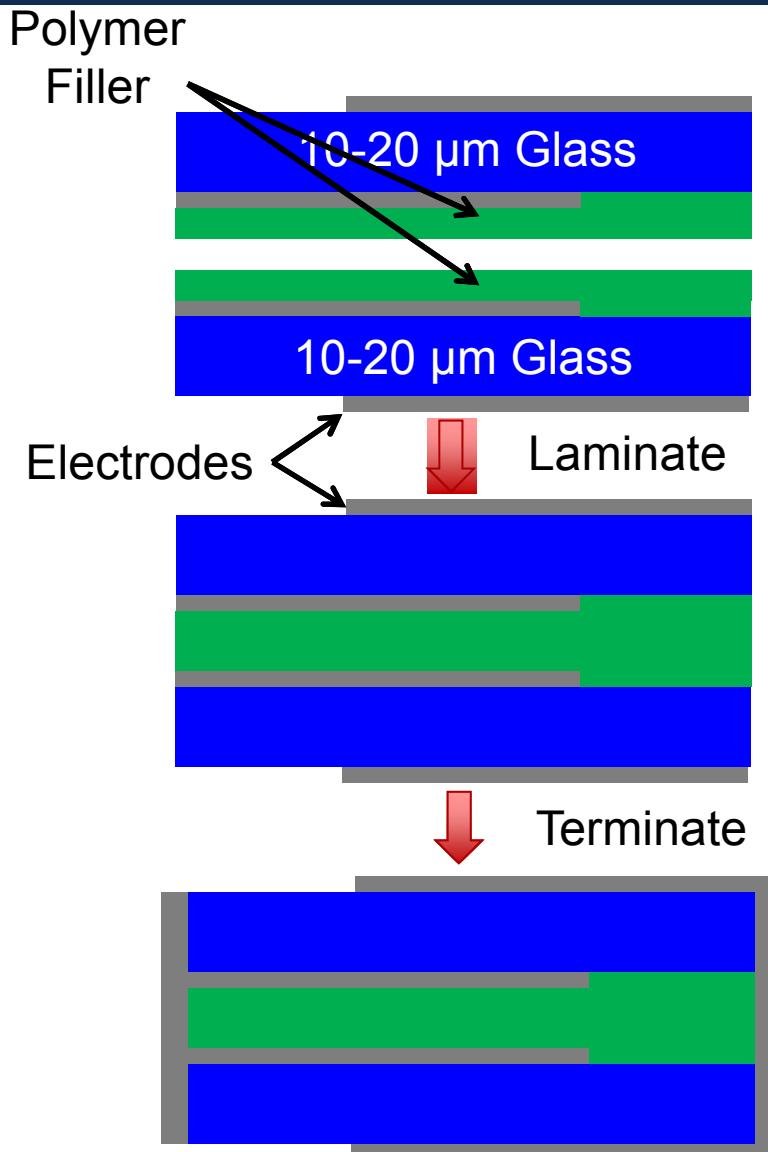


Thinning of Glass has been Demonstrated



- Glass is masked on edges – provide mechanical structure for thinned samples
- Etched in 2.5% HF solution using μ -Fab recirculating HF tank
- Reproducibly thin to from 30 μ m to 10 μ m ($\pm 3\%$)

Approach for Bonding Metallized Glass



- Thinned glass is manufactured “layer by layer”
- Need approach to physically and electrically connect multiple layers to form final capacitor
- Bonding Approach – laminate using high breakdown strength Epon 828/Jeffamine T403
 - Analogies to epoxy impregnated mica-paper capacitor construction



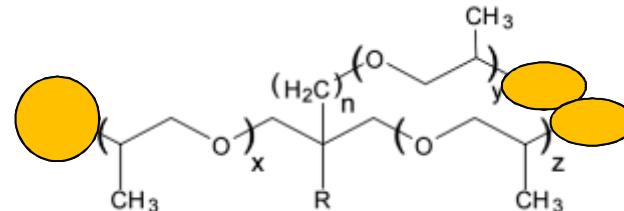
Selection of Epoxy

Epon 828 with Jeffamine T403

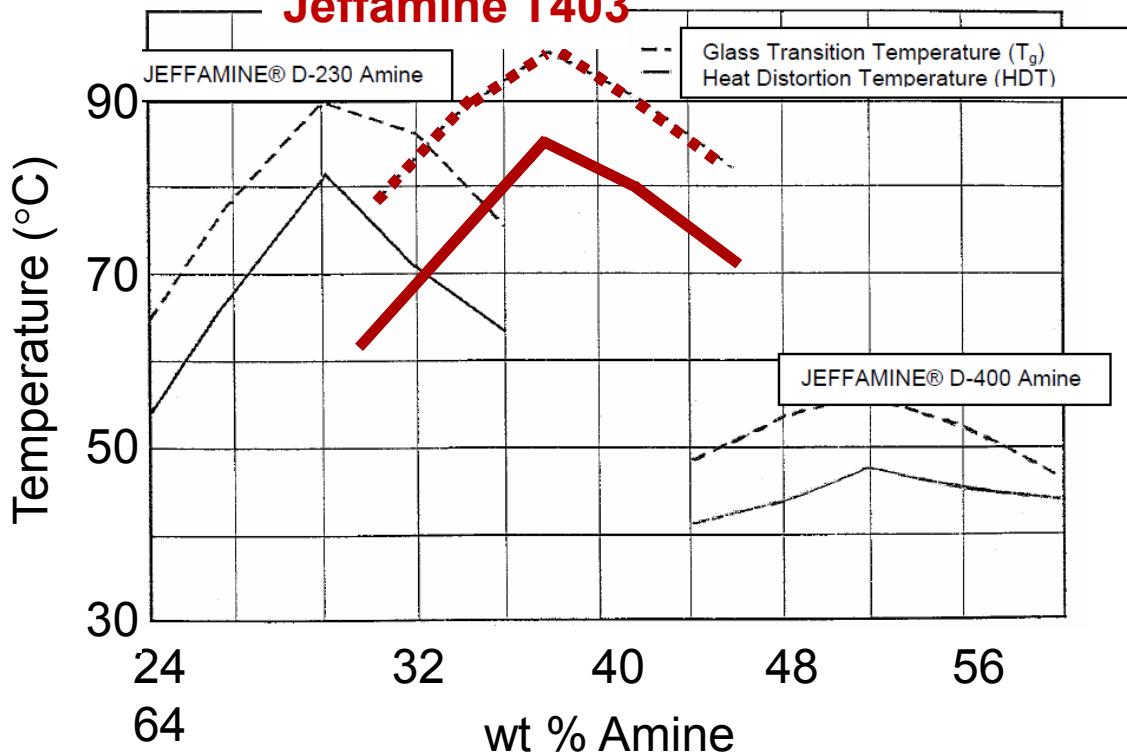
Epon 828



Triamine

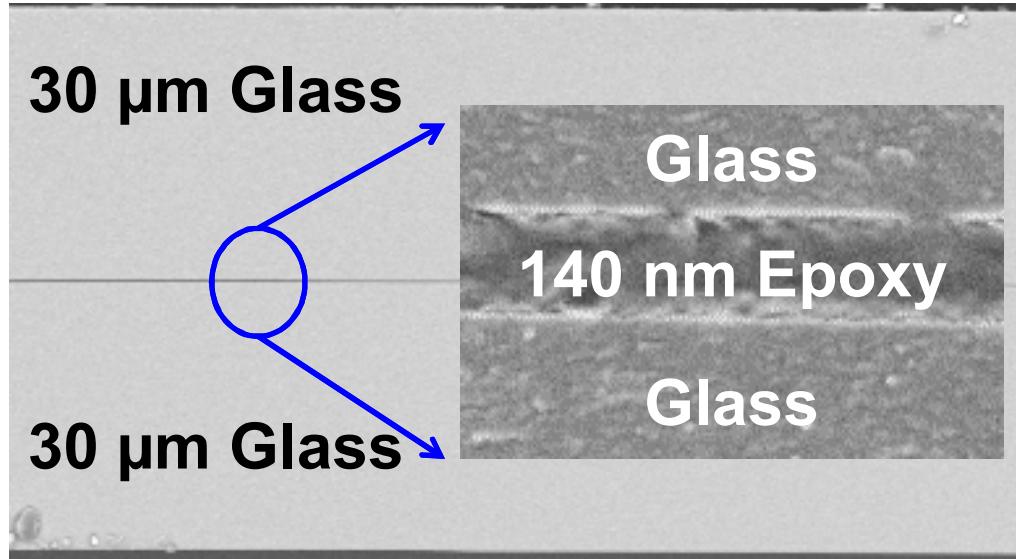
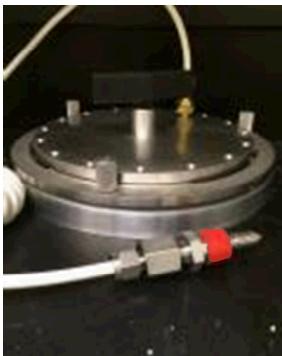
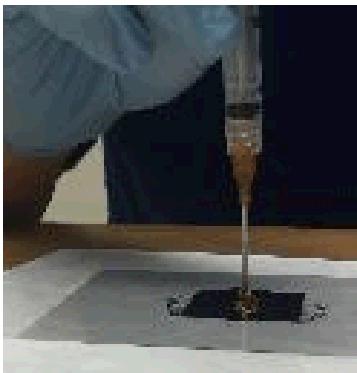


Jeffamine T403



- Lack of solvent means no solvent evacuation needed
- $T_g > 90 \text{ }^{\circ}\text{C}$ for 42 wt% Jeffamine T403
- Volume contraction during curing $\sim 5\%$

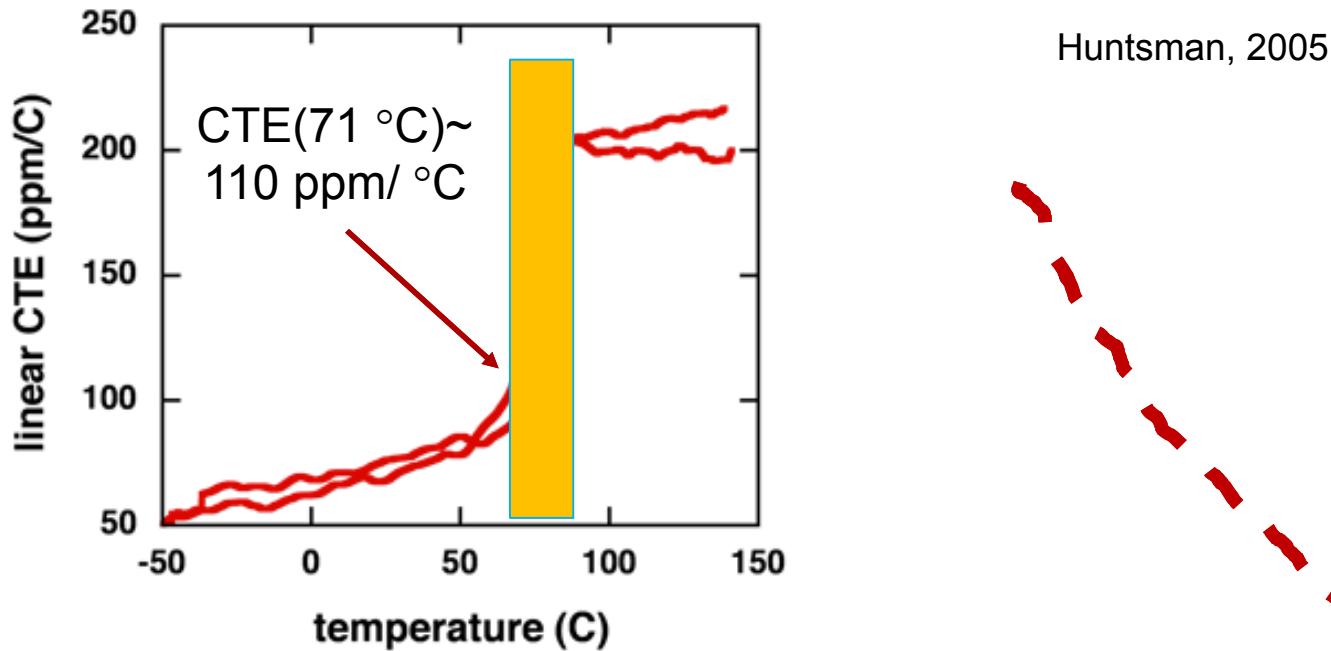
Demonstration of Bonding under Pressure



- Epoxy cured at 100 °C under uniaxial pressure of 4.2 kPa
- Uniform thickness of 138 ± 4 nm across 1" test piece



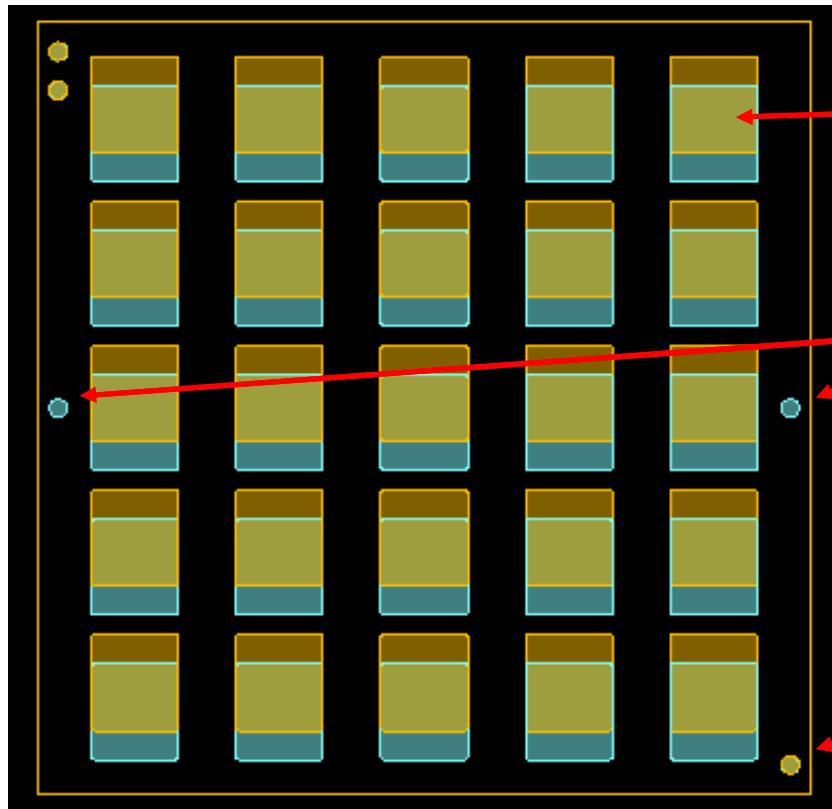
Setting of Curing Temperature



$$\alpha_{(\text{Lin})} = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right) \quad \sigma = E \frac{1}{L} \left(\frac{\partial L}{\partial T} \right) dT$$

- CTE of glass is 4.5 ppm/ $^\circ\text{C}$
- Curing at 100 $^\circ\text{C}$ induces significantly more stress than staying below T_g
- Cure at 65 $^\circ\text{C}$ requires higher pressure for similar thickness epoxy layer

Aligning Electrodes



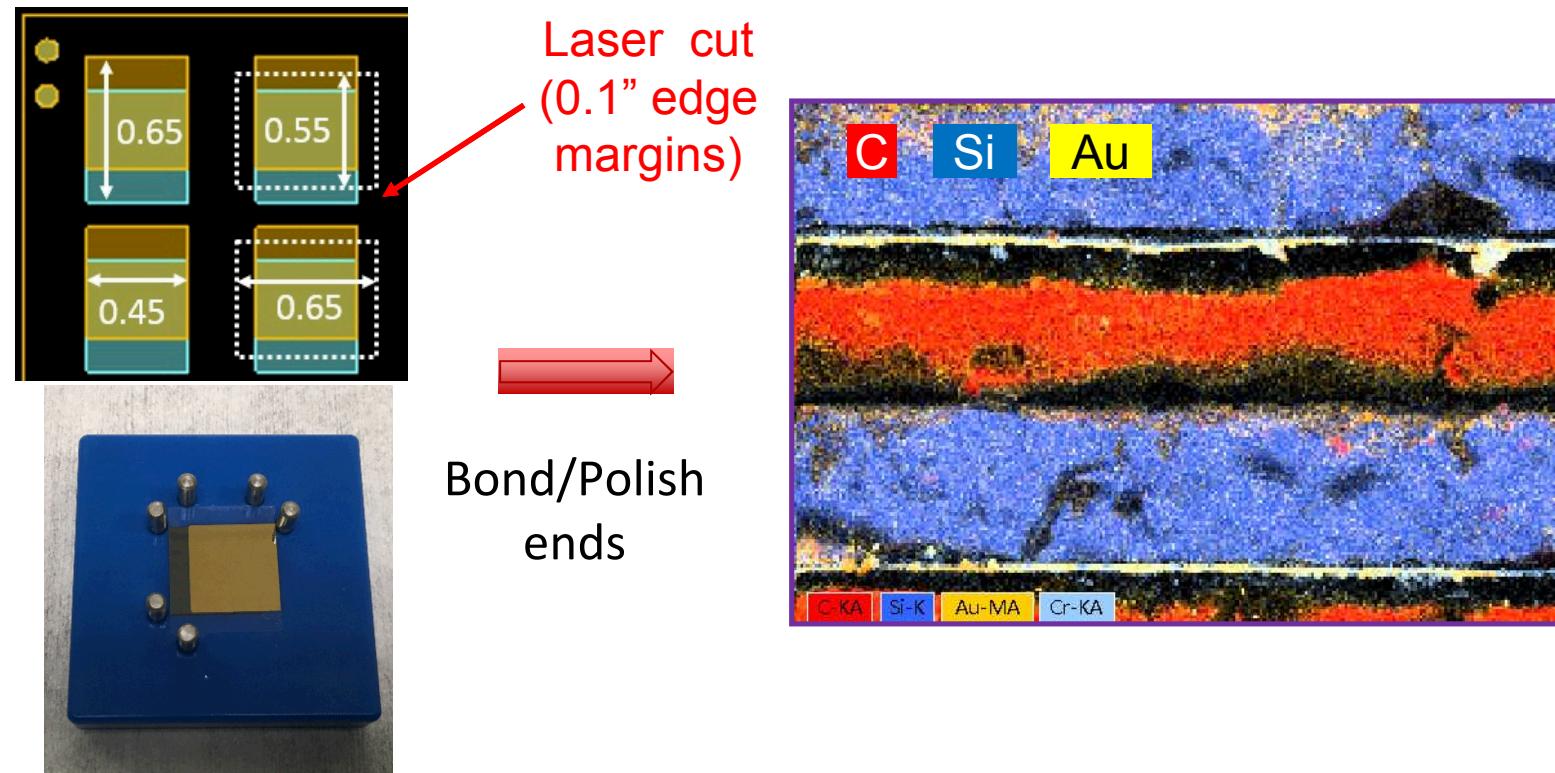
Metallized Electrodes
0.45" x 0.5" (0.15" offset)
Active area 0.35"x0.45"

Reference Marks for Laser Machining
Cut out for Alignment Fixture

Reference Marks for Aligning
Shadow Mask
for Top/Bottom Electrodes

- Alignment between subsequent layers is crucial for minimizing dead volume/maximizing energy density
- Shadow mask designed for metallizing glass – providing alignment markings
- Glass sheets subsequently cut

Fabricating Capacitor using 3D Printed Fixture

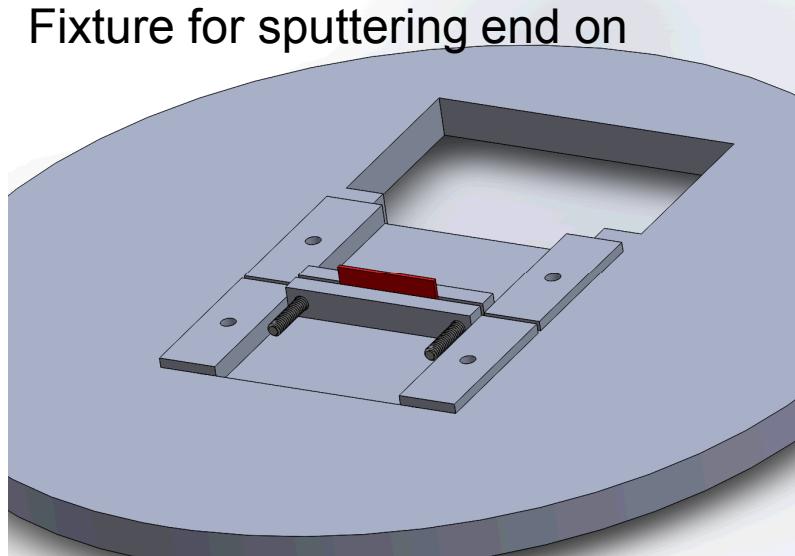


- Active area of capacitor is 0.35" x 0.45" (Total area 0.55" x 0.65")
 - 10 μm glass provides 500 pF per layer
 - Long term goal is 5 μm (990 pF per layer)

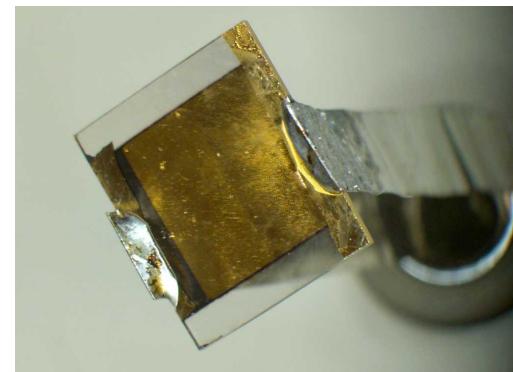


End Terminations

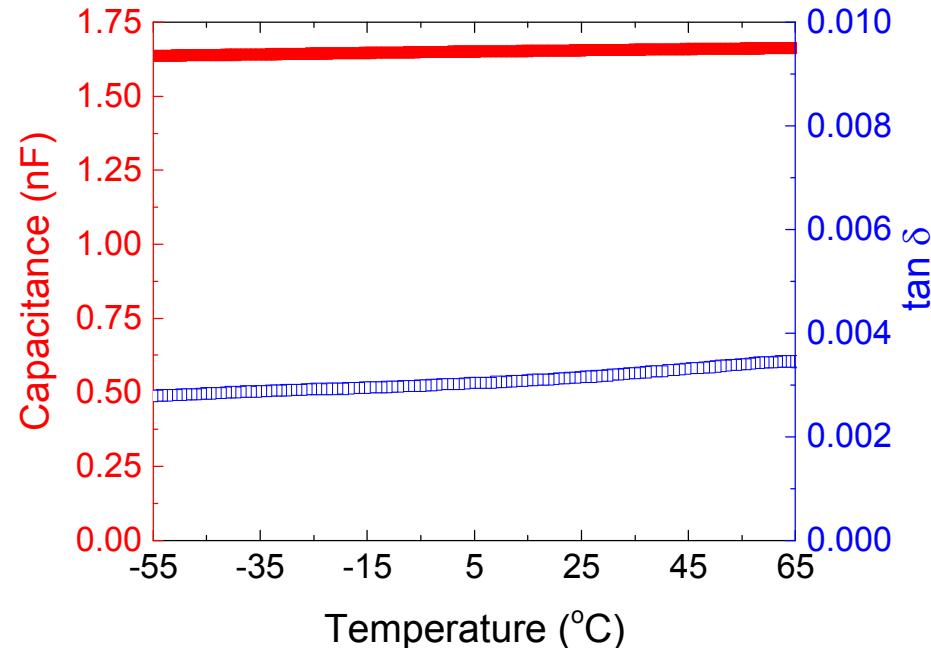
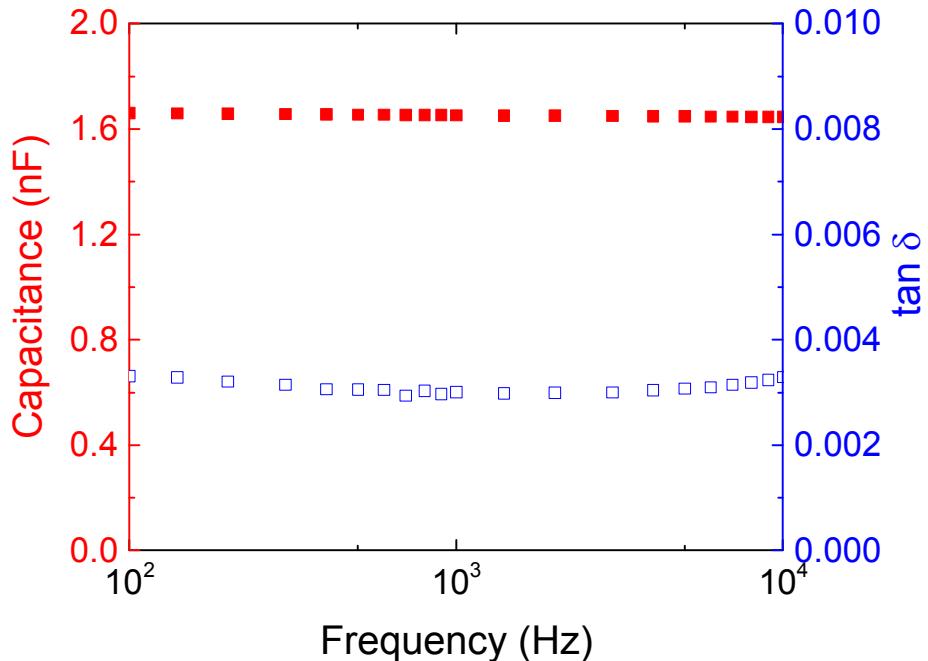
Fixture for sputtering end on



- Sputter deposit Ti (200 nm)/Pt (100 nm)/Au (200 nm)
 - Non-directional nature of deposition ensures contact to inner electrodes
- Solder leads for electrical testing



Capacitor from 30 μm Glass

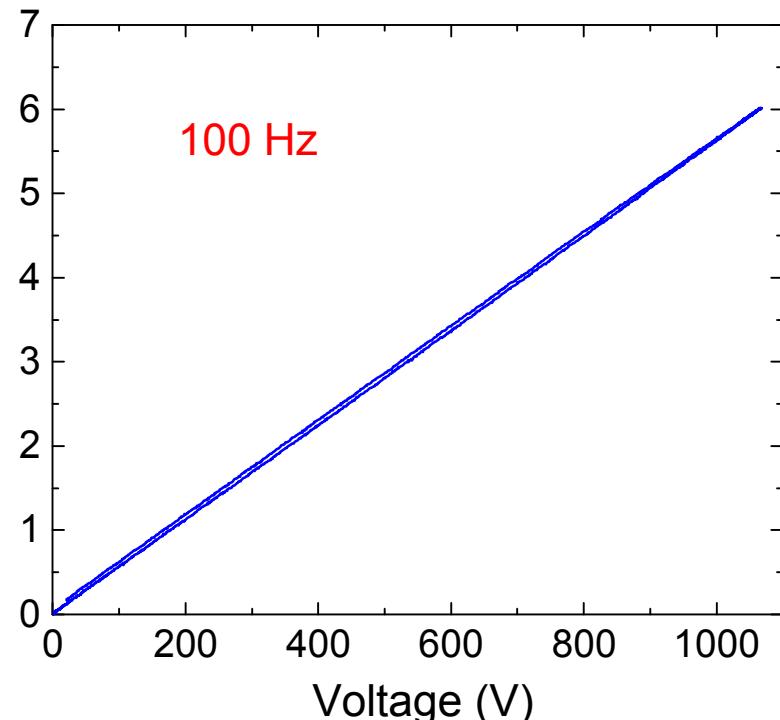
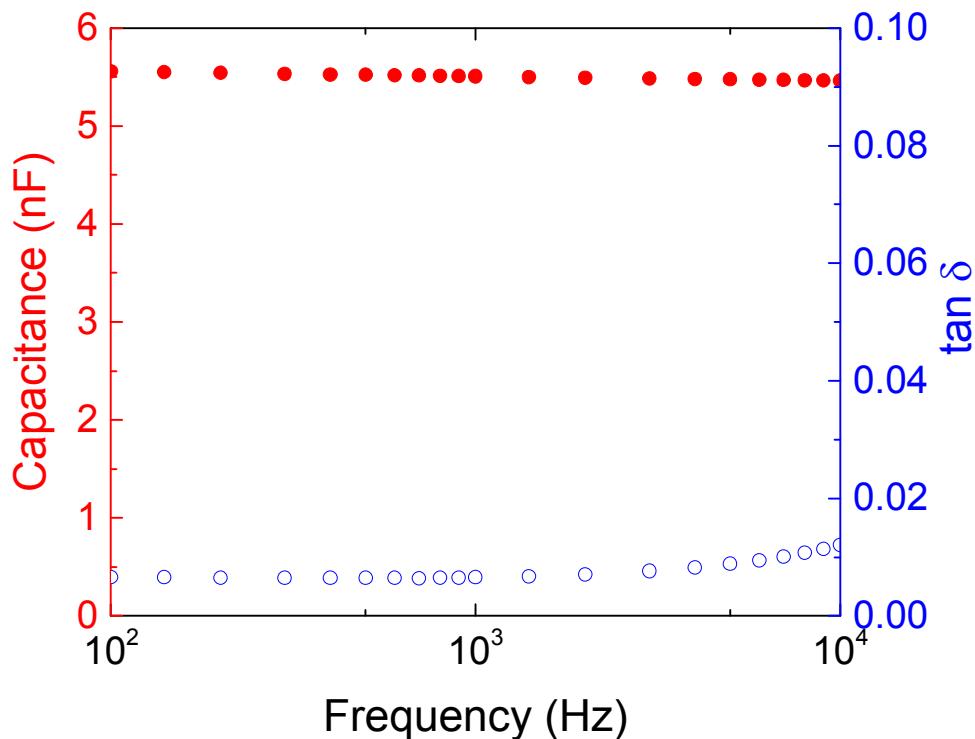


- 10 layers - 1.65 nF (indicates all layers electrically active)
- Shows better than $\pm 1\%$ stability over -55 °C to +65 °C (exceeds X4A classification)
- $R = 2.81 \times 10^{13} \Omega$ @ 65 °C ($RC = 4.7 \times 10^4$ s)
- $V_{\text{Breakdown}} = 9.74$ kV (dielectric $\Rightarrow 2.8$ J/cc, package $\Rightarrow 0.4$ J/cc); need more samples for Weibull analysis
- 150x increase in area vs. Lee report:

$$\frac{E_{b1}}{E_{b2}} = \left(\frac{\text{Area}_2}{\text{Area}_1} \right)^{1/\beta} \quad \rightarrow \quad V_B(\text{MLGC}) \sim 12\text{kV}$$



Capacitors from thinned Glass



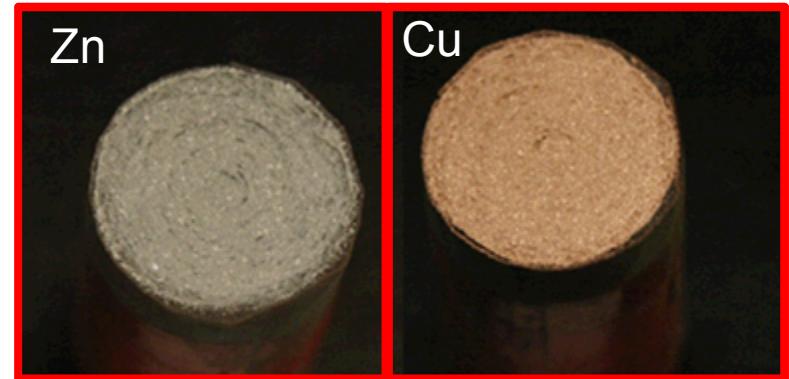
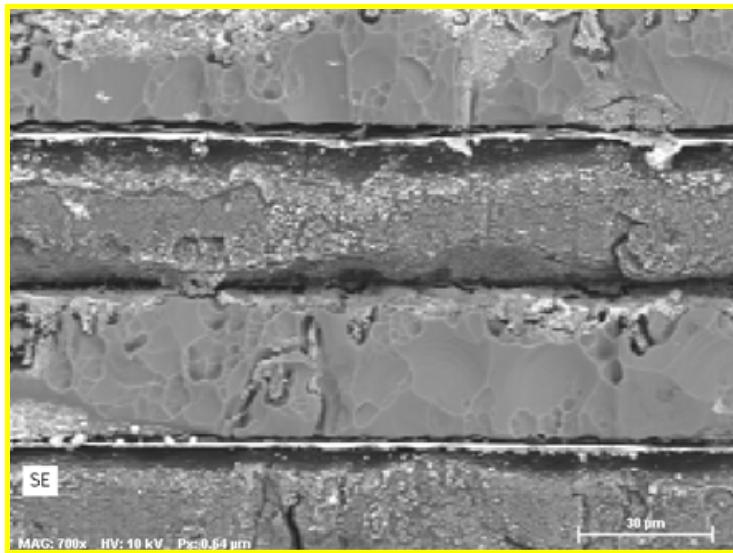
- 10 Layers – 5.5 nF @ 1 kHz
- Tested to 1 kV
 - $E = 3.2 \text{ mJ}, U = 0.09 \frac{\text{J}}{\text{cc}}$
 - 66% value of NovaCap at ceramic
- 50% of volume was from epoxy bonding layer
 - Need to optimize bonding process to reduce inactive volume





What's Next?

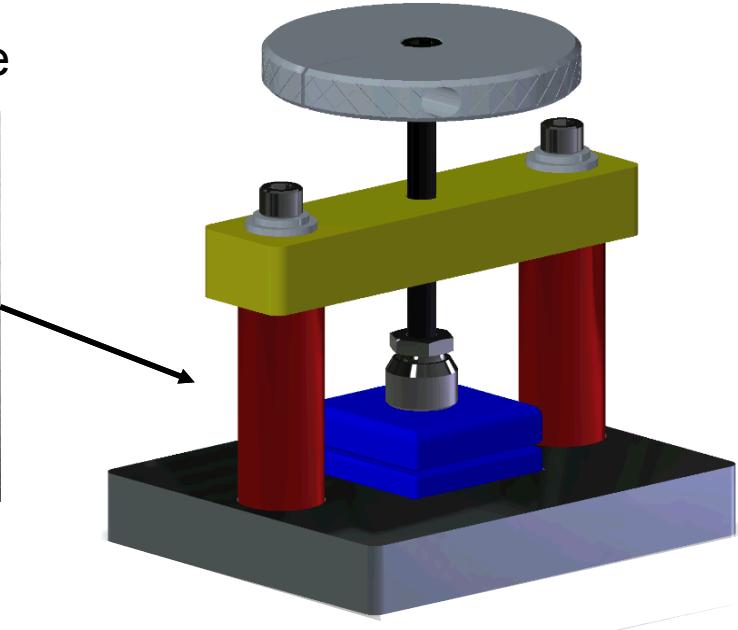
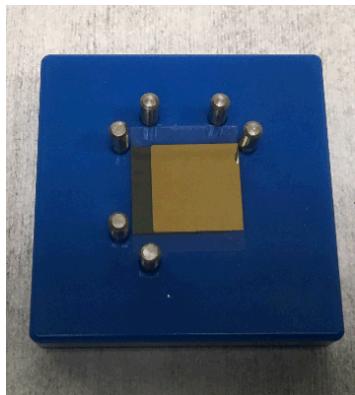
- Decrease dead-space to improve energy density
- Demonstrate more commercially viable processing





New Fixture for Controlling Pressure

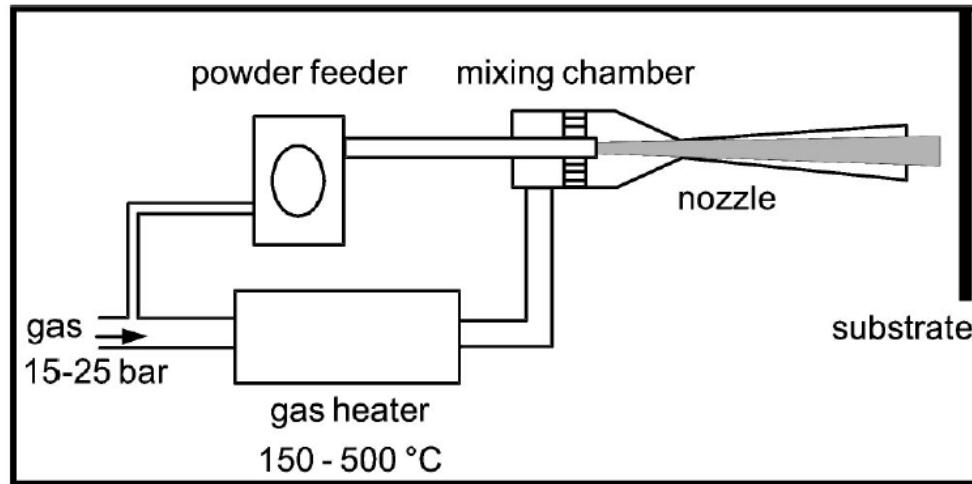
Alignment Fixture



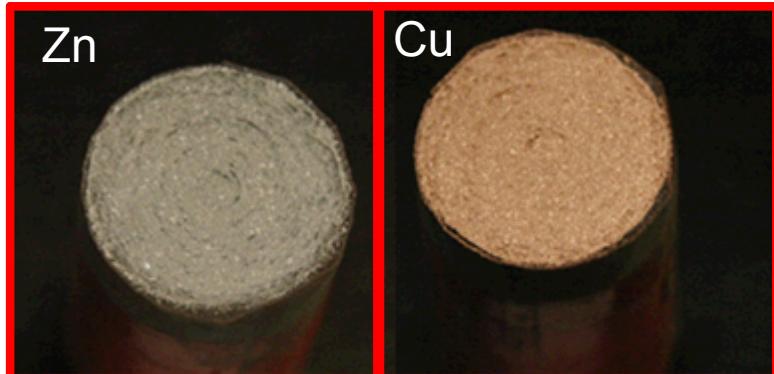
- SS construction allows fixture to be placed in oven
- Applied pressure can be controlled by torque wrench or large thumb screw

- Can “pre-cure” glass @ 65 °C for 1 hour under controlled pressure to control thickness of epoxy layer
- Remove glass from alignment fixture, clean, then proceed to final cure

Investigate Arc-Spray as Route to Apply End Terminations

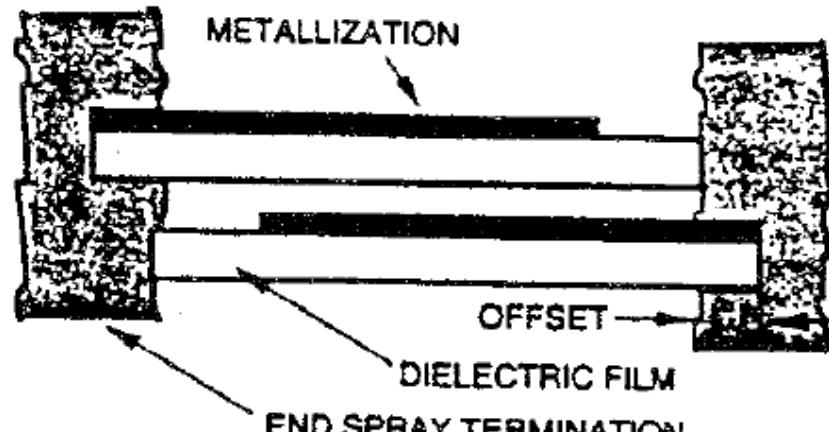


Borchers et al., JAP 2003



Pylin Sarabol, Andrew Miller

- Zn/Cu arc-spray on polymer capacitors
- Low temperature process – won't damage epoxy/glass structure
- Rapid deposition for thick films ($>10 \mu\text{m}$)
- Resistivity of Cu films $40-400 \mu\Omega\text{-cm}$ (bulk $1.7 \mu\Omega\text{-cm}$)



Ennis et al., Pulsed Power 1997

Conclusions

- Successfully demonstrate route to make solid state multi-layer glass capacitors
- Temperature range of operation determined by bonding material (Epon 828/Jeffamine T403 -55 °C to + 65 °C)
- Breakdown data suggests area scaling of Weibull data applies
 - Need to proof test glass sheets prior to incorporation to maximize energy density
 - Working on “mass production” to demonstrate Weibull statistics on packaged capacitors
- End terminations in the works.....