

# Processing of Alkali-free Glass for High Energy Density Capacitors

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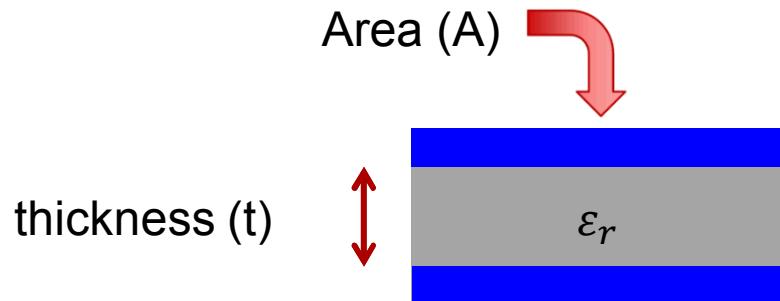


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# Outline

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

# Energy Density of Linear Dielectrics

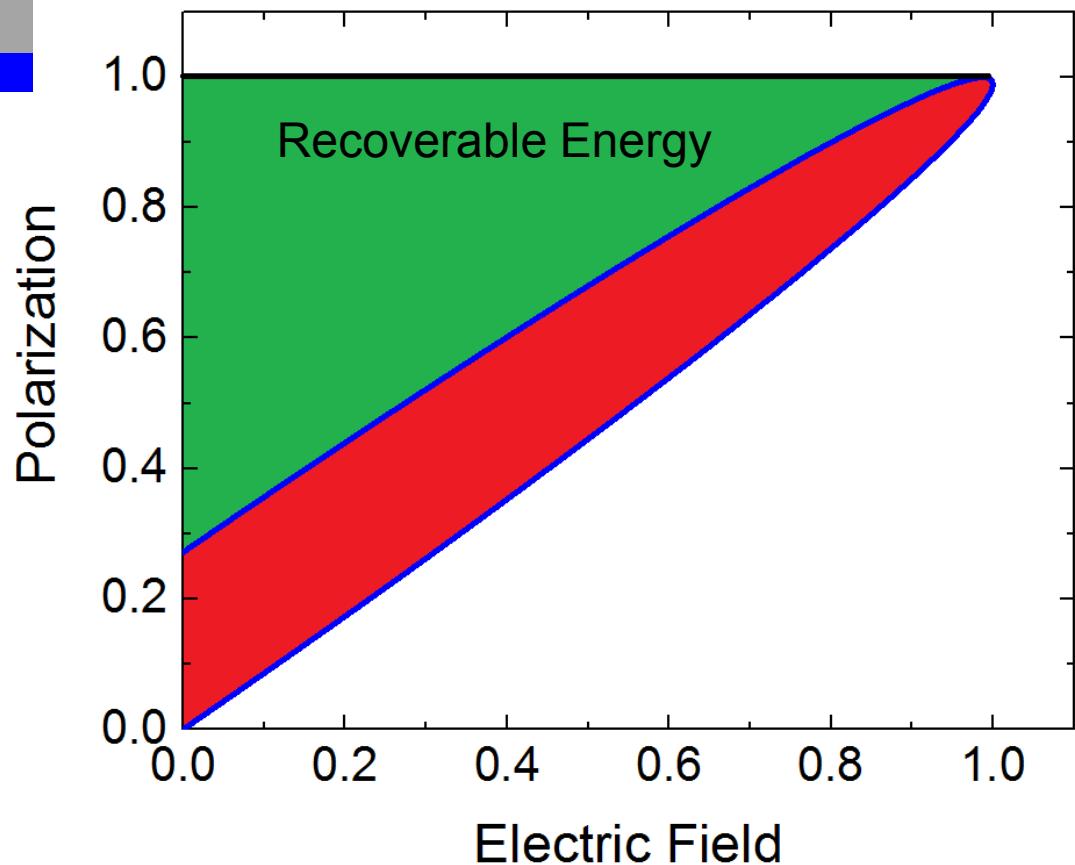


$$C = \epsilon_r \epsilon_0 \frac{A}{t}$$

$$W = \int P dE$$

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

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

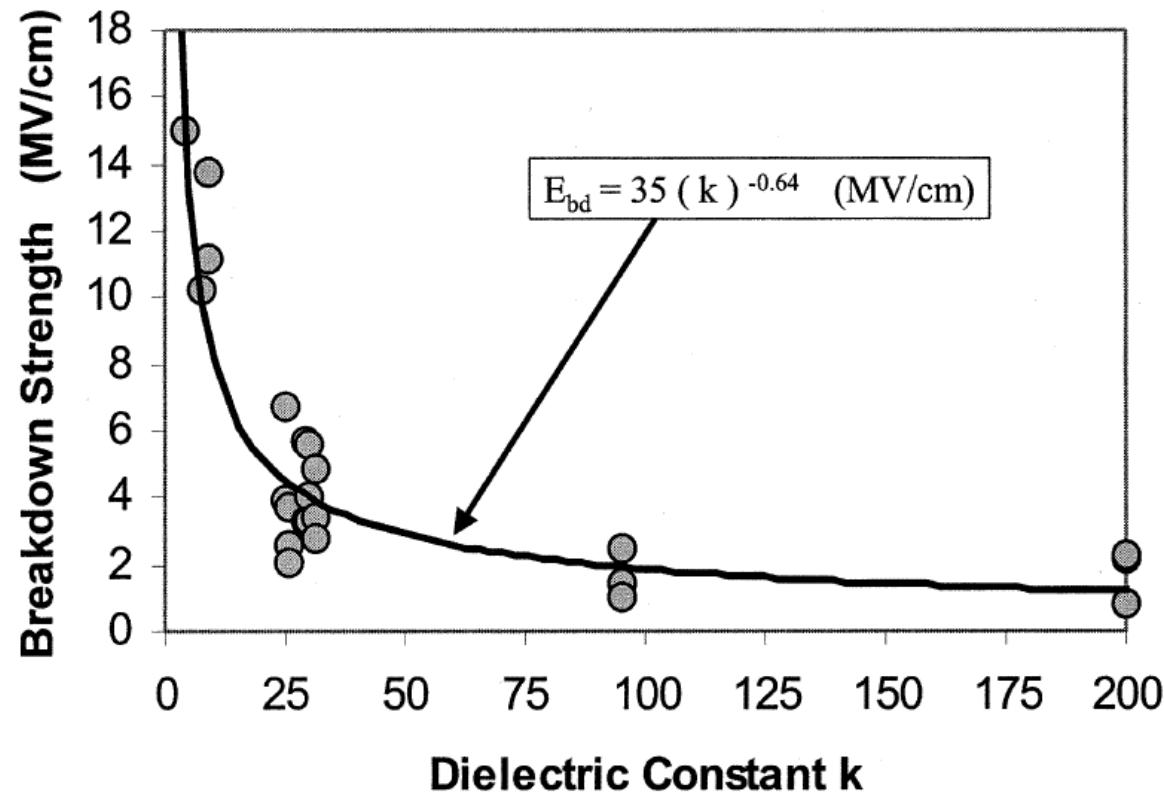


# Energy Density of Linear Dielectrics

Larger gains can be had by increasing breakdown strength

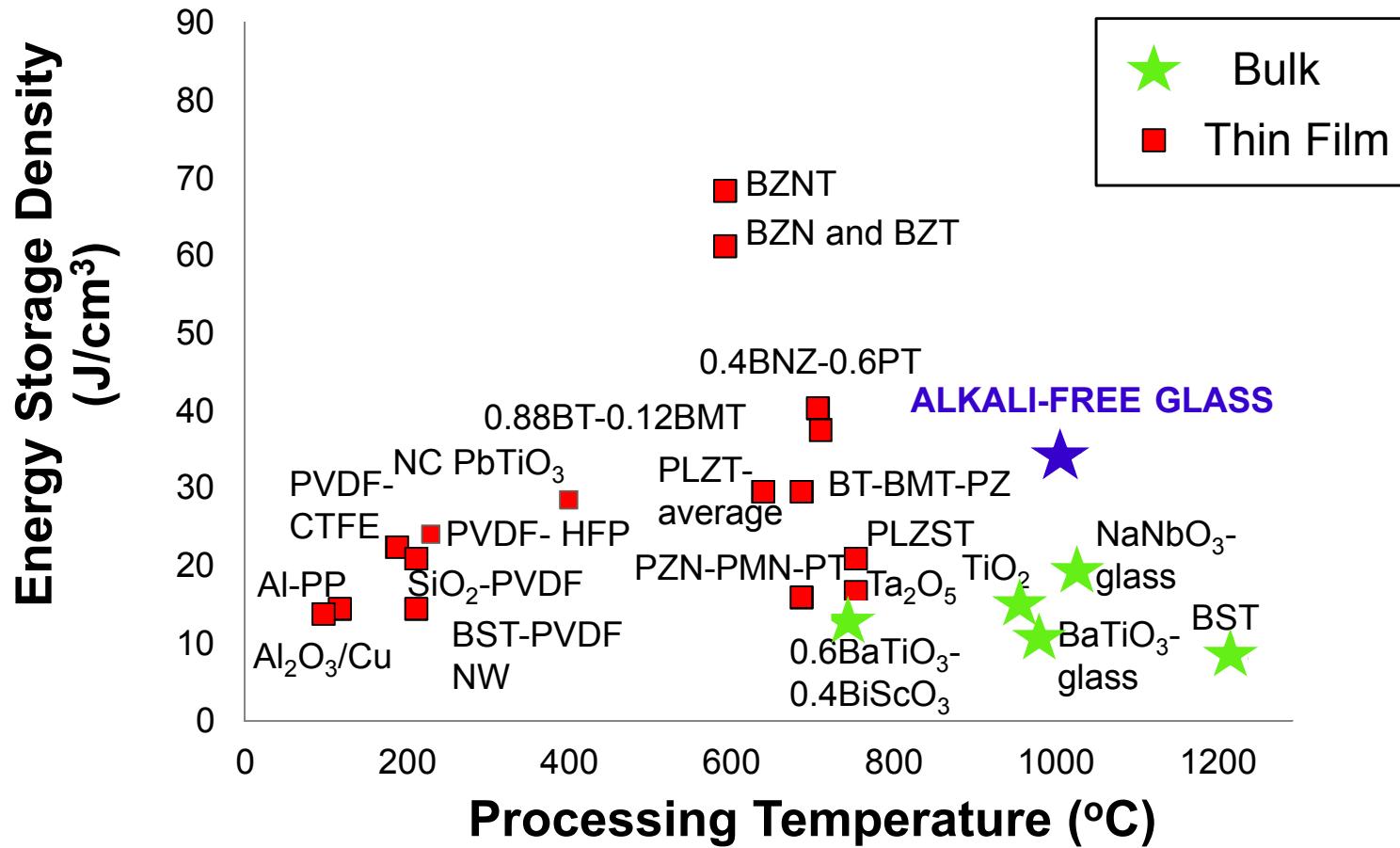
$$U = \frac{\text{Energy}}{\text{Volume}} = \frac{1}{2} \epsilon_r \epsilon_0 E^2$$

Limited value to tuning  $\epsilon_r$



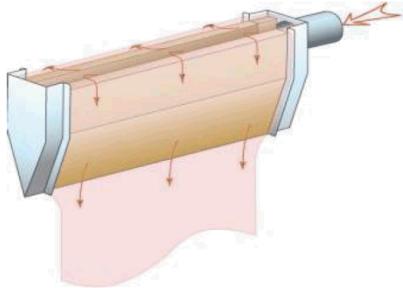
McPherson et al. IEEE TED, 2003

# Comparison of Capacitive Energy Storage Materials



- Alkali-free glass competitive with many emerging materials
- May have an advantage in manufacturing

# Alkali-Free Glasses

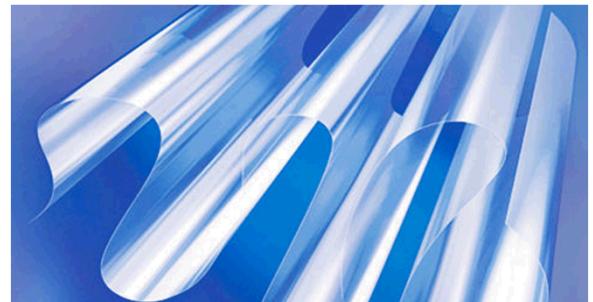


- “Overflow drawn down process”

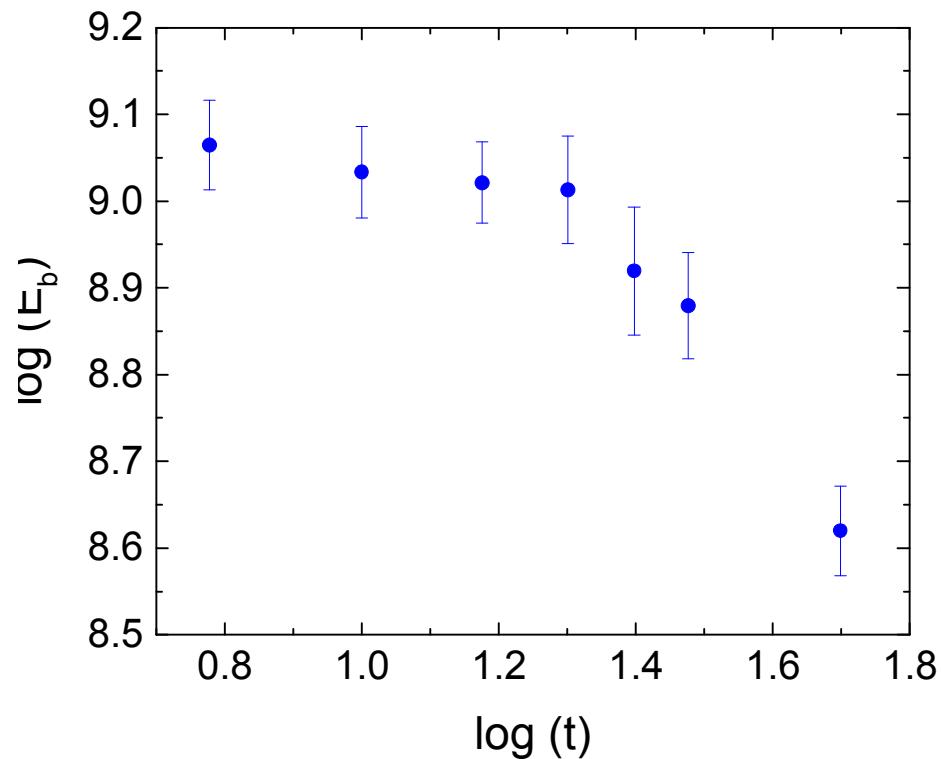
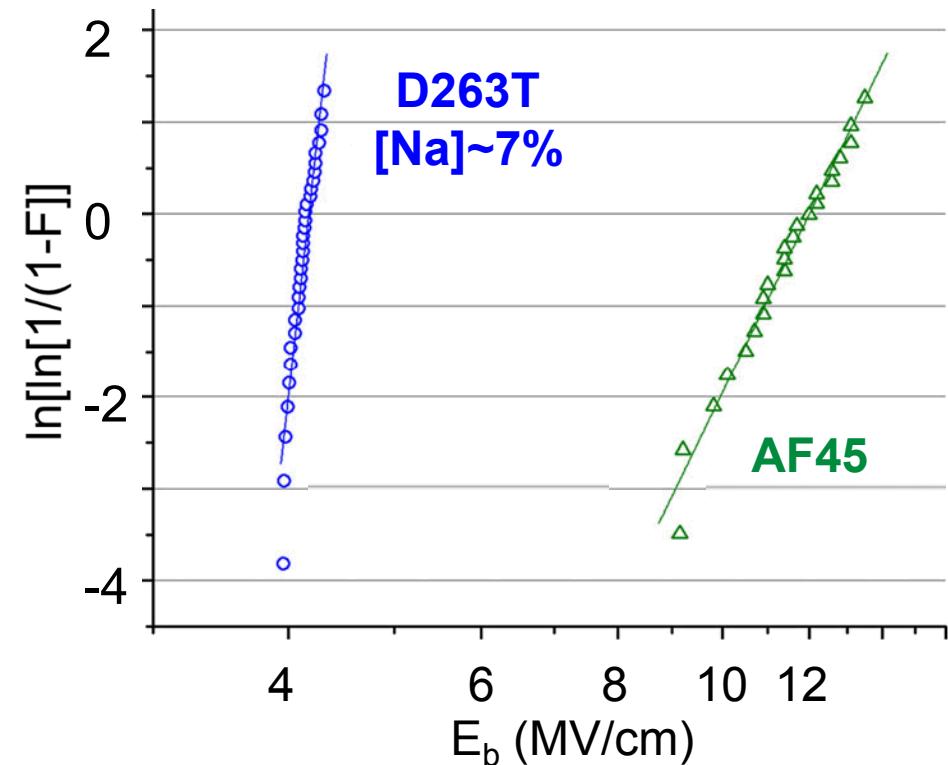


Parameter	Value
Density (g/cm <sup>3</sup> )	2.3-2.5
Young's Modulus (GPa)	73-75
$\epsilon_r$	5-6
$\tan \delta$	0.001
$\rho$ ( $\Omega^*cm$ @ 250 °C)	>10 <sup>12</sup>
Strain Point	650-700 °C

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



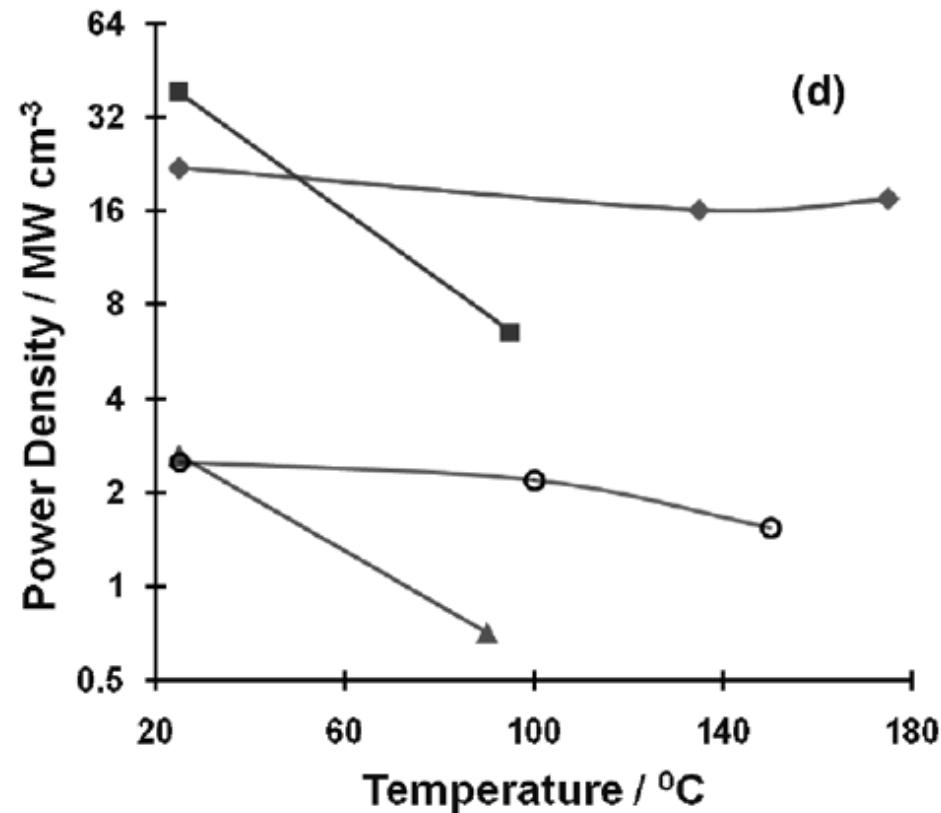
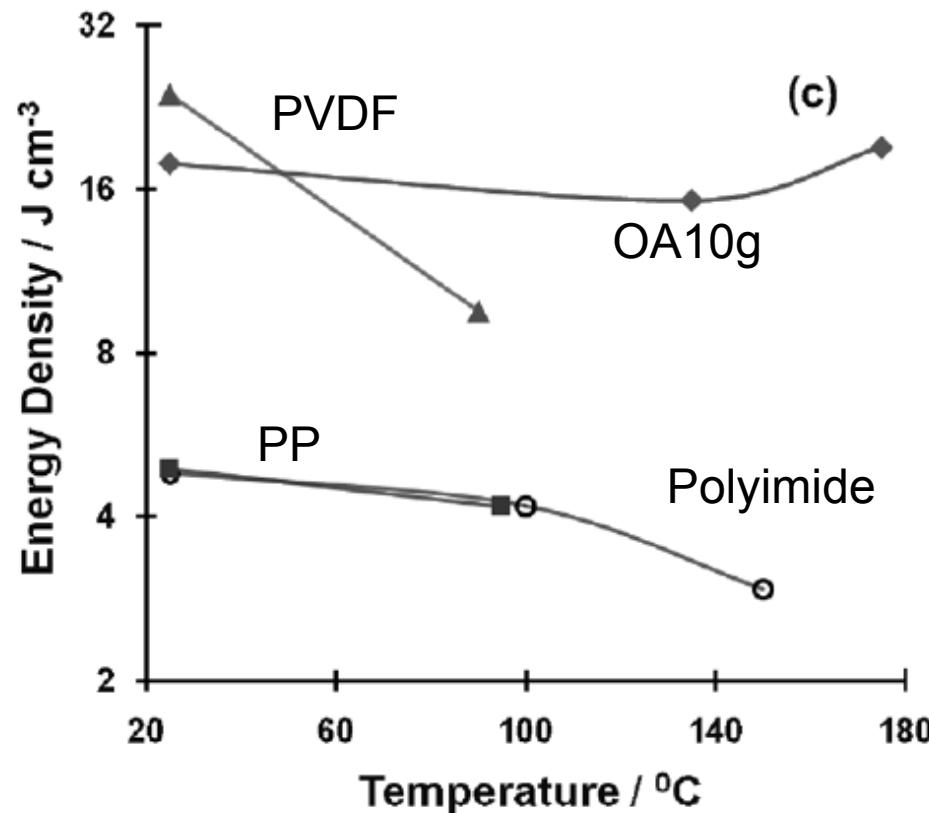
# Breakdown Strength of Alkali-free Glass



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  $t < 20 \mu\text{m}$ ,  $E_b > 10 \text{ MV/cm}$
- $U_{\text{dielectric}} \sim 35 \text{ J/cc}$

# Temperature Stability of “Flexible” Capacitor Materials



- Temperature stable HV properties beyond range achievable by most polymers
- $\text{BaTiO}_3\text{-BiScO}_3$  shows 2-3 J/cc out to 300 °C
- Concentration of Alkali-elements key to minimizing loss at high temperatures

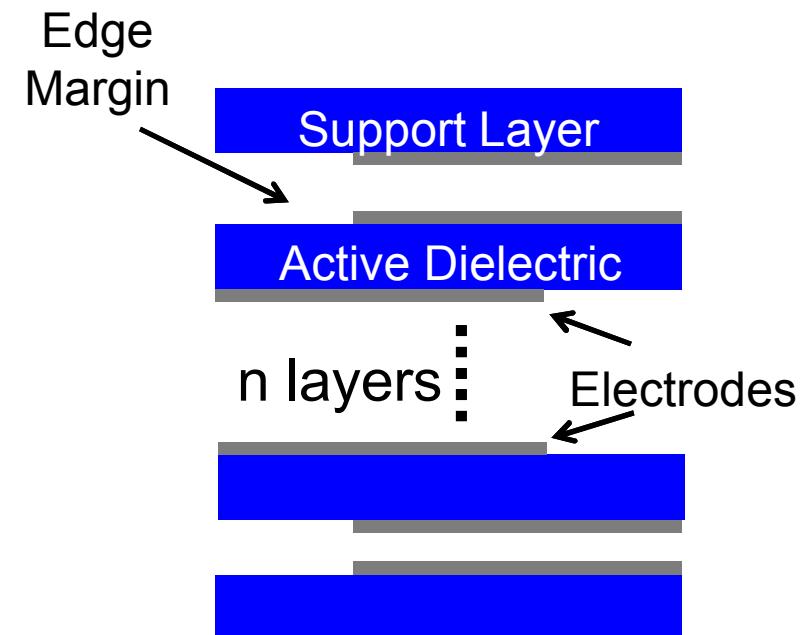
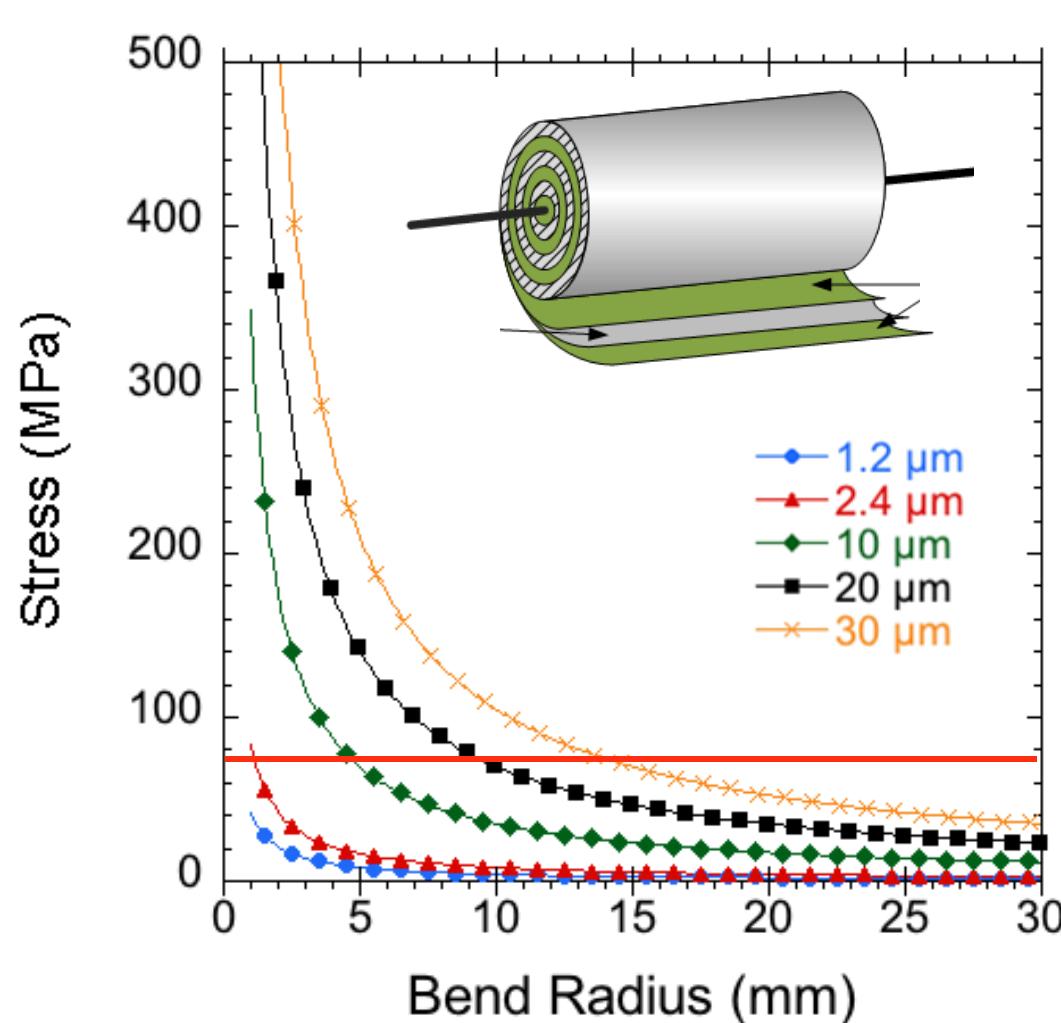
# Thinning of Glass - Motivation



5  $\mu\text{m}$  thick, 8 mm diameter

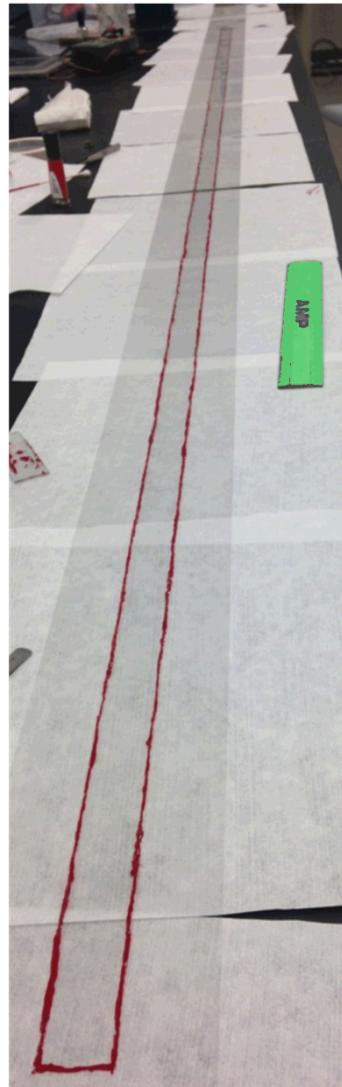
- Alkali-free glass has found wide use in cell phone, display applications
- Commercially sold in thickness  $> 100 \mu\text{m}$  (1.3 x 300 m rolls)
- $\epsilon_r \sim 5-6 \Rightarrow$  Need massive area ( $> 20 \text{ cm}^2$ ) to achieve 1 nF capacitance

# Thinned Glass Capacitors Designs



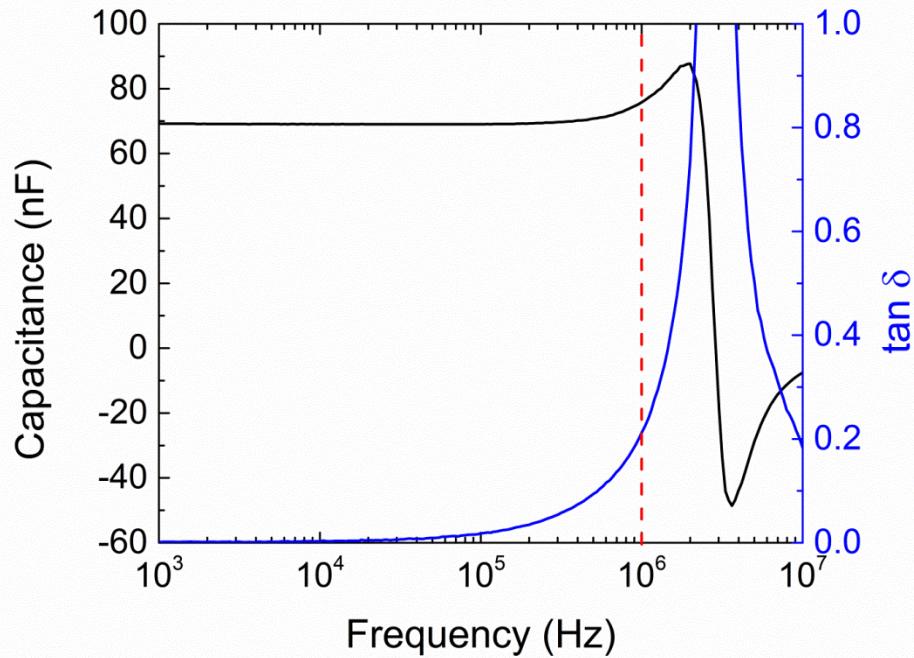
- Top/Bottom sheets for physical support
- Edge margin to avoid flashover
  - Needs insulating fluid to avoid triple points

# Fabrication of a Wound Capacitor



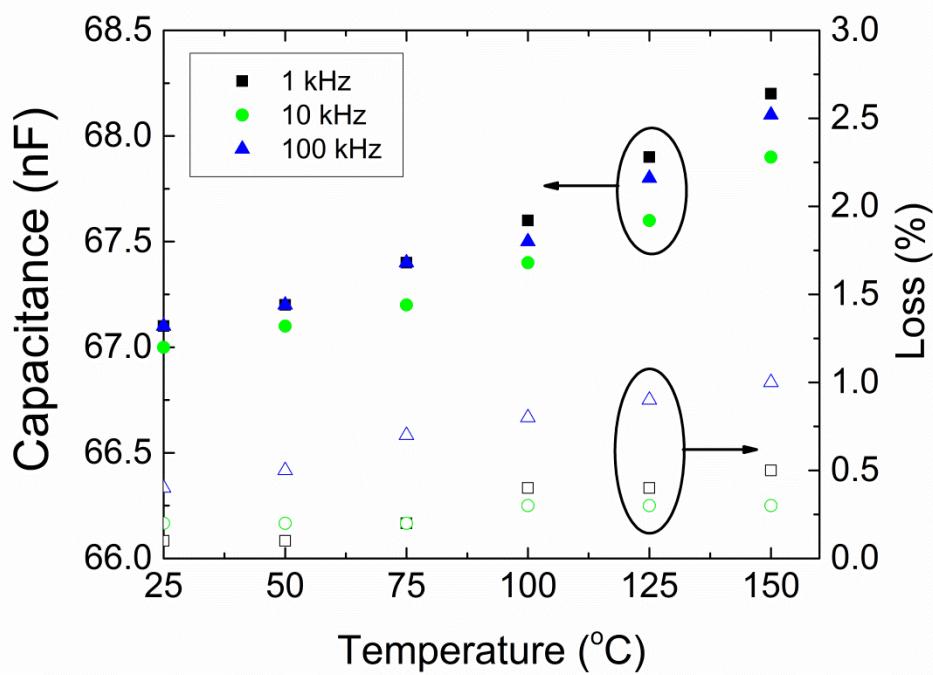
- 2.7 m long piece of 50  $\mu\text{m}$  thick NEG Glass
- Designed to have electrode tabs to limit electrode resistance and inductance effects
- 12  $\mu\text{m}$  polypropylene sheet glued around edges to prevent flashover
- Wound around 5.5 inch diameter spool

# Electrical Properties of Wound Capacitor



- Show good temperature stability to  $150^{\circ}\text{C}$  (low frequencies)
- $U_{\text{dielectric}} \sim 10 \text{ mJ/cc}$ ,  $U_{\text{capacitor}} \sim 0.5 \text{ pJ/cc}$

- Self-resonance above 1 MHz
- $L \sim 90 \text{ nH}$

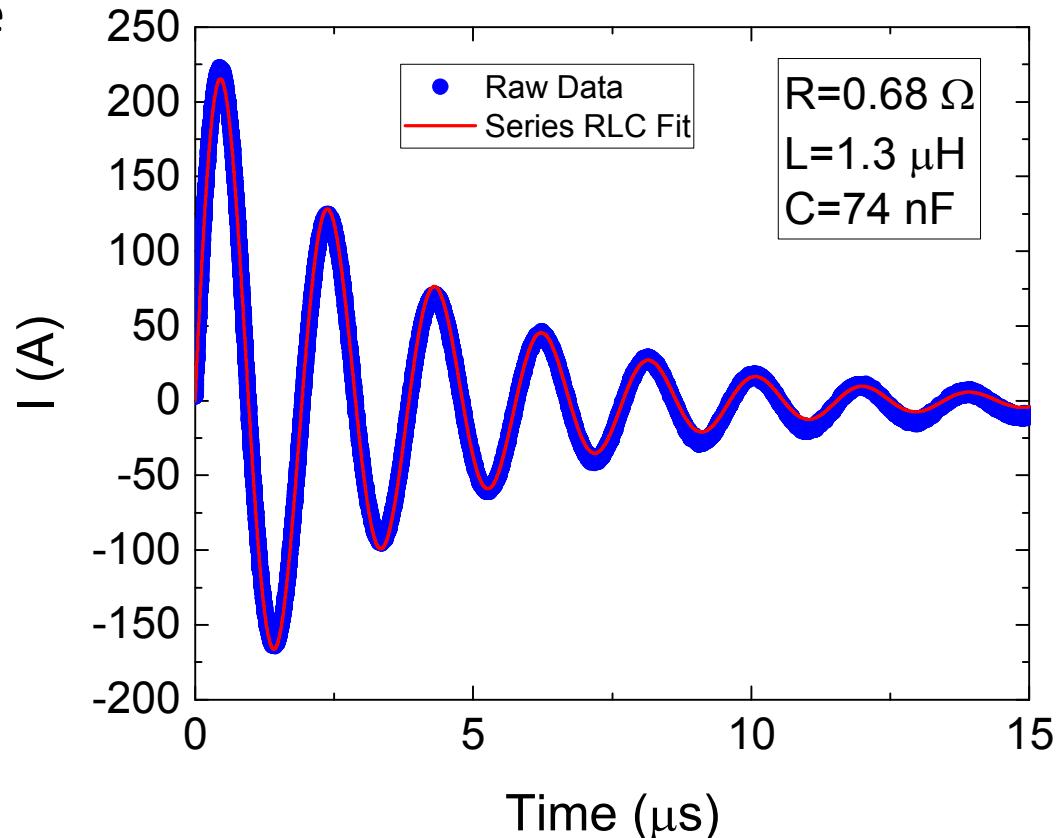


# Pulsed Discharge of Wound Capacitor

- Underdamped RLC discharge

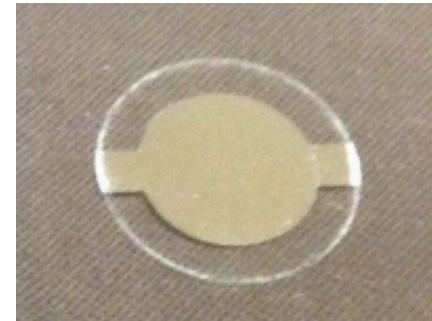
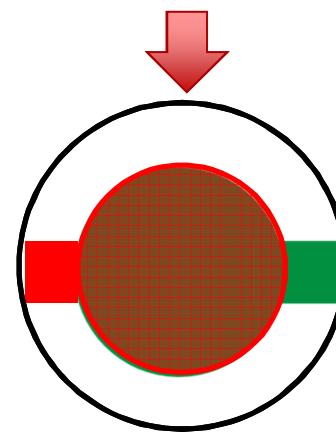
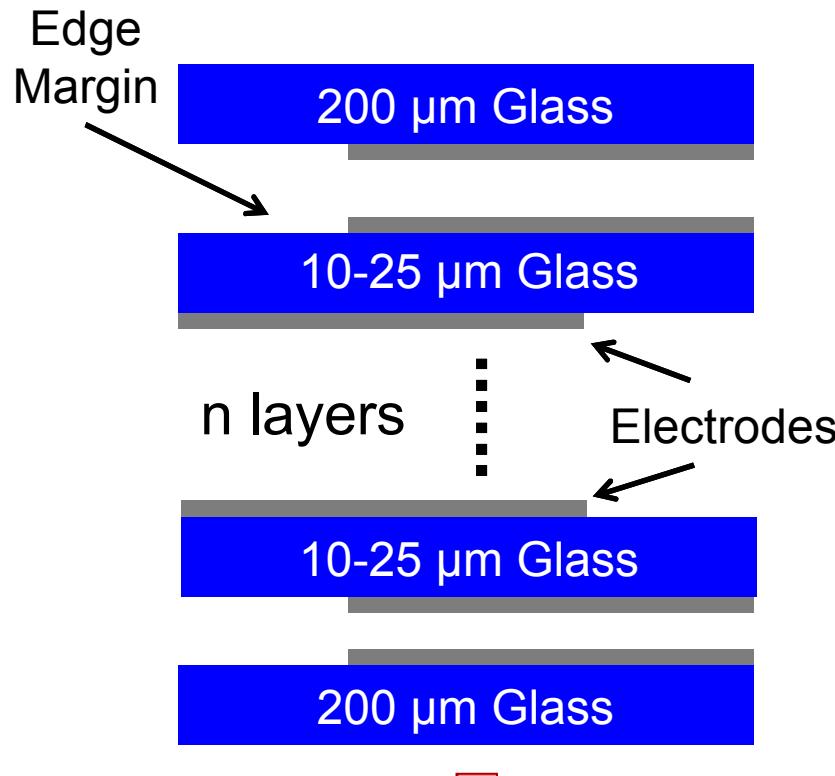
$$I(t) = \frac{V_0}{\omega_0 L} e^{\left(-\frac{Rt}{2L}\right)} \sin(\omega_0 t)$$

$$\omega_0 = \sqrt{\frac{1}{LC} - \left(\frac{R}{2L}\right)^2}$$



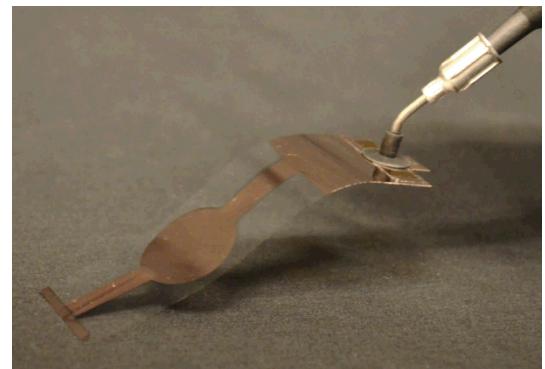
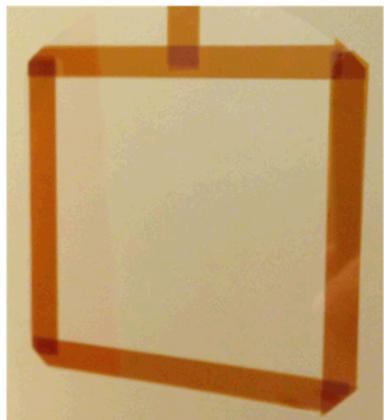
- Charged to 1000 V
- Could not compensate for lead inductance.

# Fabrication Approach for Multi-layer Glass Capacitor



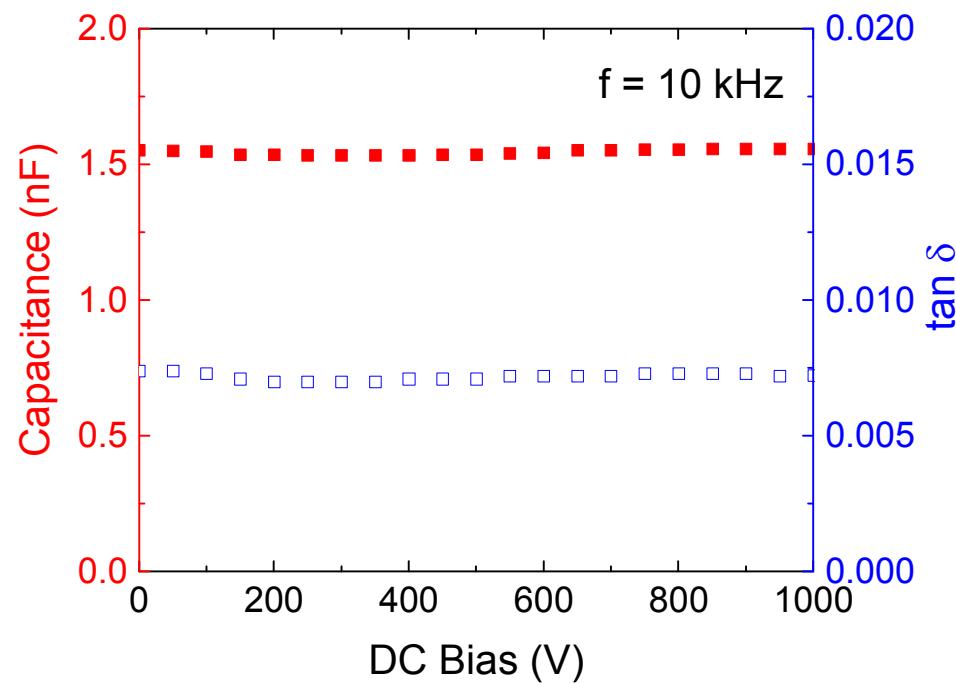
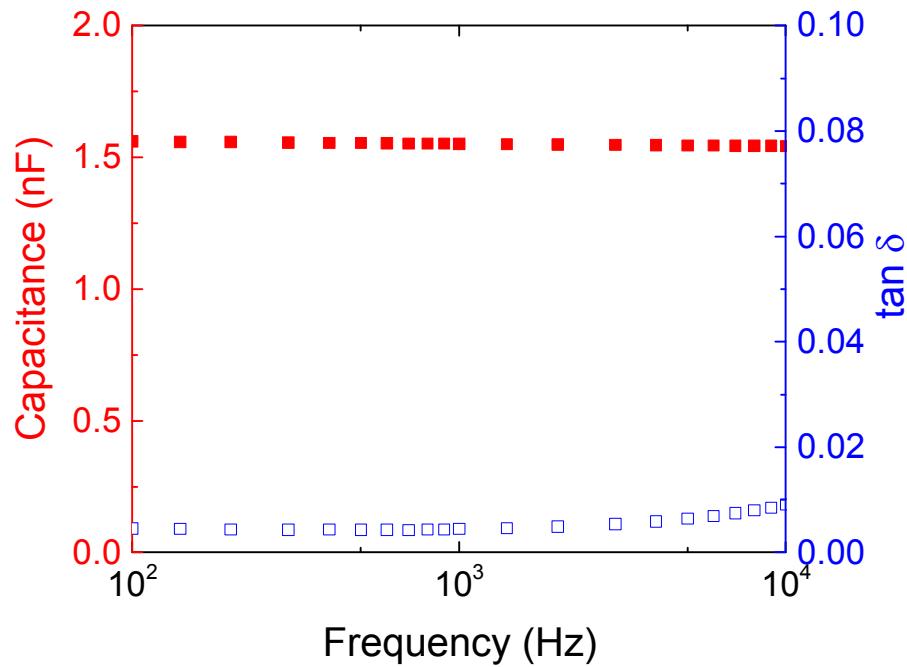
- Pattern 0.75" diameter electrode with edge tab
  - Electrode deposition top and bottom – rotated 180°
- Laser cut glass to form individual capacitor layer
  - Edge margin is 0.125" ( $\sim 10$  kV hold off voltage in air)

# Thinning of Glass - Process



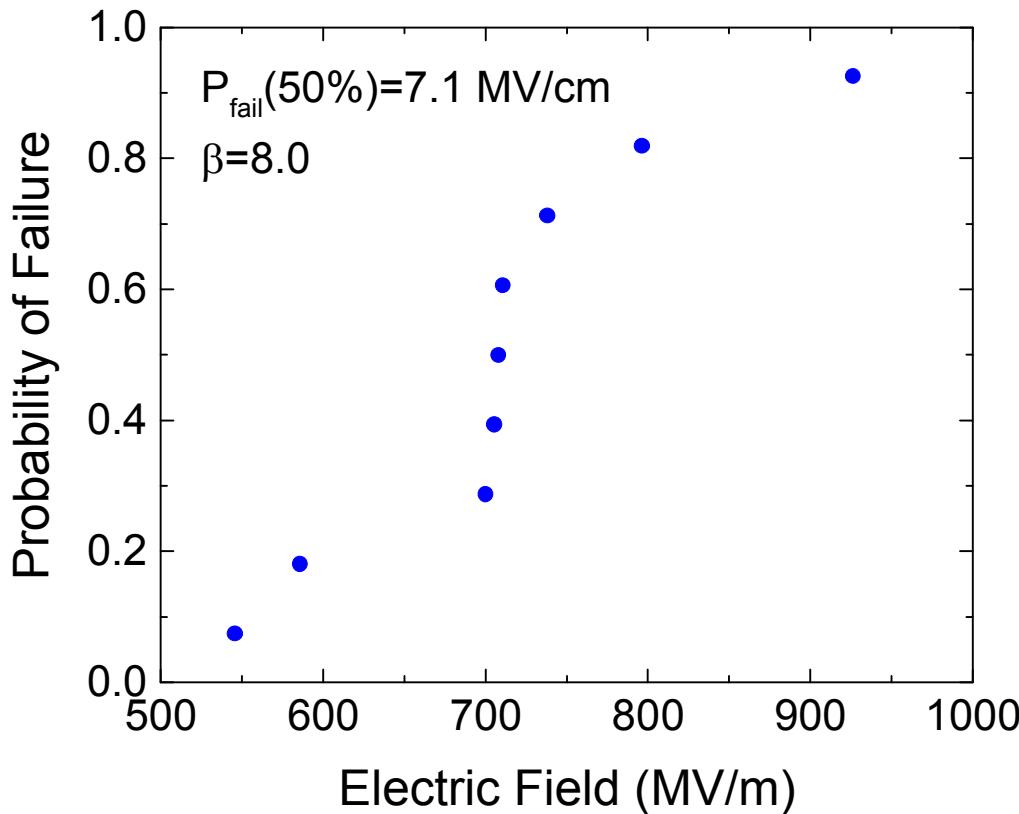
- Glass is masked on edges – provide mechanical structure for thinned samples
- Etched in 2.5% HF solution ( $0.01 \mu m/s$ )
- Ti/Pt contacts

# Electrical Properties of nF Sized “Bulk” Capacitors



- Corning Willow thinned to  $\sim 25$   $\mu\text{m}$  thickness
- Electrode size = 1 inch ( $5.07 \text{ cm}^2$ )
- Flat frequency response with no tunability at 1 kV
- $\rho > 10^{15} \Omega \cdot \text{cm}$

# Breakdown Characteristics of Thinned Corning Willow Glass

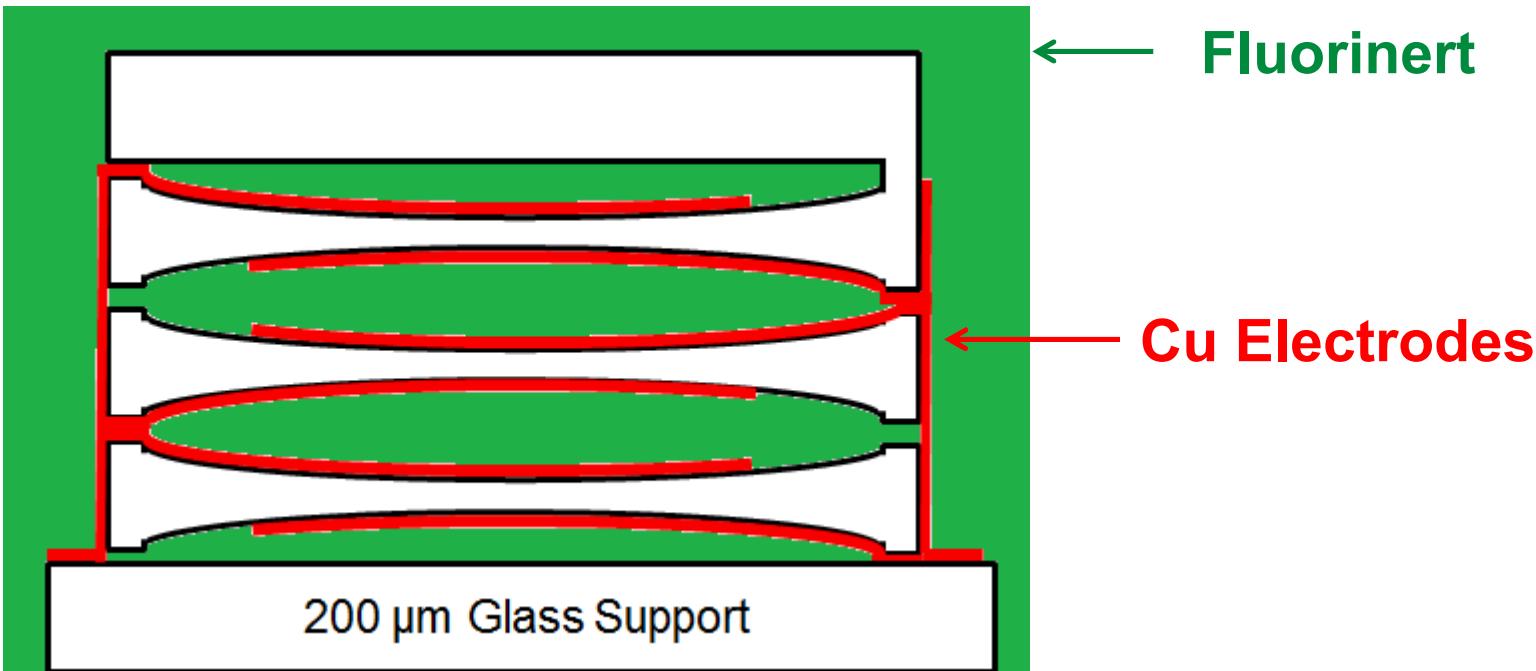


- $t \sim 19 \mu\text{m}$  (estimated from capacitance)
- Area  $\sim 9.6 \text{ mm}^2$  (Lee et al. Area  $\sim 1.6 \text{ mm}^2$ )

$$\frac{E_{b1}}{E_{b2}} = \left( \frac{Area_2}{Area_1} \right)^{1/\beta}$$

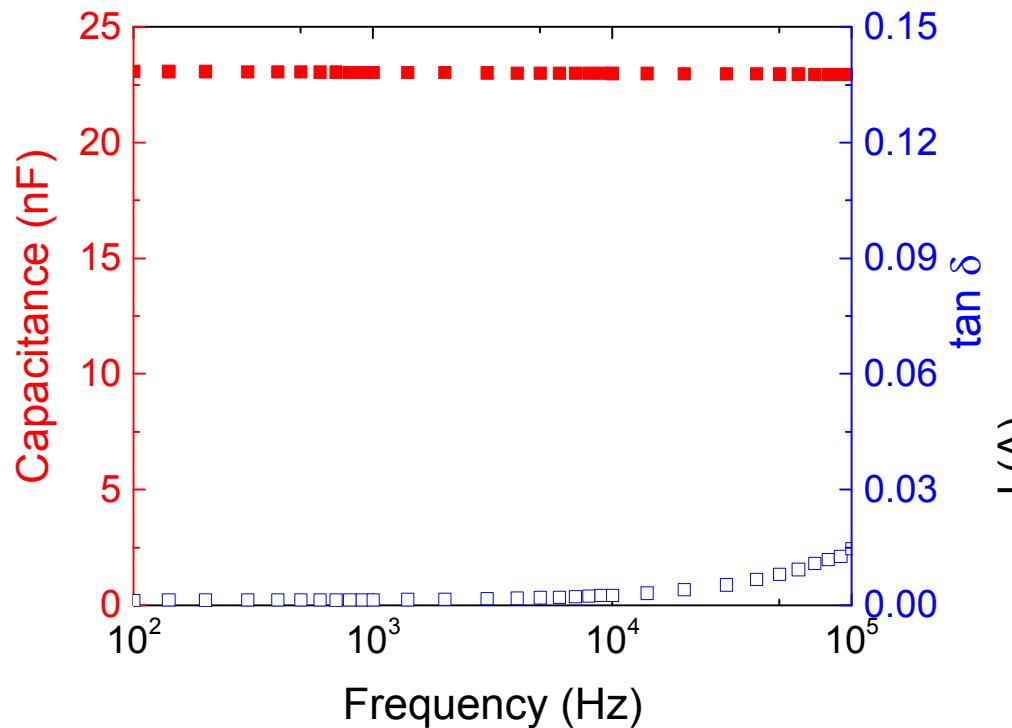
- Breakdown strength scales with area (greater probability of sampling defects)
- Weibull Statistics prediction of  $E_b$  of AF45 = 8.0 MV/cm

# Fabrication of Large Area/Multi-Layer Capacitor

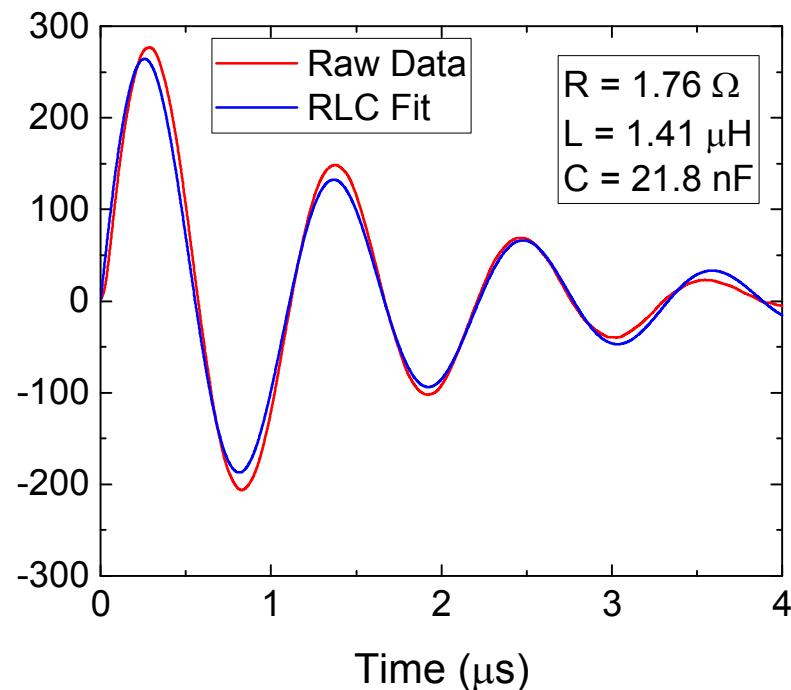


- Left 200  $\mu\text{m}$  thick support frame around 25  $\mu\text{m}$  thick thinned glass (60 mm  $\times$  60 mm)
- Immersed in Fluorinert for measurement
- Layers bonded together using air dried silver paint

# Properties of Multi Layer Glass Capacitor



Pulsed Discharge – 2.5 kV



- $C(1 \text{ kHz}) = 23.0 \text{ nF}$ ,  $\tan \delta = 0.001$
- $U_{\text{dielectric}} \sim 0.24 \text{ J/cc}$  – need to improve end termination to push  $E_{\text{applied}}$
- $U_{\text{capacitor}} \sim 70 \text{ mJ/cc}$  - can increase by increasing  $n$ , decreasing edge margin, using thinner support layers

# Conclusions



- Alkali-free glasses show great promise for high energy density capacitors
  - Literature reports of
    - $E_b > 1 \text{ GV/m}$
    - $U_{\text{dielectric}} \sim 35 \text{ J/cc}$
    - Alkali content is crucial for high energy density and temperature stability
  - Challenging to make and handle!
    - With sufficiently thin glass, wound capacitors are possible
    - Our approach – thin and build multi-layer capacitor
      - Have process for thinning to  $10 \mu\text{m}$  (1-2 nF per layer)
      - Have process to electrode and cut individual layers
      - Stacking:
        - » Demonstrate 23 nF on 3 layer stack with  $36 \text{ cm}^2$  electrodes
        - » Next step: stack laser cut layers to build 10-100 nF capacitor

# Acknowledgements



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