

# Towards High Energy Density Glass Capacitors

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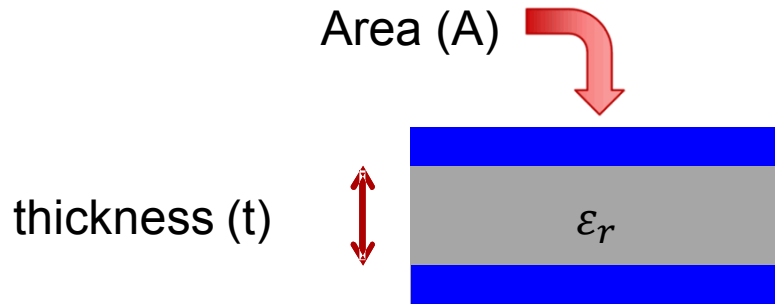
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# Outline



- 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

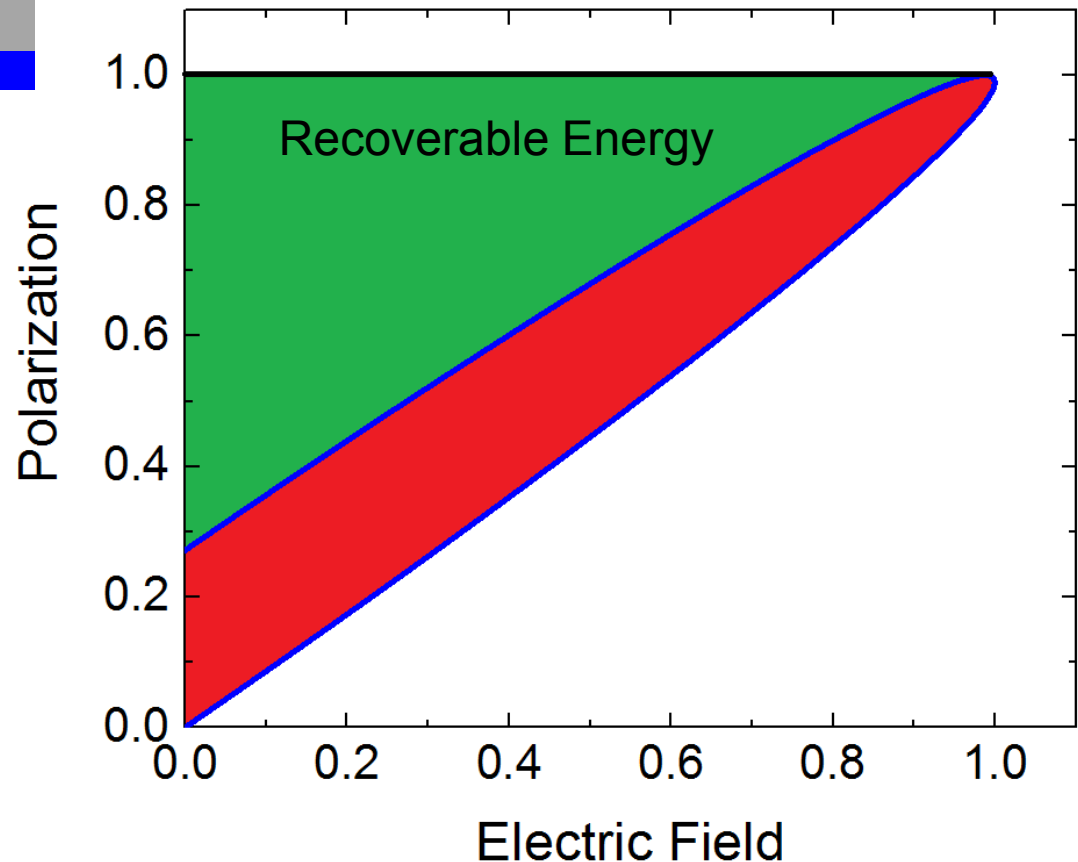


$$C = \epsilon_r \epsilon_0 \frac{A}{t}$$

$$W = \int P dE$$

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

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

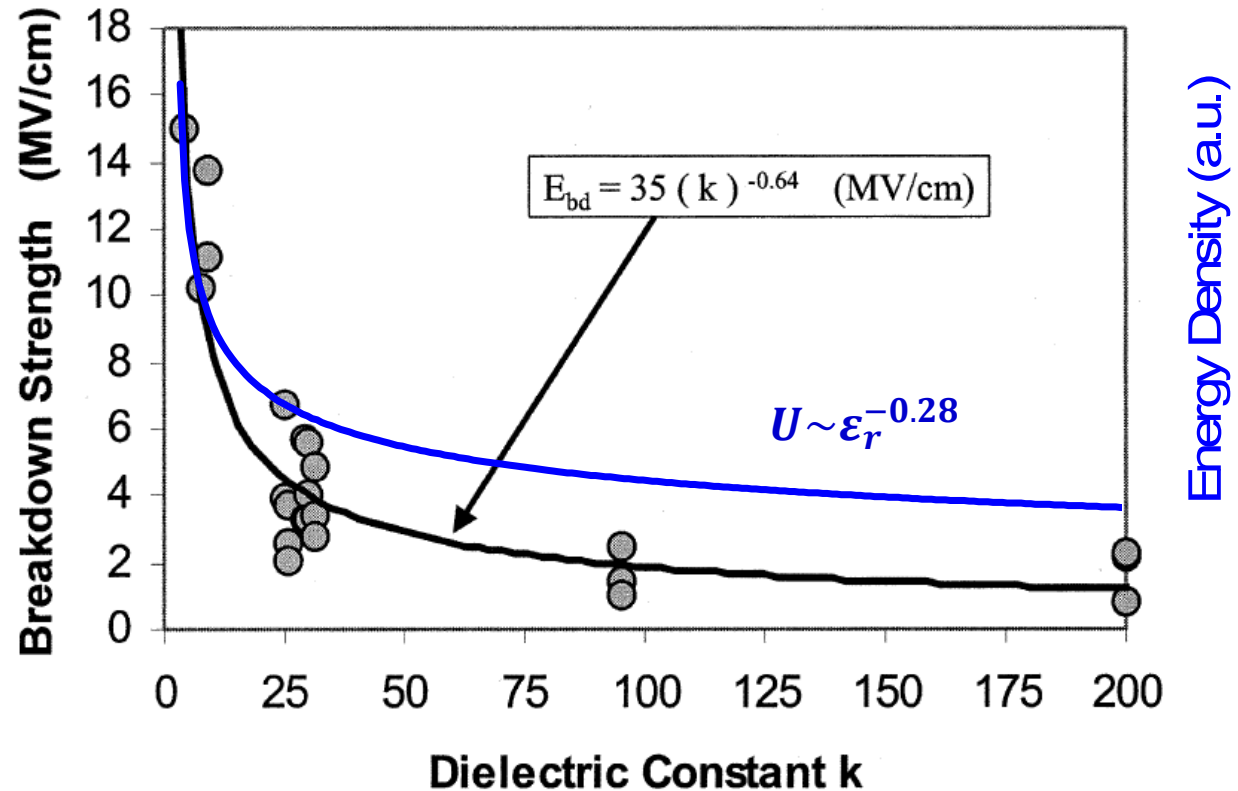


# Trends in Breakdown Strength of Dielectrics

Larger gains from  
increasing breakdown  
strength

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

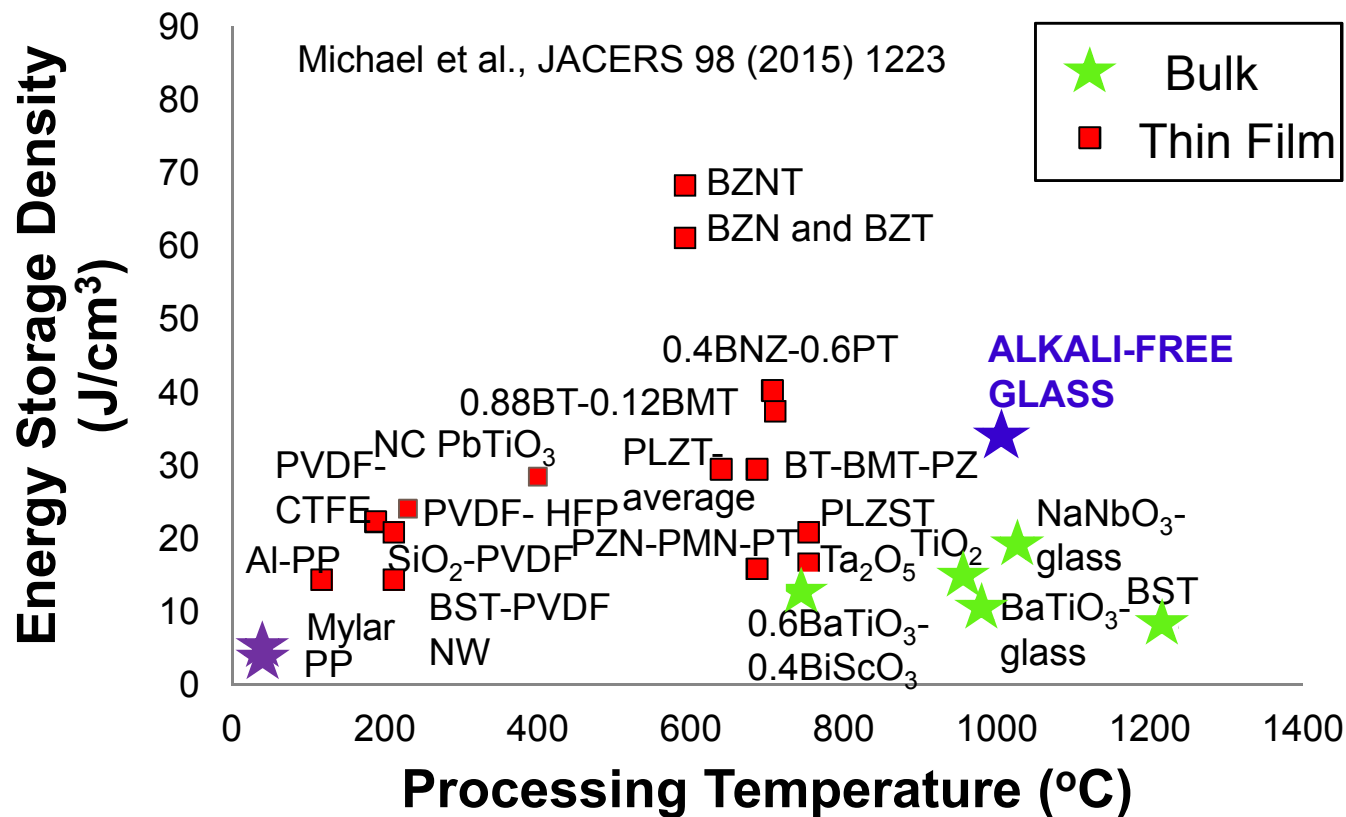
Limited value to tuning  $\epsilon_r$



McPherson et al. IEEE TED, 2003

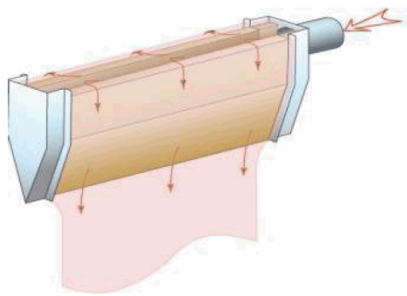
- Thermochemical modeling suggests link between polarizability and bond strength
  - Increasing permittivity in inorganic compounds will invariably lead to decrease in energy density due to drop in  $E_B$**

# 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?

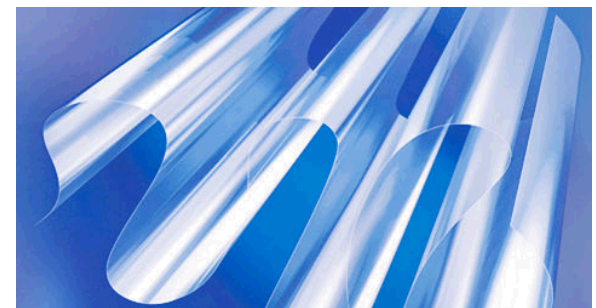
# Alkali-Free Glasses



- “Overflow drawn down process”



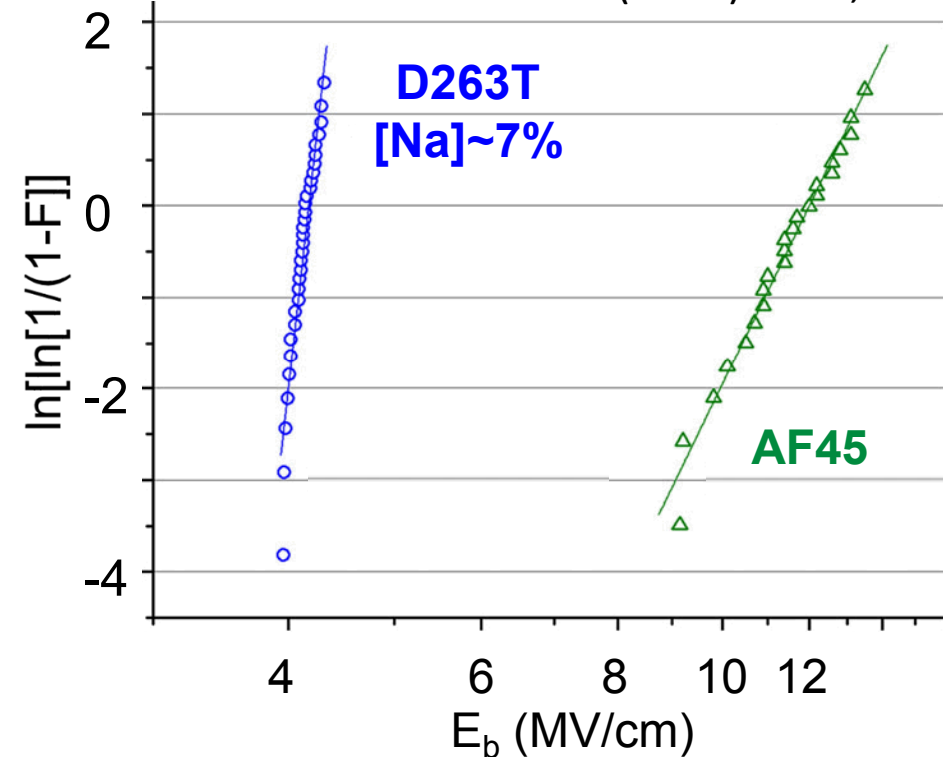
Parameter	Value
Density (g/cm <sup>3</sup> )	2.3-2.5
Young's Modulus (GPa)	73-75
$\epsilon_r$	5-6
$\tan \delta$	0.001
$\rho$ ( $\Omega \cdot \text{cm}$ @ 250 °C)	$>10^{12}$
Strain Point	650-700 °C



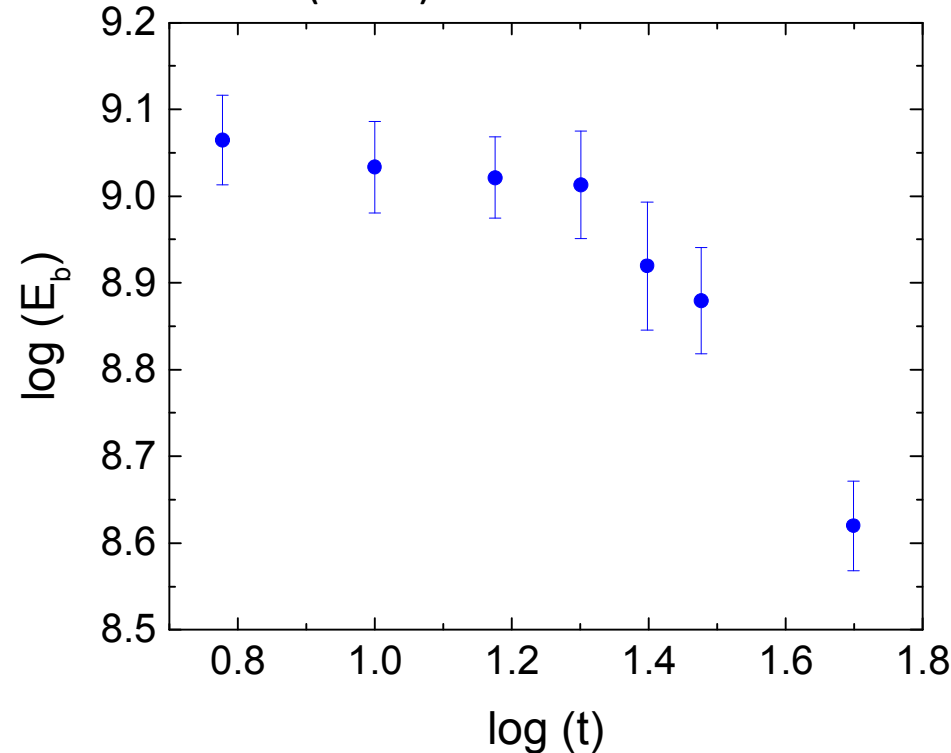
- Sold by many vendors world wide
- Boro-alumino-silicate glass category
- Sold in thicknesses  $\sim 100 - 200 \mu\text{m}$
- $[\text{Na}] < 350 \text{ ppm}$  (typical)

# Breakdown Strength of Alkali-free Glass

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



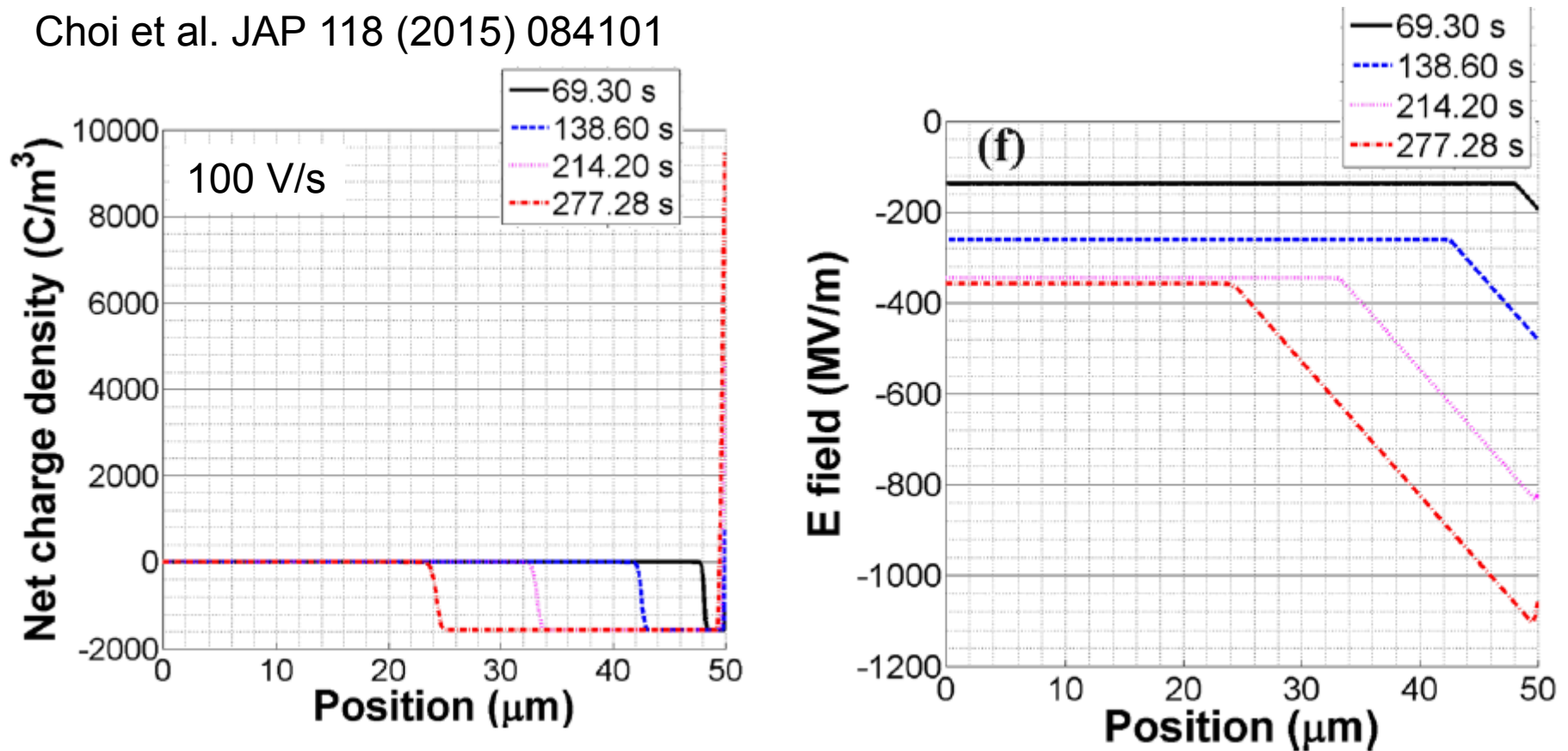
Parameter	D263T	AF45
$t$ ( $\mu\text{m}$ )	30	19
$E_b$ (MV/cm)	4.2	12
$\beta$	47.9	10.7



- 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

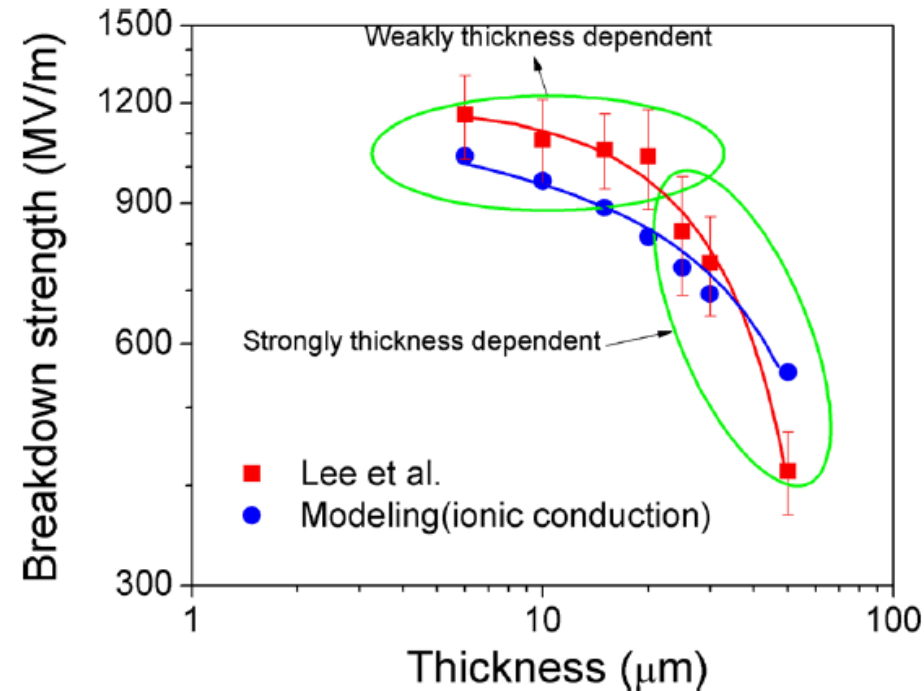
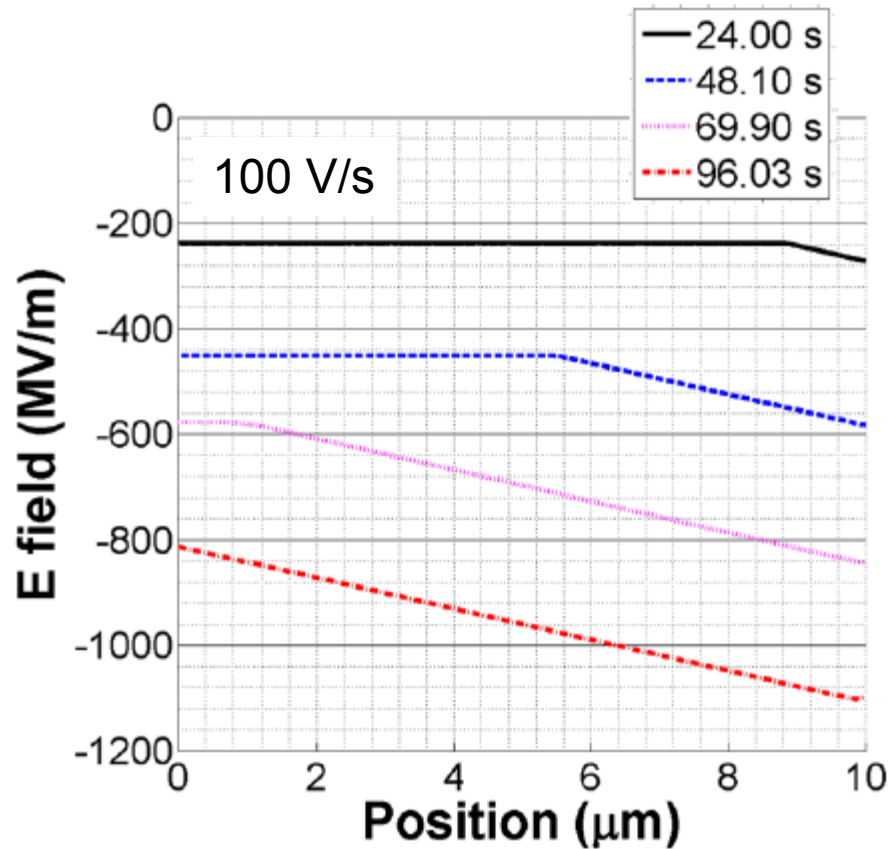


- Mobile ions ( $Na^+$ ) depleted from anode, giving rise to field enhancements that can lead to breakdown



# 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

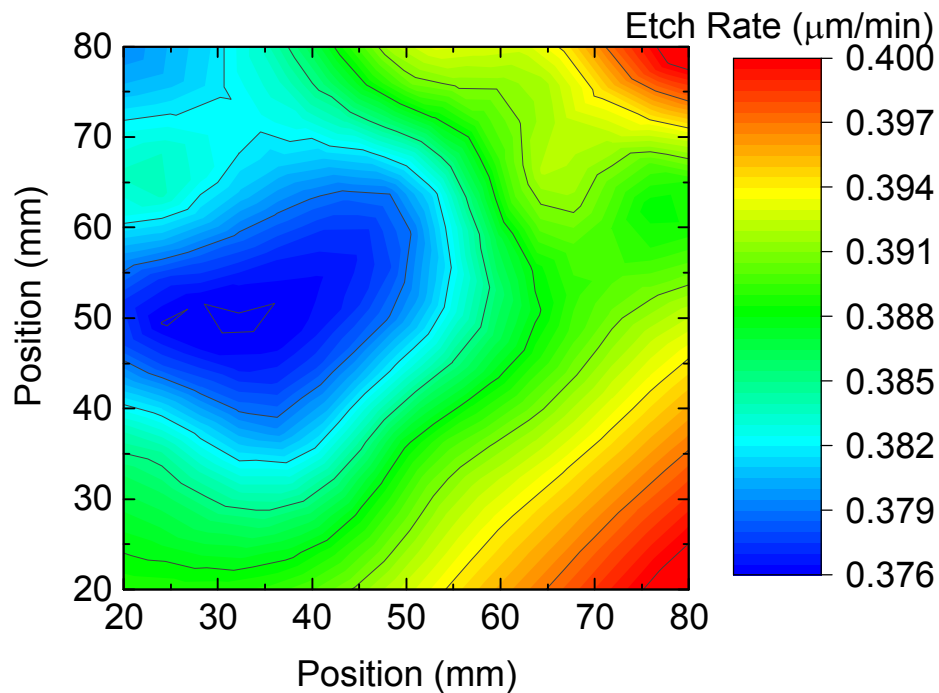
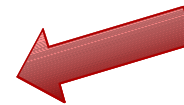
# What do we want?



- 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

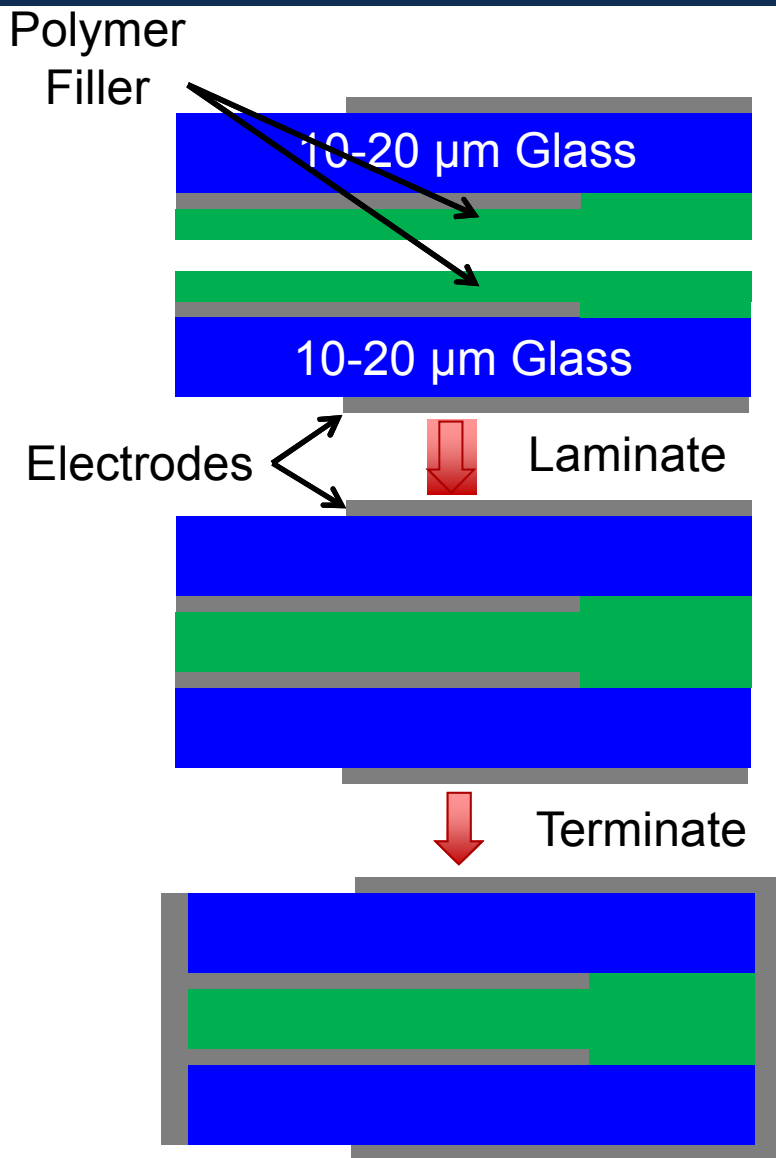


# Thinning of Glass has been Demonstrated

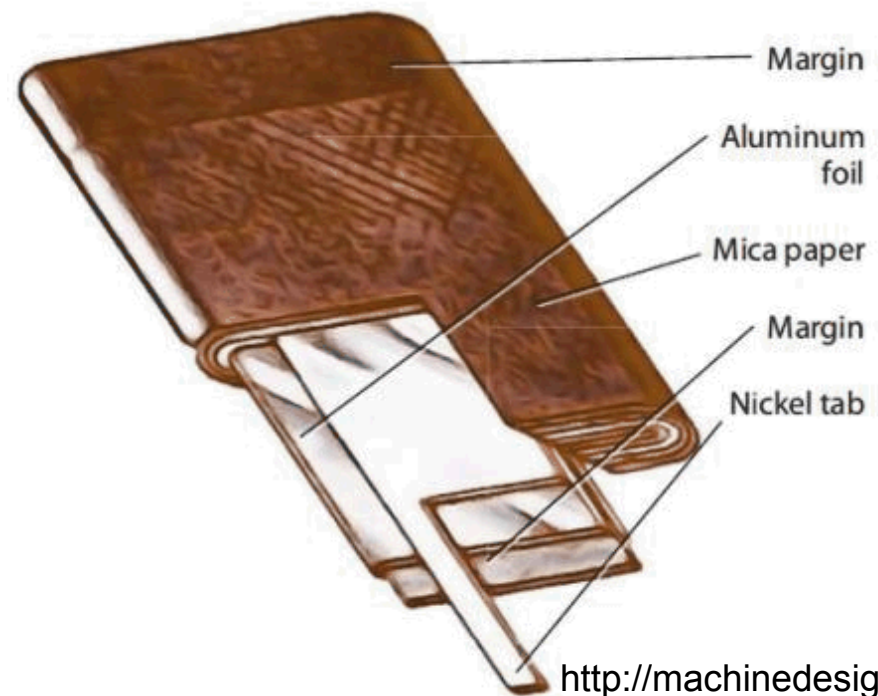


- Glass is masked on edges – provide mechanical structure for thinned samples
- Etched in 2.5% HF solution using  $\mu$ -Fab recirculating HF tank
- Reproducibly thin to from 30  $\mu\text{m}$  to 10  $\mu\text{m}$  ( $\pm 3\%$ )

# 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

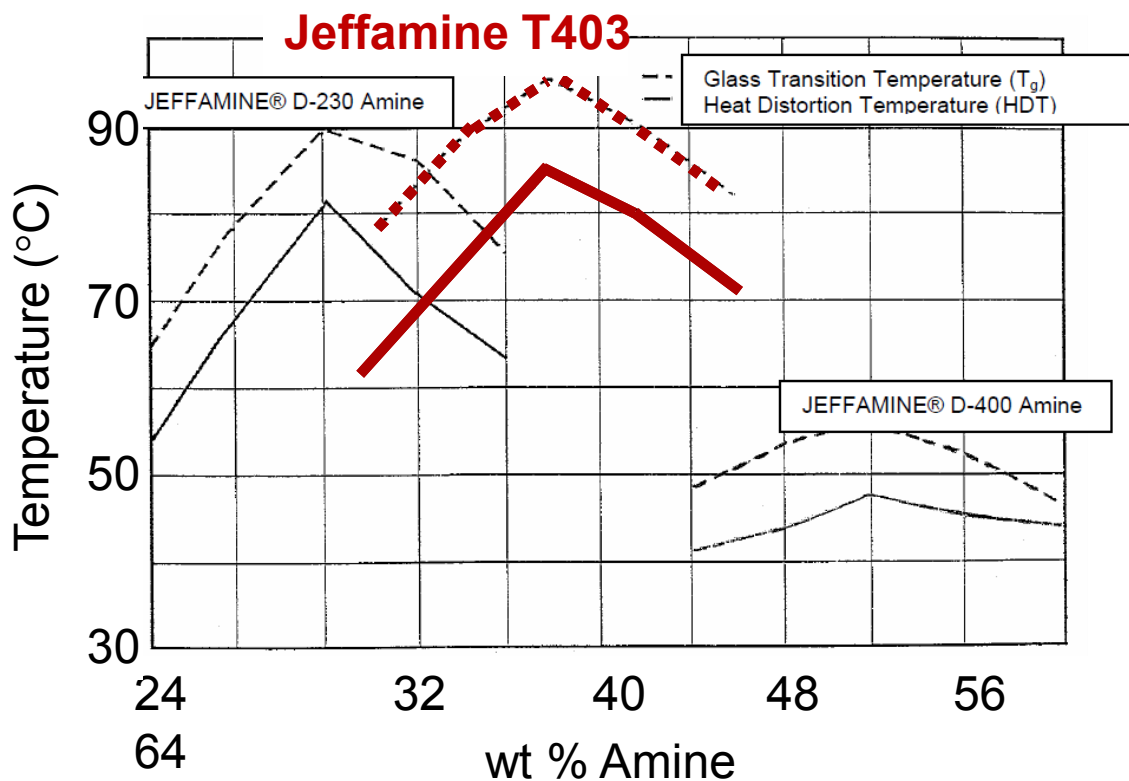
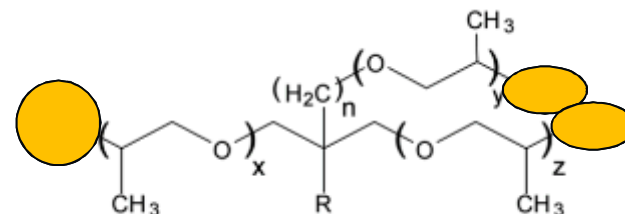


# Selection of Epoxy

Epon 828 with Jeffamine T403

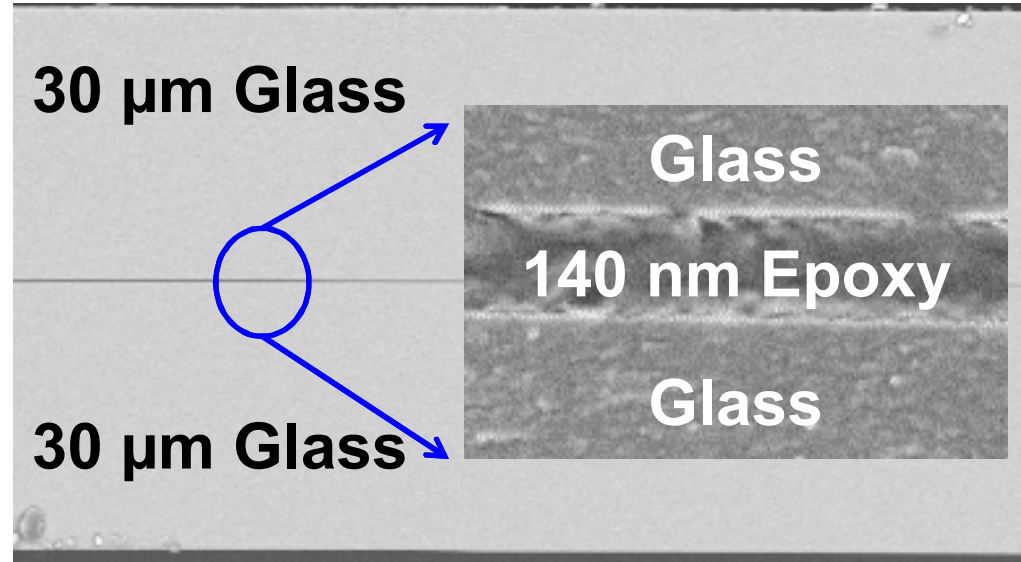
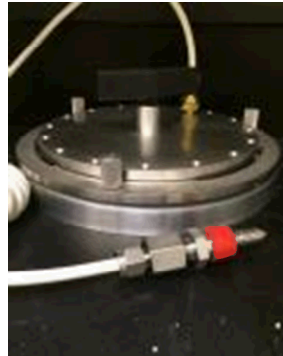
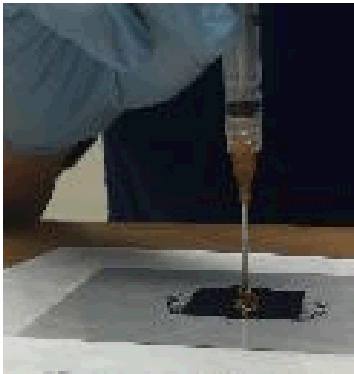
**Epon 828**

**Triamine**



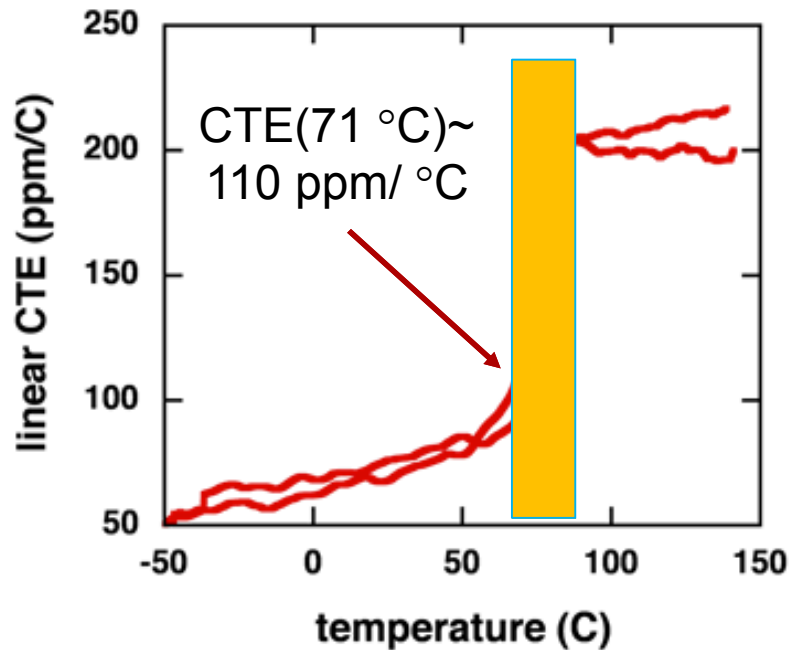
- Lack of solvent means no solvent evacuation needed
- $T_g > 90^\circ\text{C}$  for 42 wt% Jeffamine T403
- Volume contraction during curing ~5%

# Demonstration of Bonding under Pressure

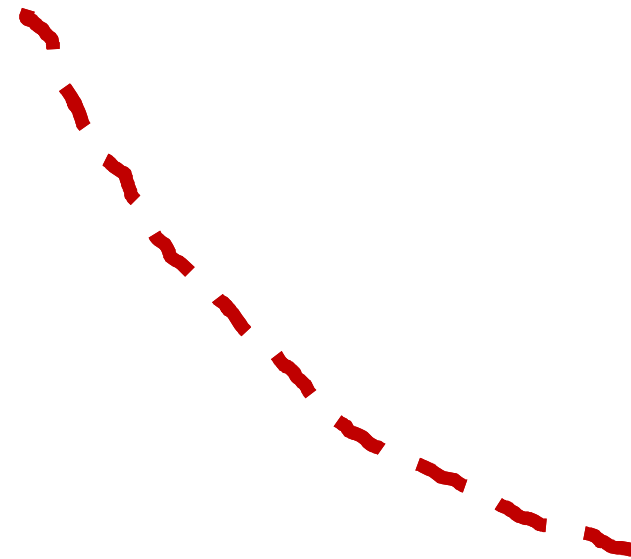


- Epoxy cured at 100 °C under uniaxial pressure of 4.2 kPa
- Uniform thickness of  $138 \pm 4$  nm across 1" test piece

# Setting of Curing Temperature



Huntsman, 2005

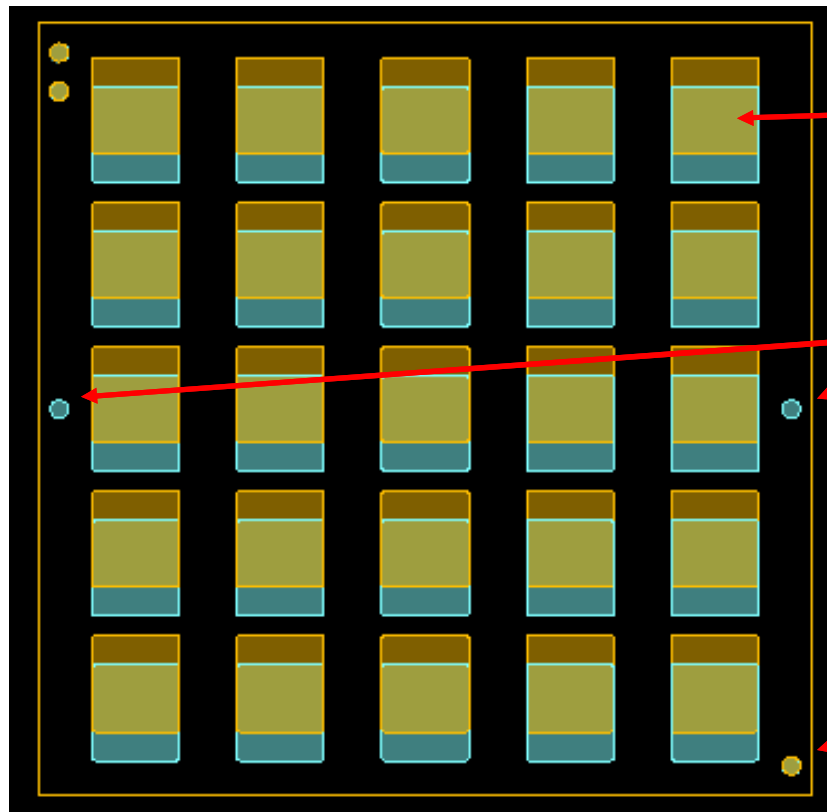


$$\alpha_{(\text{Lin})} = \frac{1}{L} \left( \frac{\partial L}{\partial T} \right) \quad \sigma = E \frac{1}{L} \left( \frac{\partial L}{\partial T} \right) dT$$

- CTE of glass is 4.5 ppm/°C
- Curing at 100 °C induces significantly more stress than staying below  $T_g$
- Cure at 65 °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"

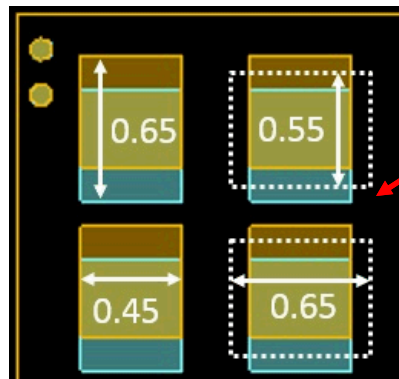
Reference Marks for Laser Machining  
Cut out for Alignment Fixture

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



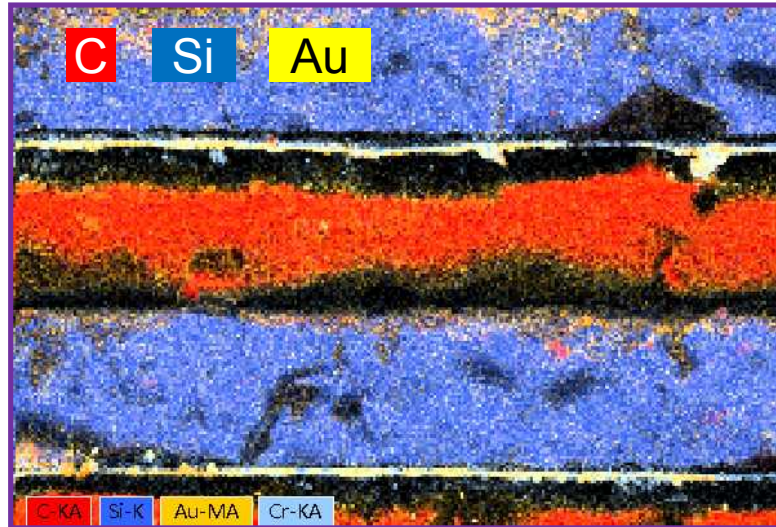
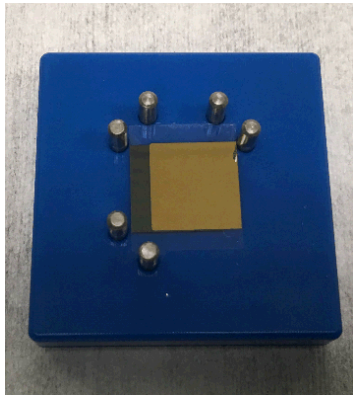
# Fabricating Capacitor using 3D Printed Fixture



Laser cut  
(0.1" edge  
margins)



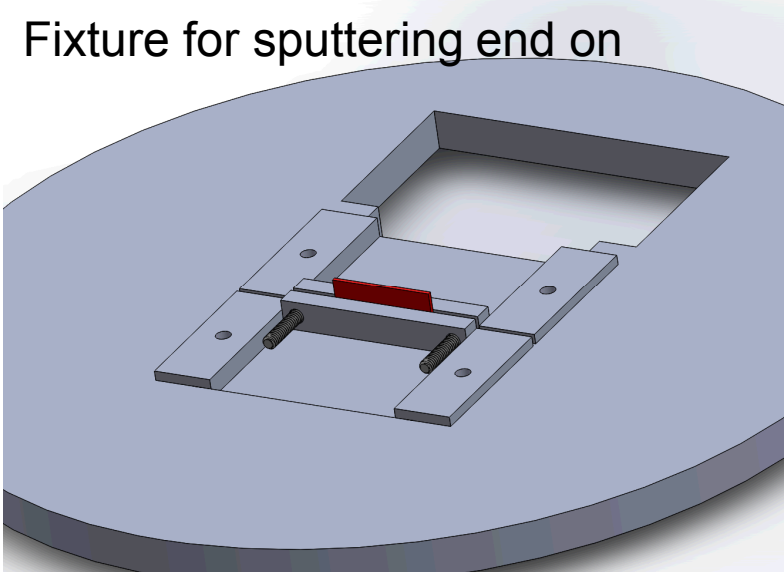
Bond/Polish  
ends



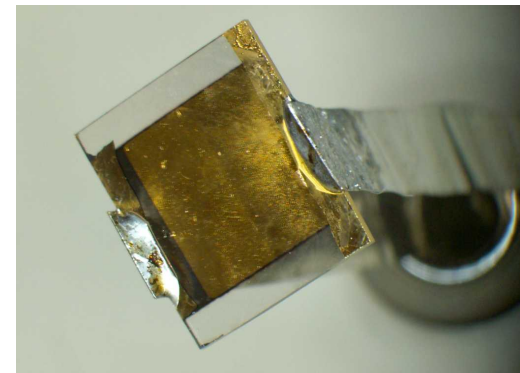
- Active area of capacitor is 0.35"x0.45" (Total area 0.55"x0.65")
  - 10  $\mu\text{m}$  glass provides 500 pF per layer
  - Long term goal is 5  $\mu\text{m}$  (990 pF per layer)

# End Terminations

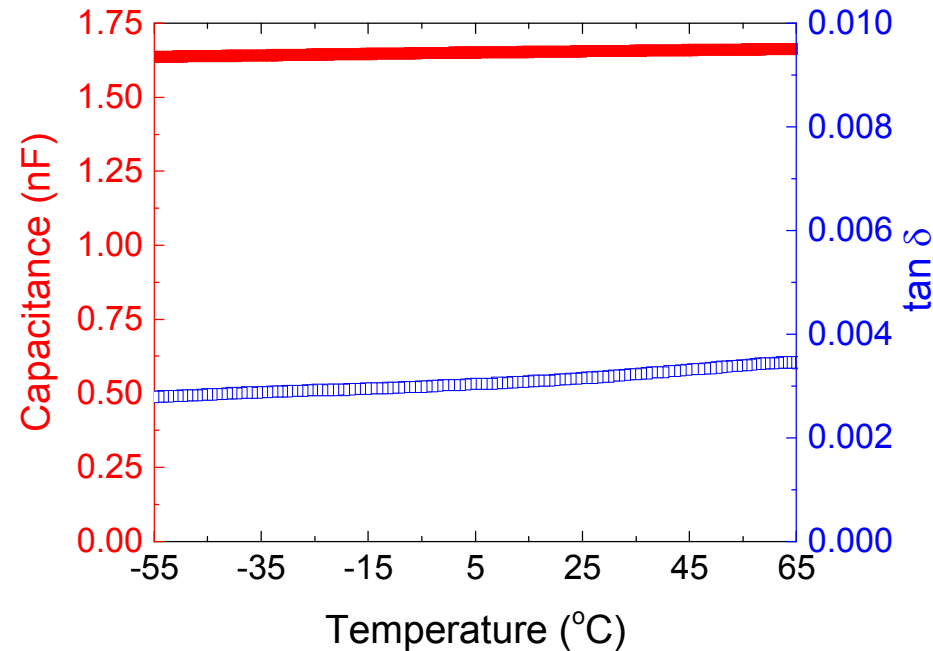
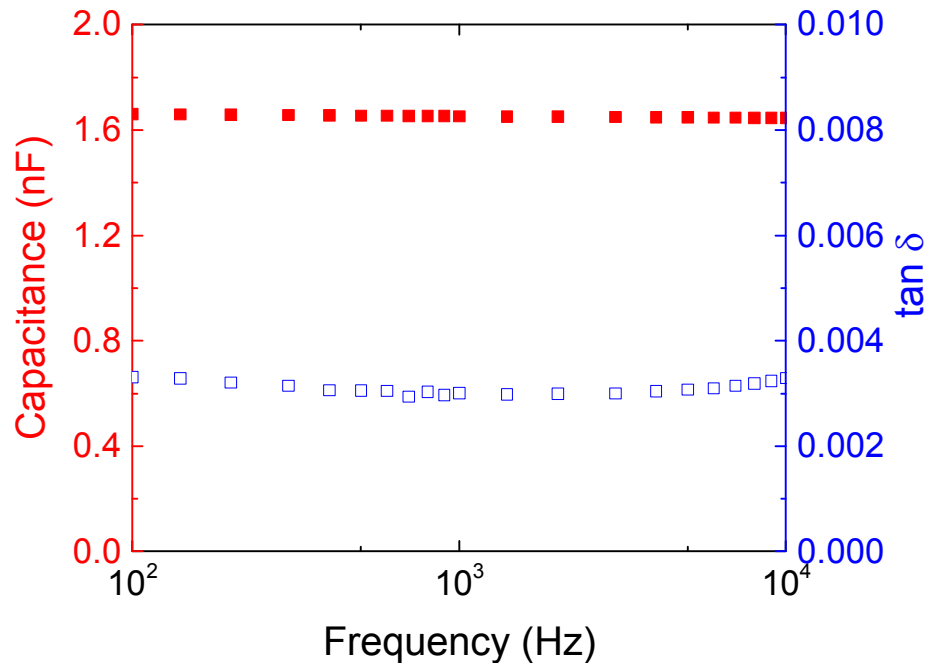
Fixture for sputtering end on



- 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

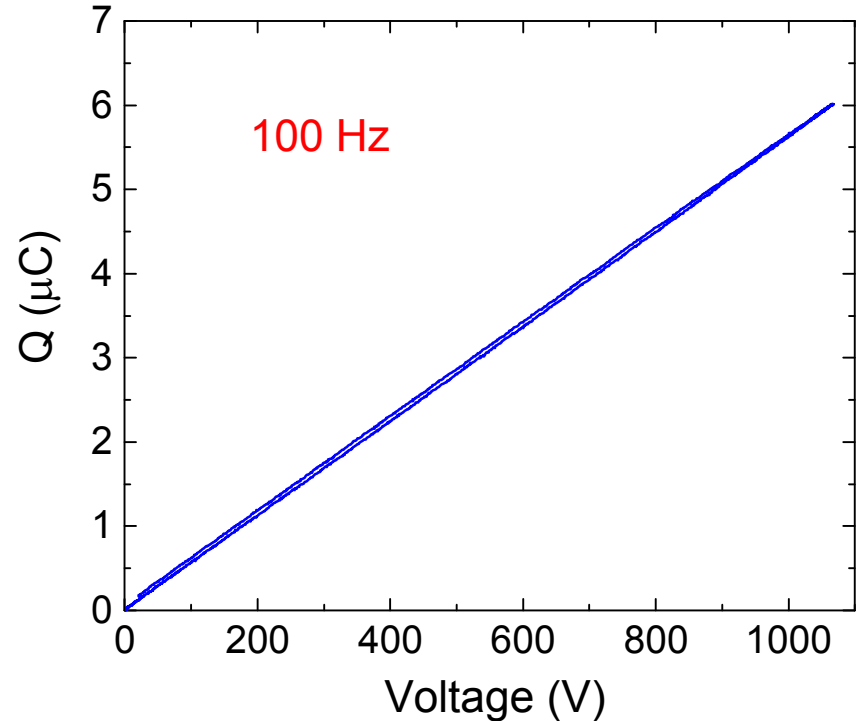
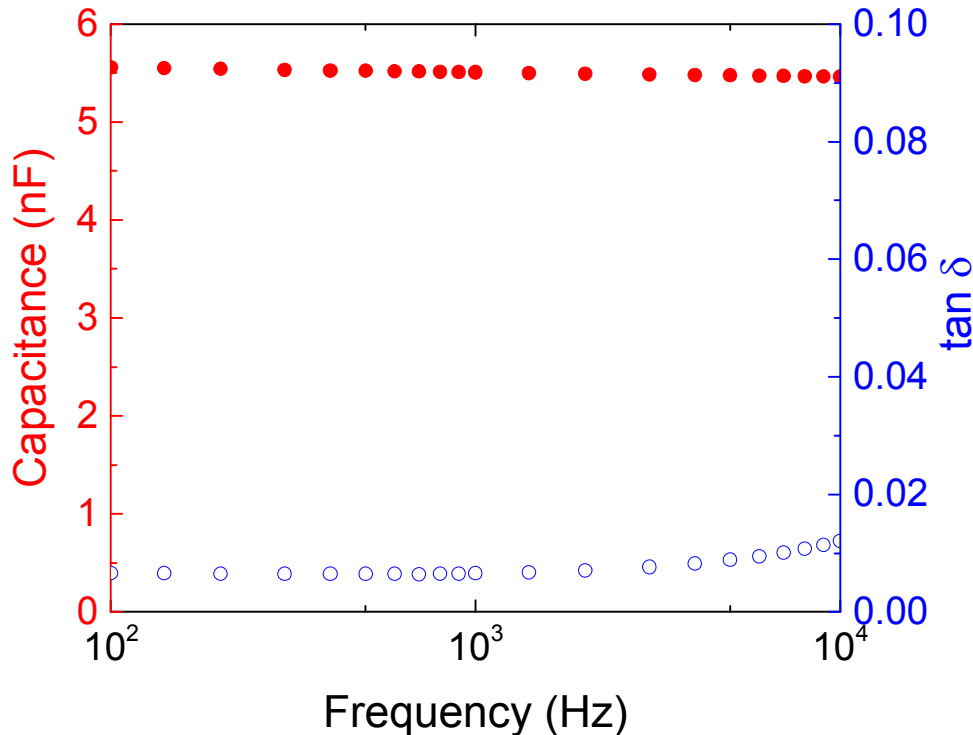


# Capacitor from 30 $\mu\text{m}$ Glass



- 10 layers - 1.65 nF (indicates all layers electrically active)
- Shows better than  $\pm 1\%$  stability over -55  $^{\circ}\text{C}$  to +65  $^{\circ}\text{C}$  (exceeds X4A classification)
- $R = 2.81 \times 10^{13} \Omega$  @ 65  $^{\circ}\text{C}$  ( $RC = 4.7 \times 10^4 \text{ s}$ )
- $V_{\text{Breakdown}} = 9.74 \text{ kV}$  (dielectric  $\Rightarrow 2.8 \text{ J/cc}$ , package  $\Rightarrow 0.4 \text{ J/cc}$ ); need more samples for Weibull analysis
- 150x increase in area vs. Lee report:  $\frac{E_{b1}}{E_{b2}} = \left( \frac{\text{Area}_2}{\text{Area}_1} \right)^{1/\beta} \Rightarrow V_B(\text{MLGC}) \sim 12 \text{ kV}$

# Capacitors from thinned Glass



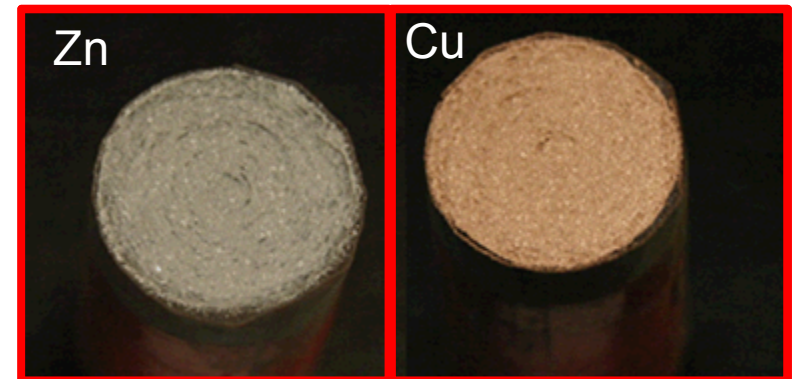
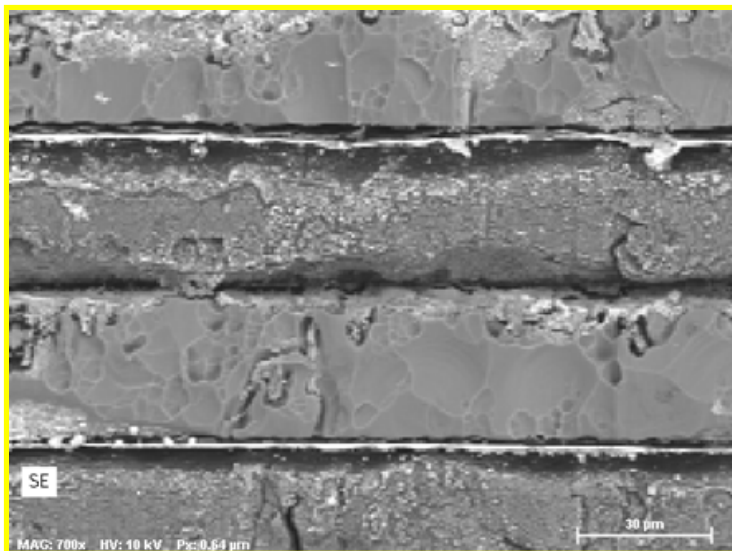
- 10 Layers – 5.5 nF @ 1 kHz
- Tested to 1 kV
  - $E = 3.2 \text{ mJ}, U = 0.09 \frac{\text{J}}{\text{cc}}$
  - 66% value of NovaCap at ceramic

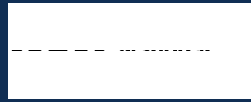


- 50% of volume was from epoxy bonding layer
  - Need to optimize bonding process to reduce inactive volume

# What's Next?

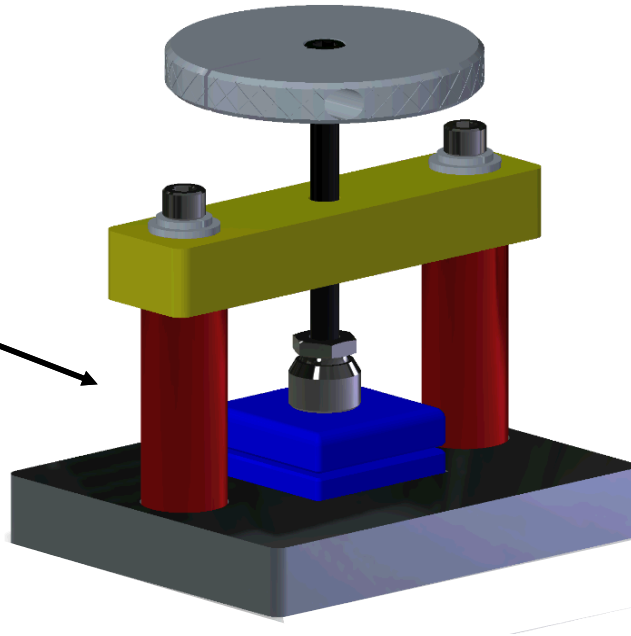
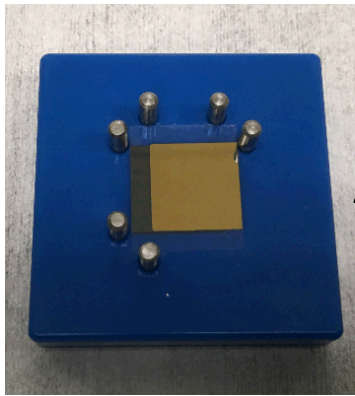
- Decrease dead-space to improve energy density
- Demonstrate more commercially viable processing





# New Fixture for Controlling Pressure

Alignment Fixture

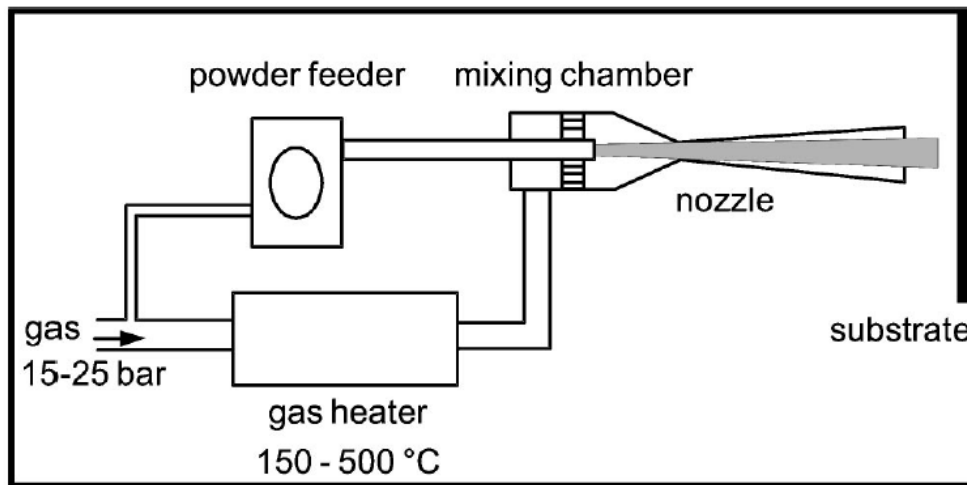


- SS construction allows fixture to be place in oven
- Applied pressure can be controlled by torque wrench or large thumb screw

- 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

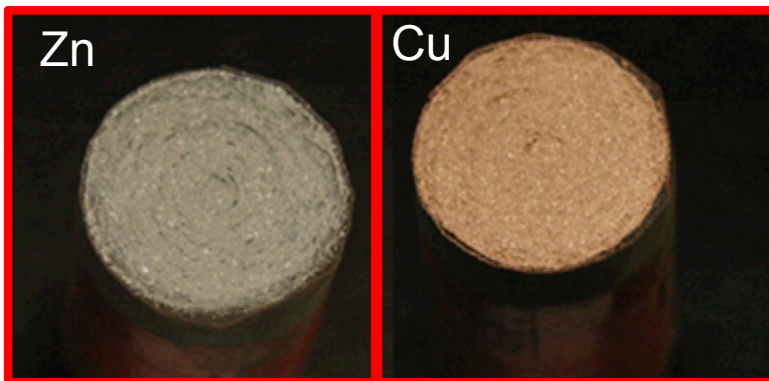


# Investigate Arc-Spray as Route to Apply End Terminations

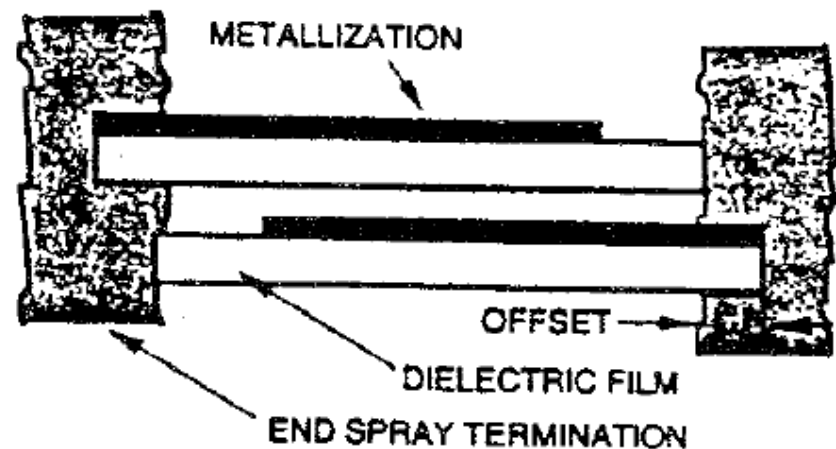


- Zn/Cu arc-spray on polymer capacitors
- Low temperature process – won't damage epoxy/glass structure
- Rapid deposition for thick films ( $>10 \mu\text{m}$ )
- Resistivity of Cu films 40-400  $\mu\Omega\cdot\text{cm}$  (bulk 1.7  $\mu\Omega\cdot\text{cm}$ )

Borchers et al., JAP 2003



Pylin Sarobol, Andrew Miller



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.....