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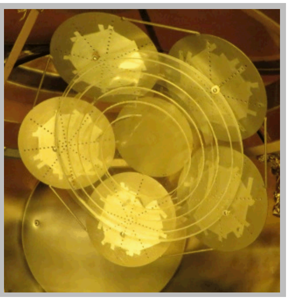

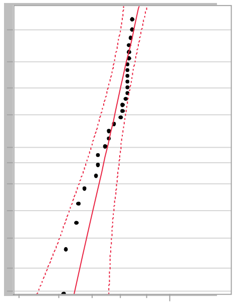

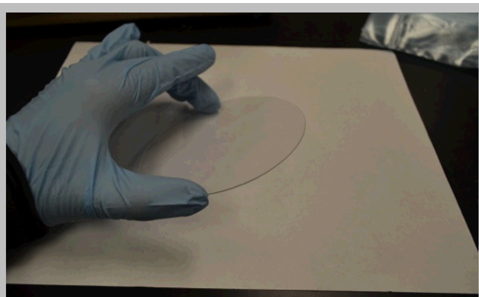

Alkali-free Glass for High Energy Density Capacitors

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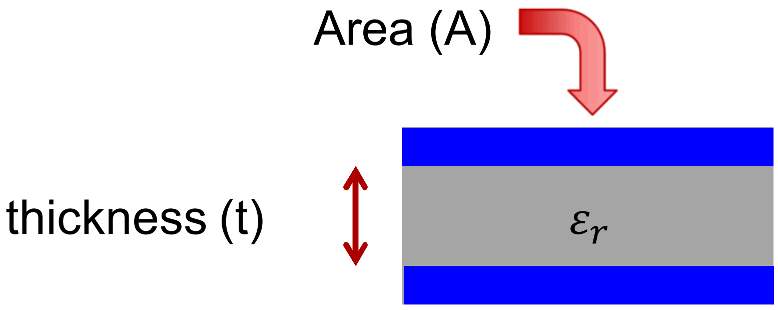
Outline

- 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

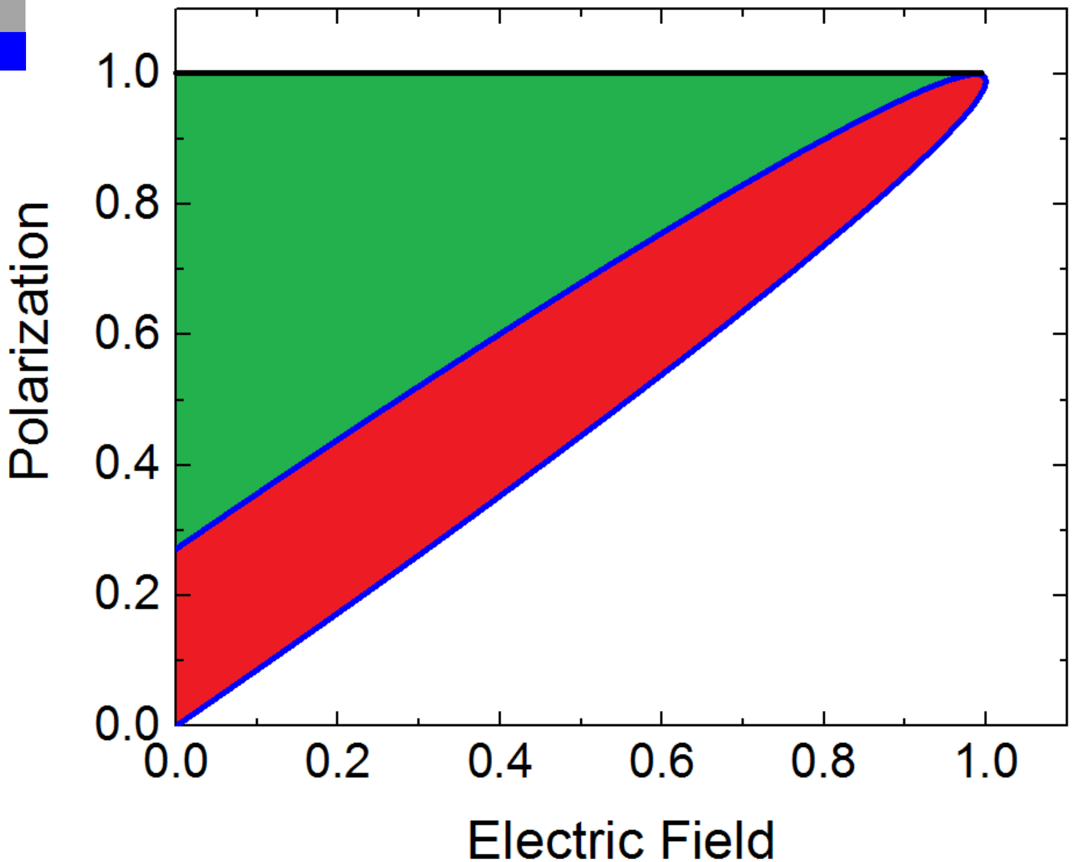


$$C = \varepsilon_r \varepsilon_0 \frac{A}{t}$$

$$W = \int P dE$$

$$W = \frac{1}{2} C V^2 = \frac{1}{2} \varepsilon_r \varepsilon_0 \frac{A}{t} V^2$$

$$U = \frac{Energy}{Volume} = \frac{1}{2} \varepsilon_r \varepsilon_0 E^2$$



Energy Density of Linear Dielectrics

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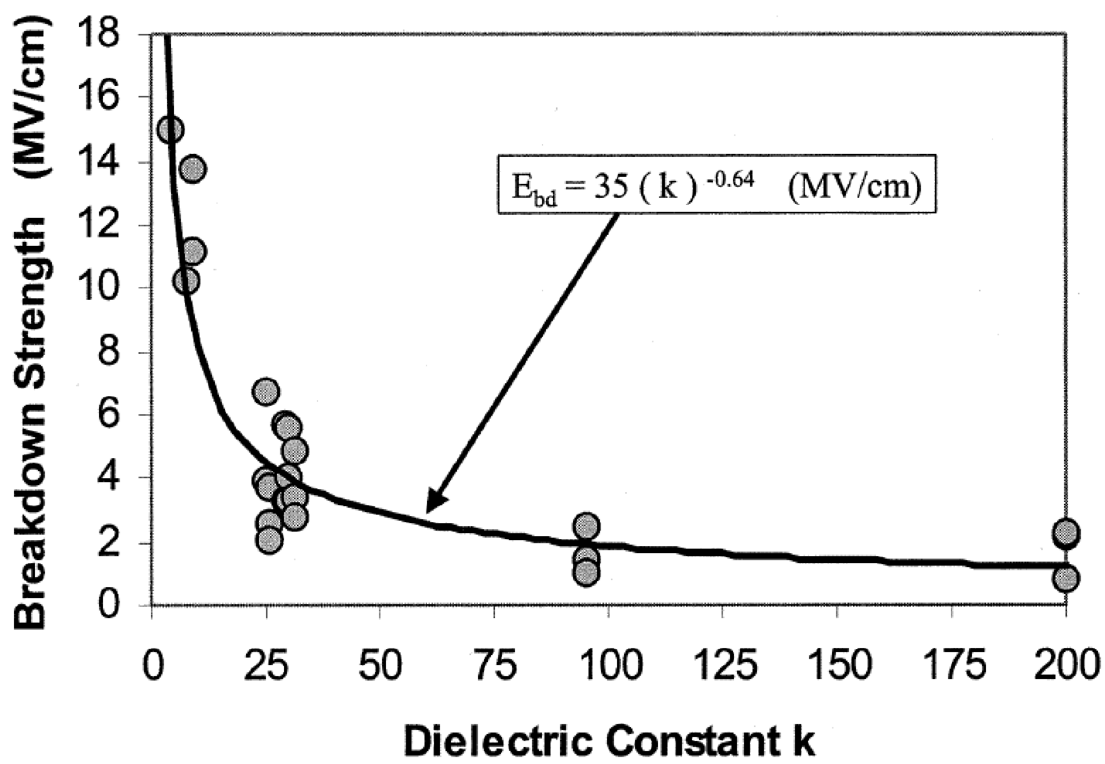
Larger gains can be had by increasing breakdown strength

$$U = \frac{Energy}{Volume} = \frac{1}{2}\varepsilon_r \varepsilon_0 E^2$$

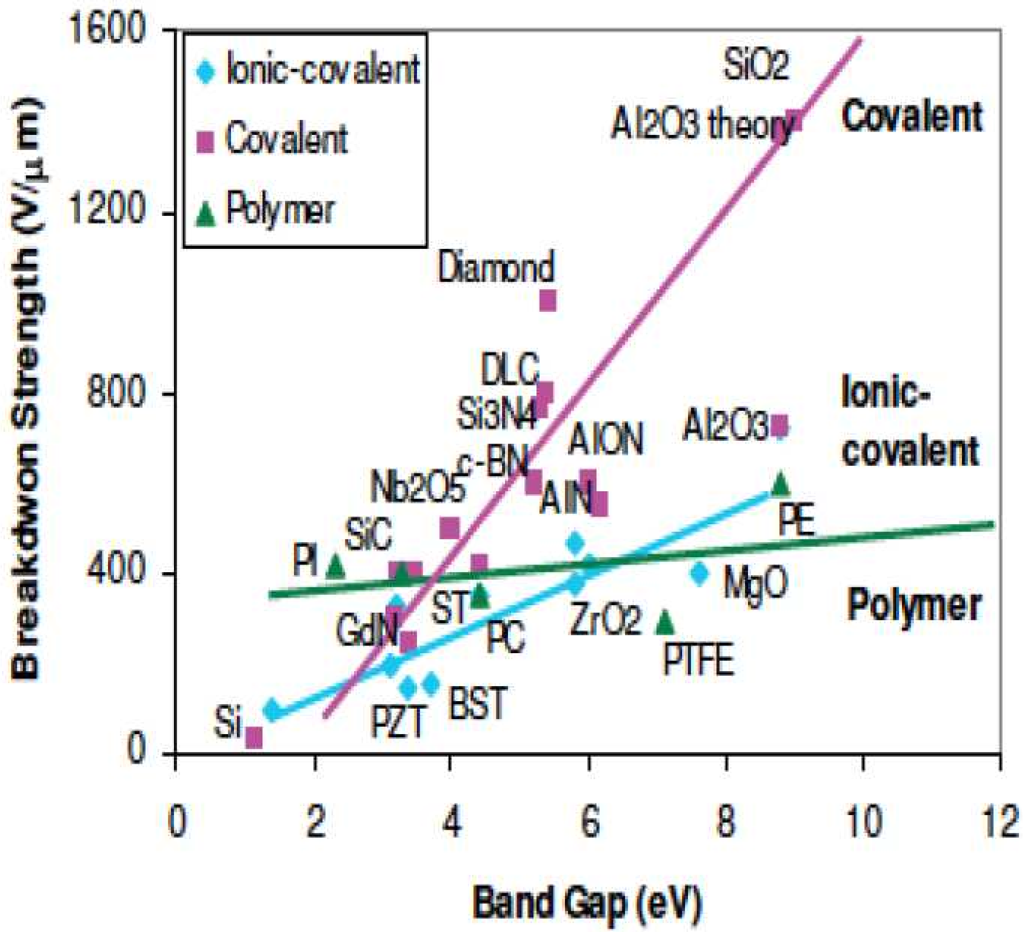
Limited value to tuning ε_r



McPherson et al. IEEE TED, 2003

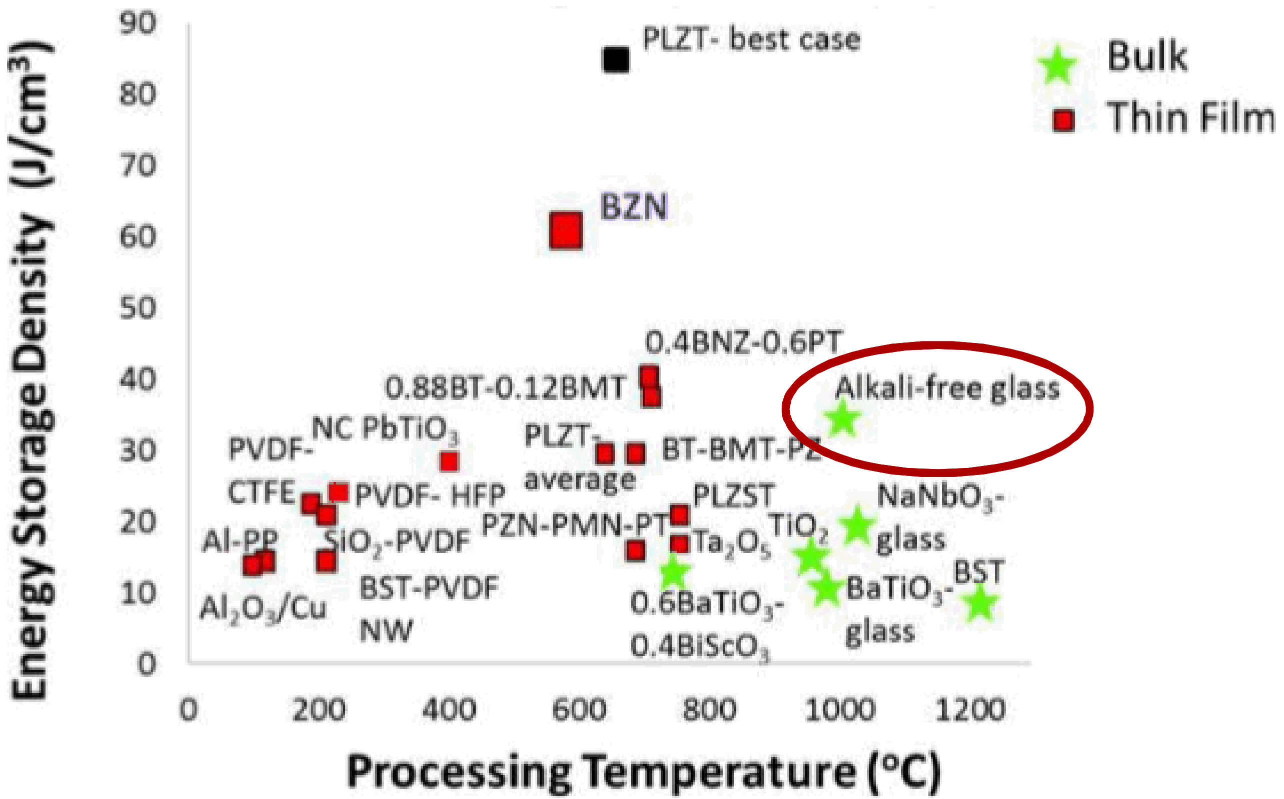
Glass as a Dielectric Material

- Covalently bonded materials have higher bond strength – larger band gaps – higher breakdown strength
- Si-O bond very strong (460 kJ/mol)
- Glasses lack grain boundaries
- Modifiers allow limited tuning of permittivity



Tan et al. ICSD 2007

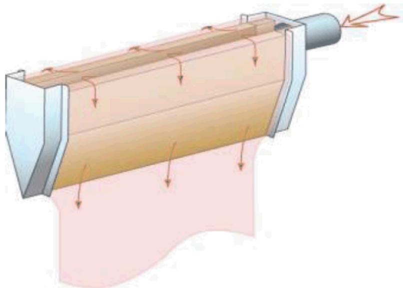
Capacitive Energy Storage Materials



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

Michael et al., JACERS 2015

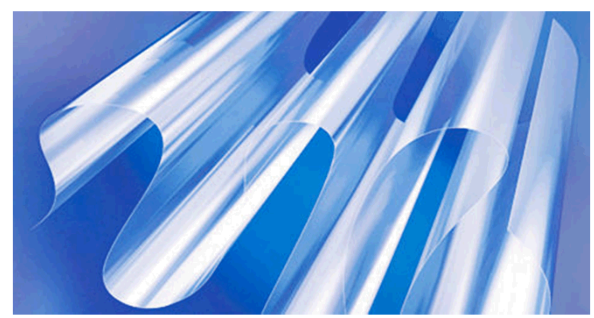
Alkali-Free Glasses



- "Overflow drawn down process"

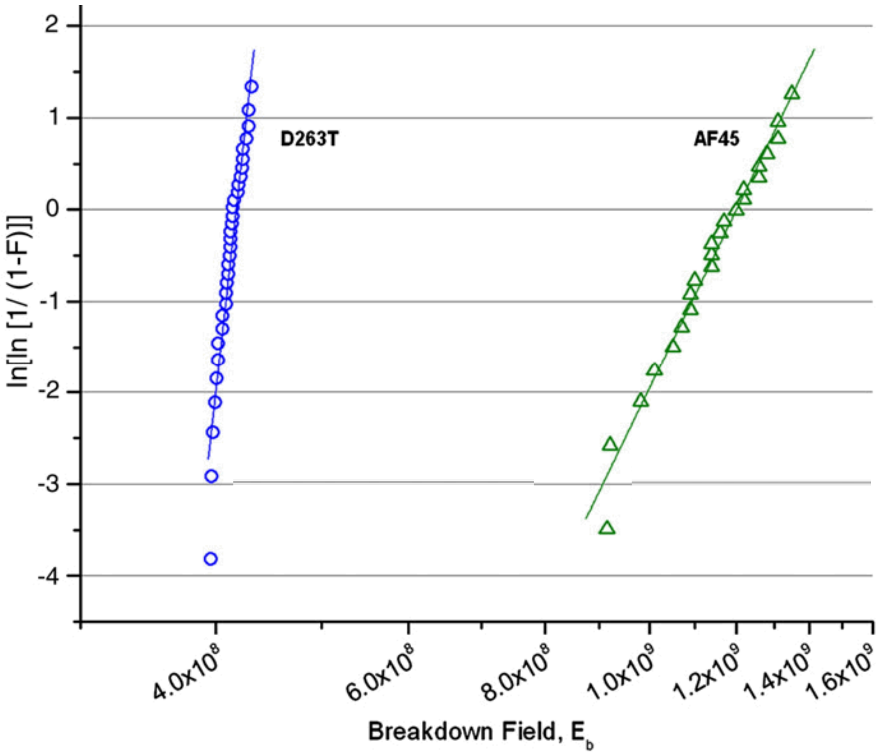
Parameter	Value
Density (g/cm^3)	2.3-2.5
Young's Modulus (GPa)	73-75
ε_r	5-6
tan δ	0.001
ρ (Ω*cm @ 250 °C)	$>10^{12}$
Strain Point	650-700 °C

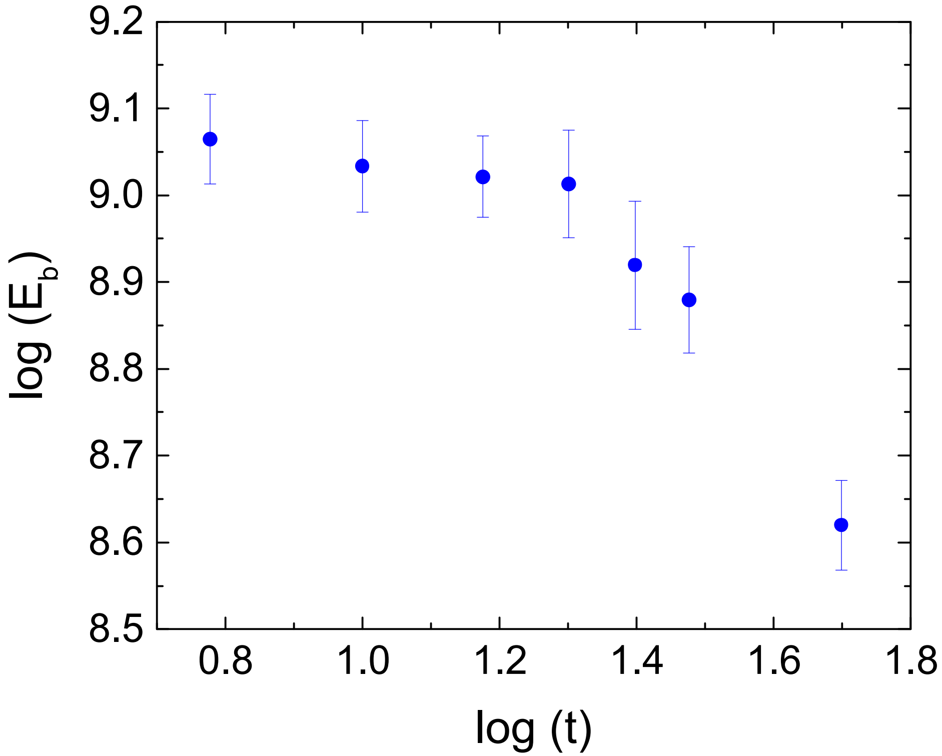
- Sold by many vendors world wide
- Boro-alumino-silicate glass category
- Sold in thicknesses ~ 100 – 200 µm
- [Na] < 350 ppm



http://www.neg.co.jp/JP/technology/pdf/idw11.pdf

Breakdown Strength of Alkali-free Glass





Parameter	D263T	AF45
t (μm)	30	19
E_b (GV/m)	0.42	1.2
β	47.9	10.7

- Schott AF45 glass etched via sonicating in HF
- For t < 20 μm, E_b > 1 GV/m
- U_{stored}~35 J/cc

Smith et al. ML 2009, Lee et al. JACS 2010

Temperature Stability of Alkali-Free Glass

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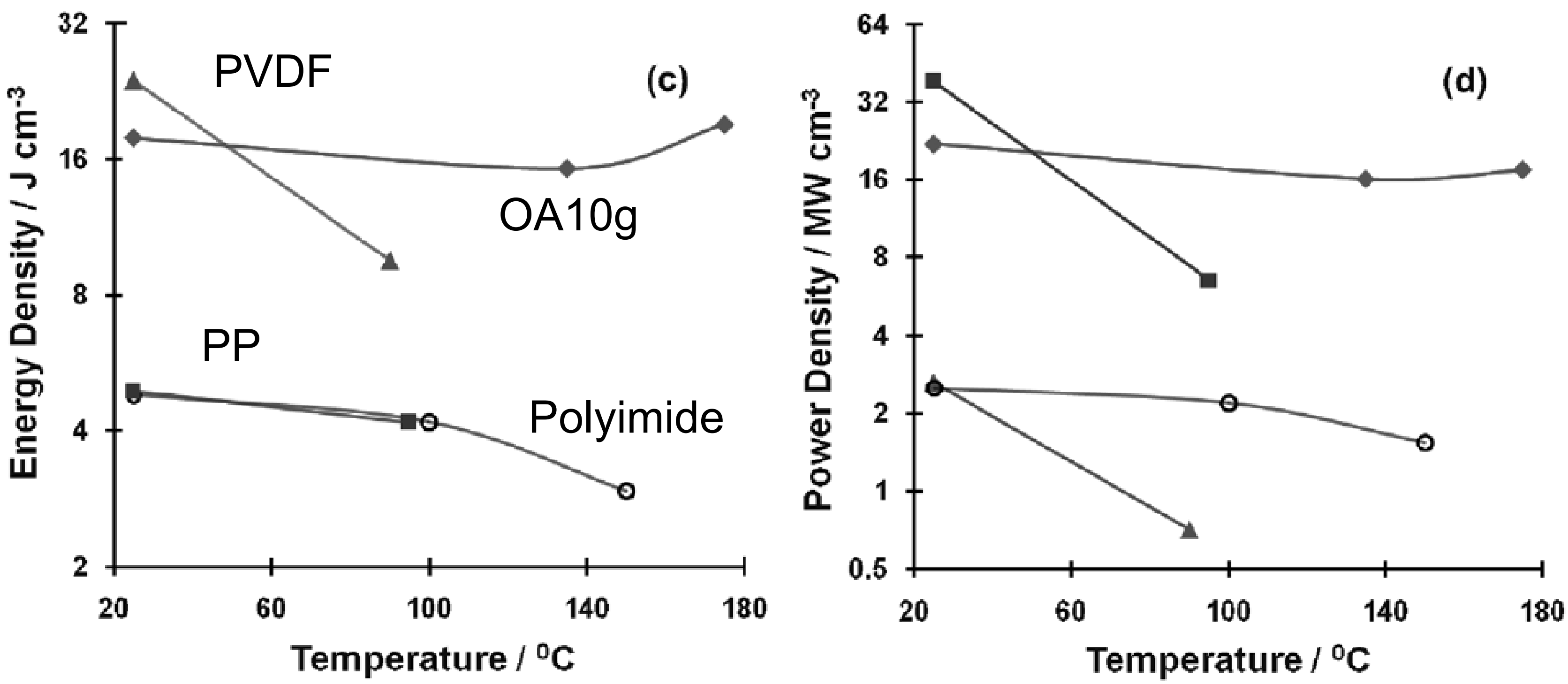
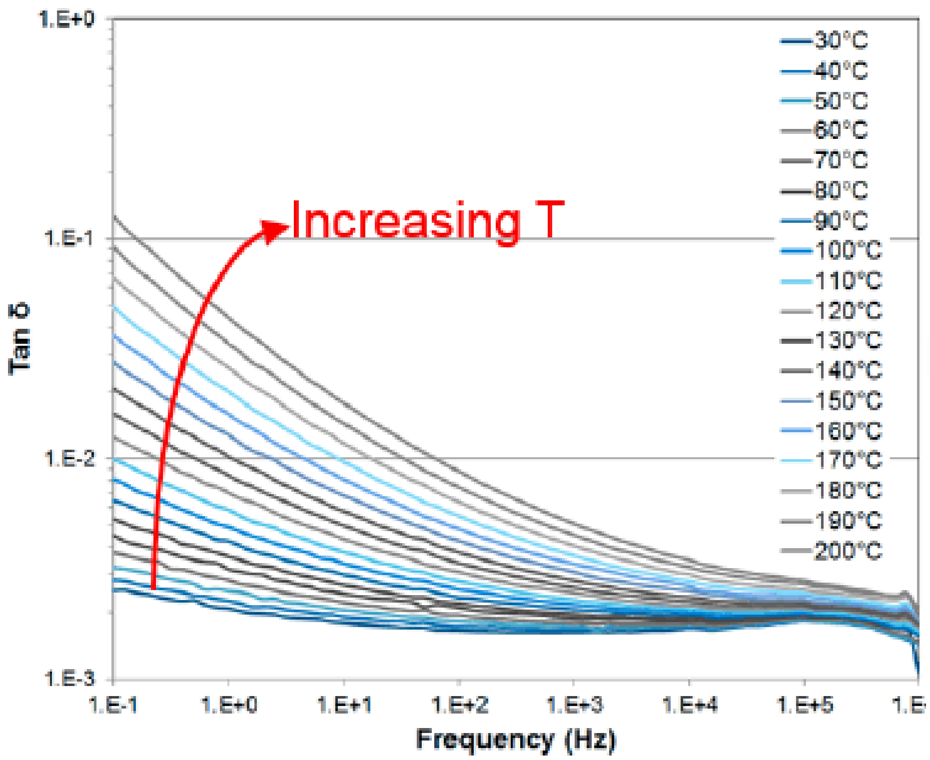


- Temperature stable HV properties beyond range achievable by most polymers

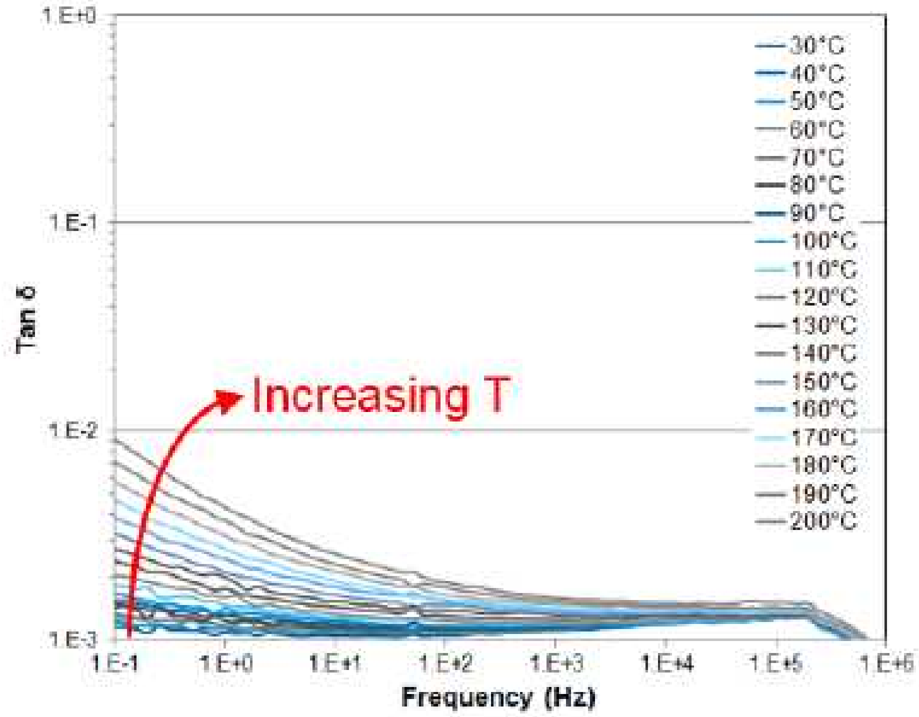
Manoharan et al. *Energy Technology* 2013

Effect of Trace Alkali Levels

Schott AF32: 0.076% Alkali Content



NEG OA-10g: 0.017% Alkali Content



- "Alkali-free"=low Alkali content
- Level of impurities critical

Petay et al. *MRS Proc.* 2014

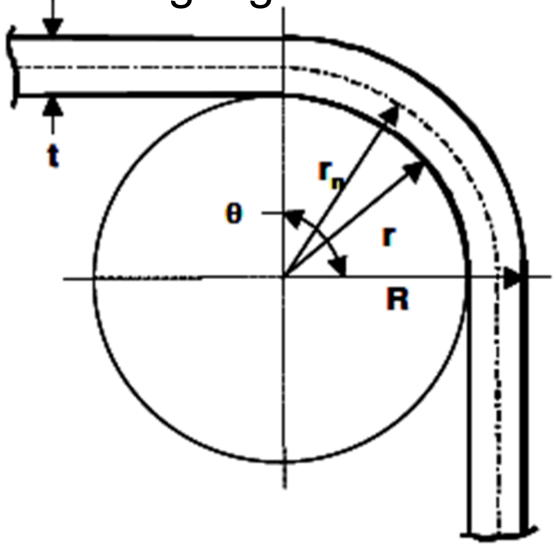
Thinning of Glass - Motivation

5 µm thick, 8 mm diameter

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

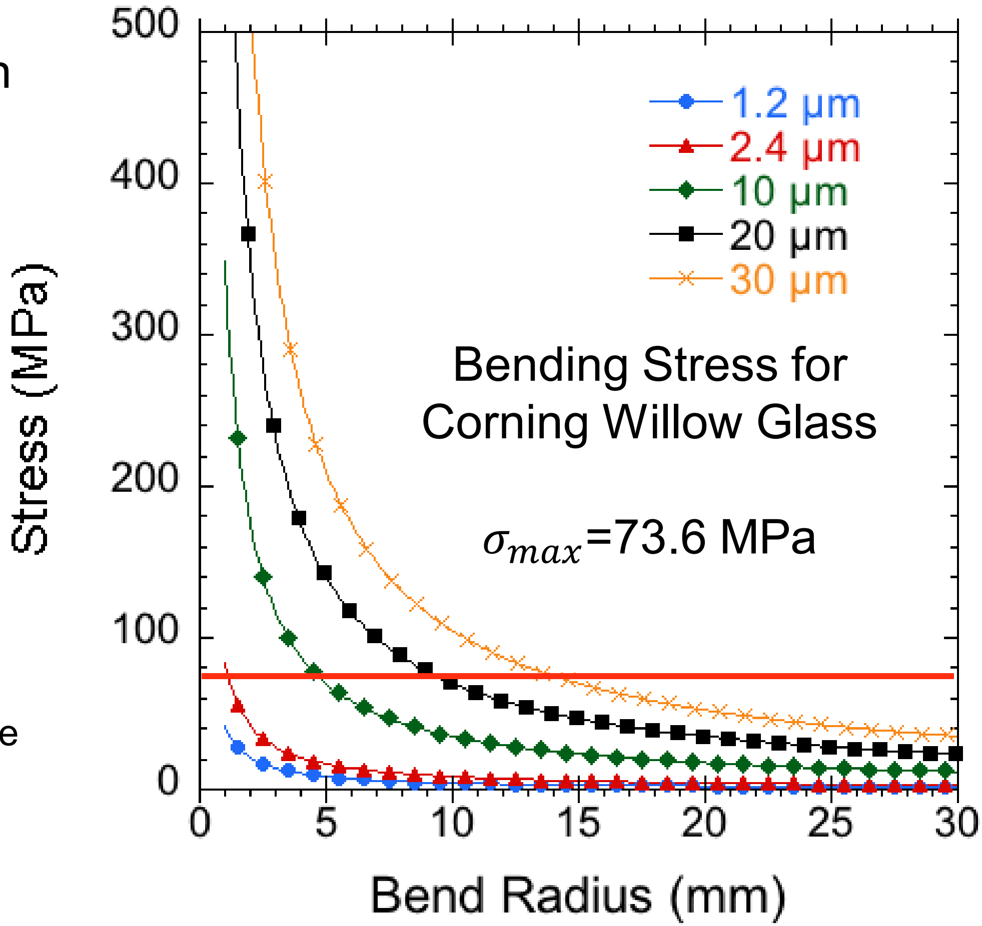
Thinned Glass for Wound Capacitors

What is the critical bend radius for high strength glass sheets?

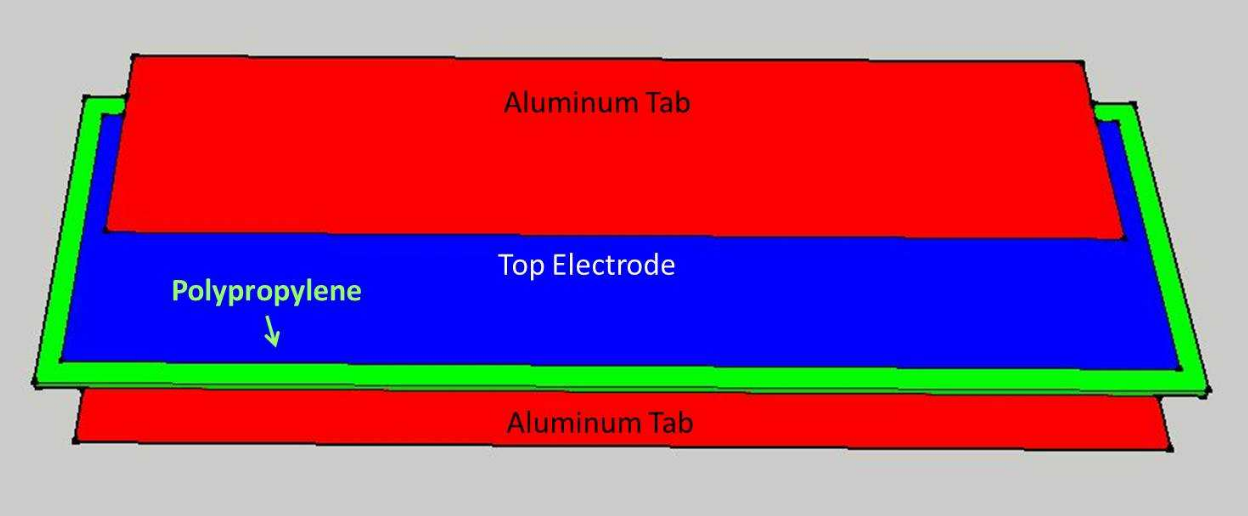


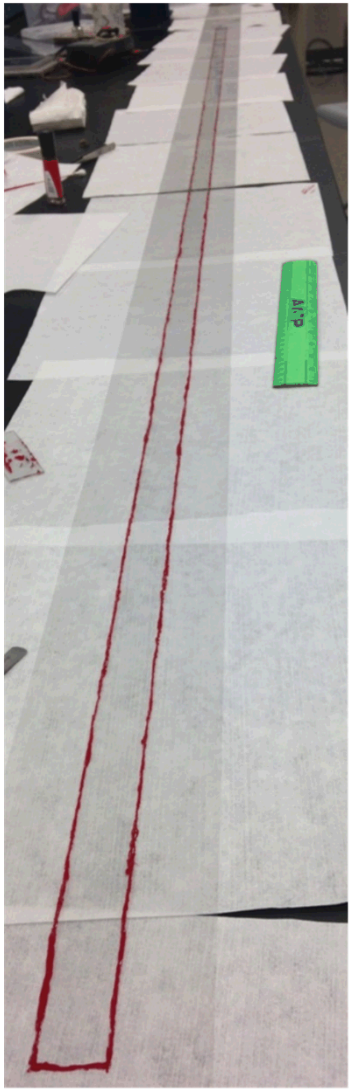
Terry Khaled, "Calculation of bend radii from tensile elongation data" Report ANM-112N-03-11 (2003).

$$\sigma = \frac{Yt}{2R},\ Y = \text{Young's modulus}$$



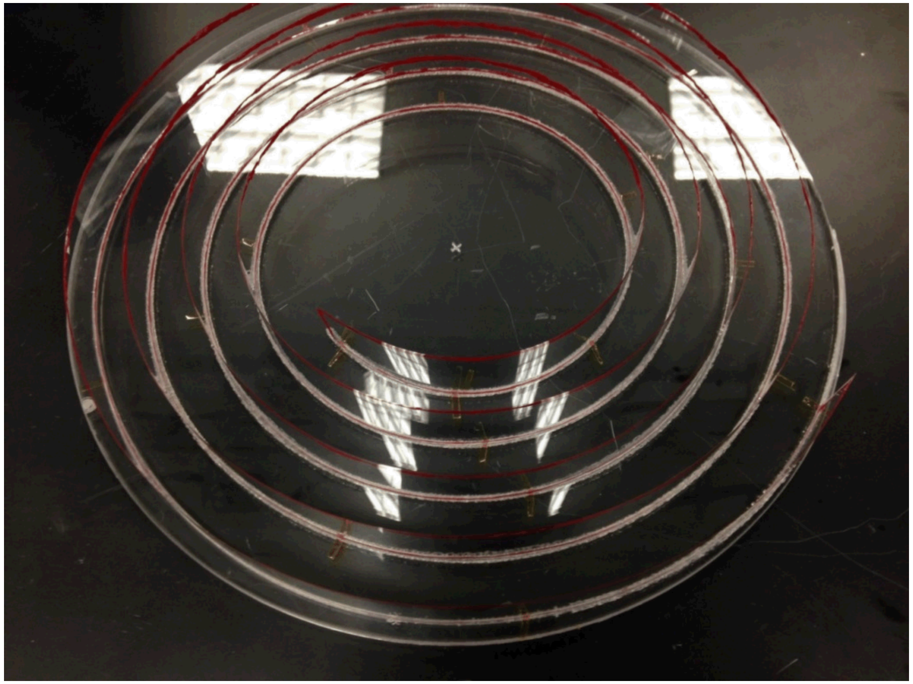
Fabrication of a Wound Capacitor

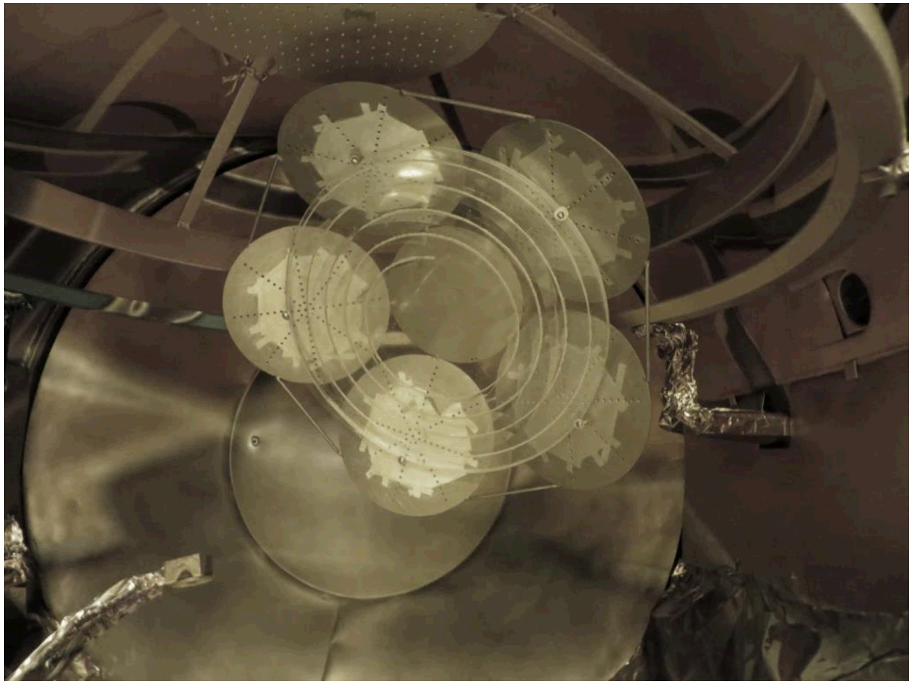




- 2.7 m long piece of 50 µm thick NEG Glass
- Designed to have electrode tabs to limit electrode resistance and inductance effects
- 12 µm polypropylene sheet glued around edges to prevent flashover

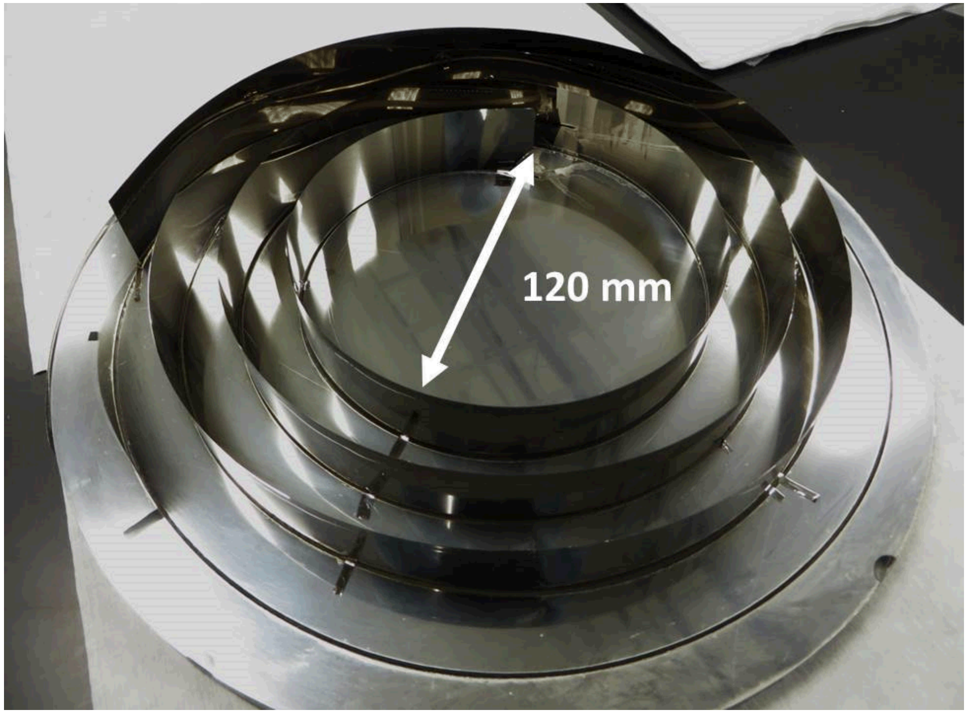
Electroding 2.7 m of Glass at a University

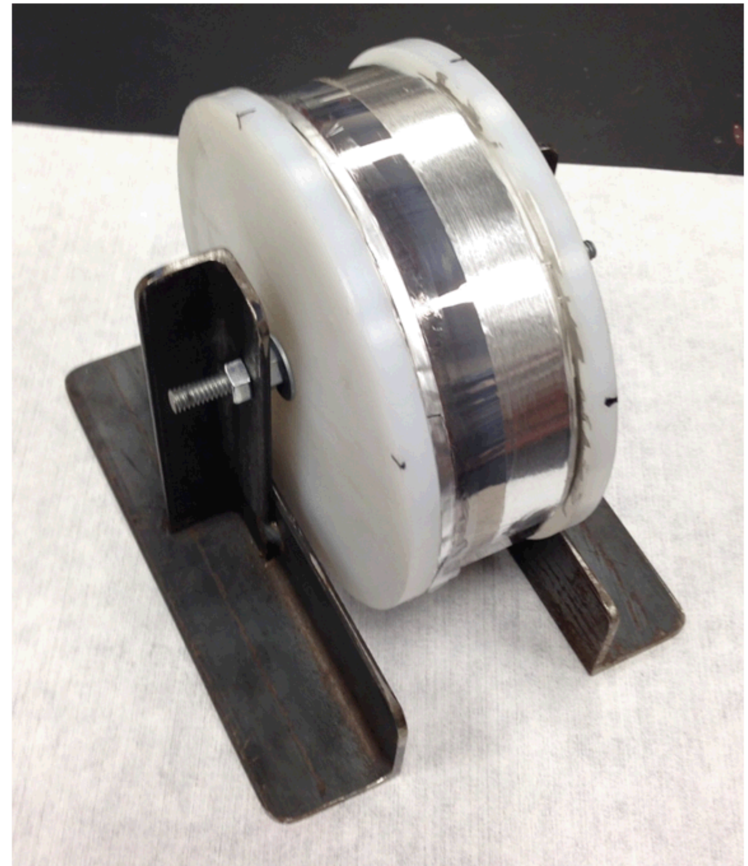




- Wound in Archimedean spiral (equal separation between rings)
- Mounted in groves laser cut into acrylic plate
- Deposited Al electrodes in Semicore evaporator
- Rinse and repeat….

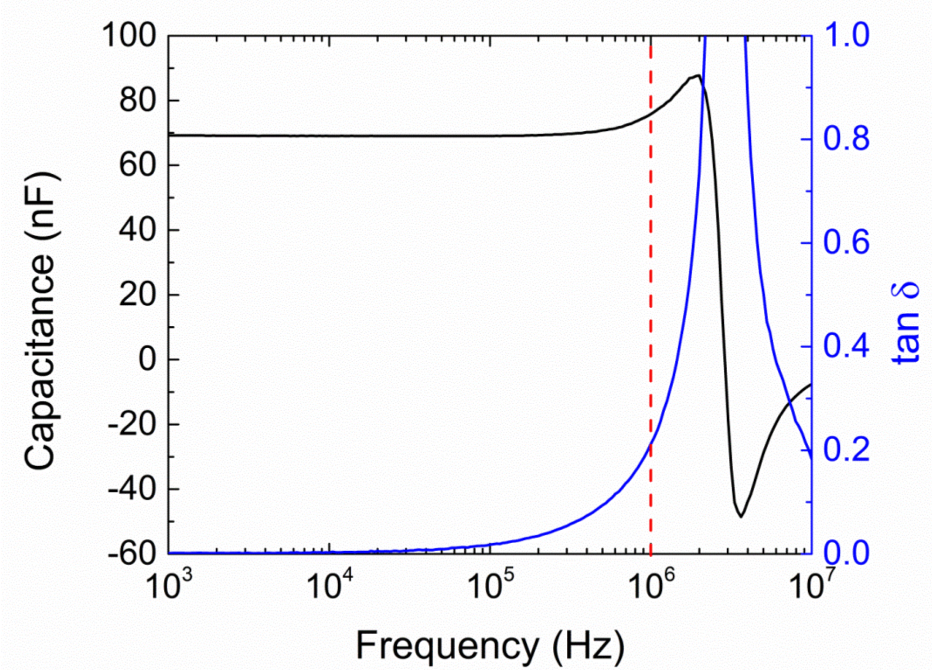
Winding of Capacitor





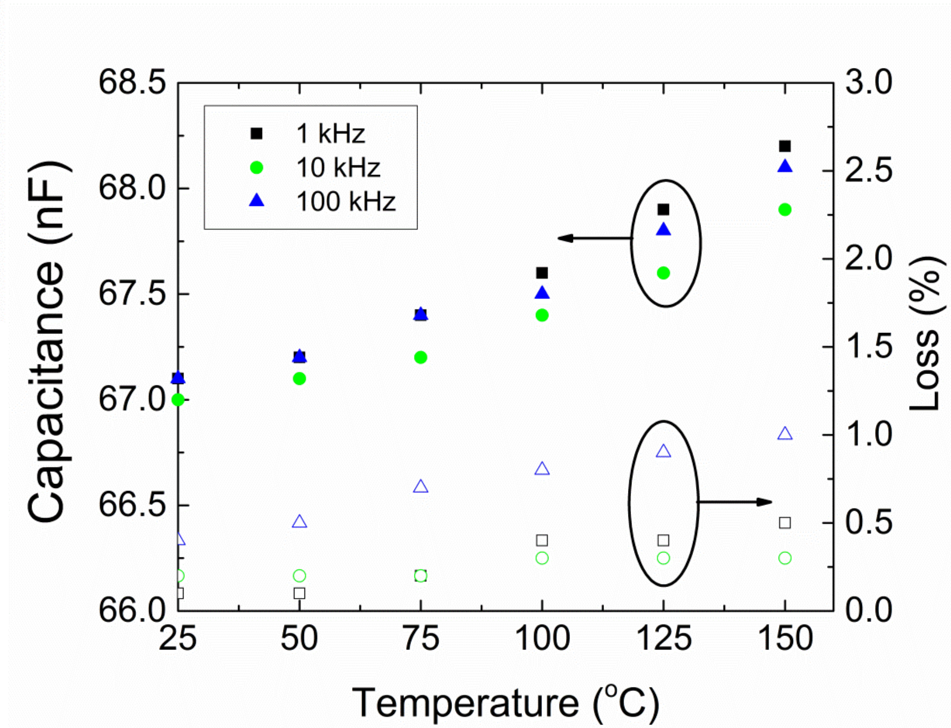
- Wound around 5.5 inch diameter spool

Electrical Properties of Capacitor



- Self-resonance above 1 MHz
- L~90 nH

- Show good temperature stability to 150 °C (low frequencies)



Routes to Higher Capacitance

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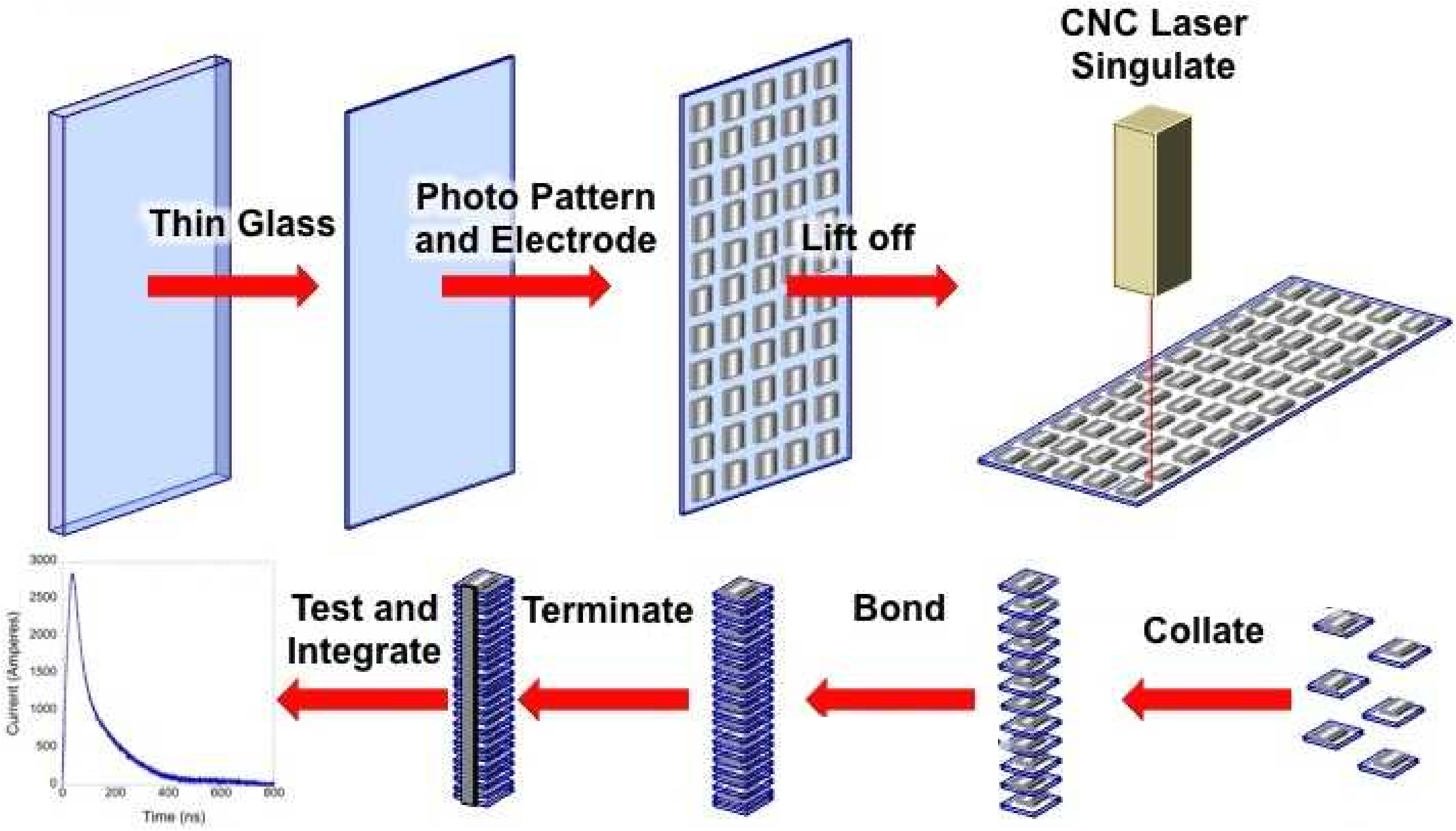
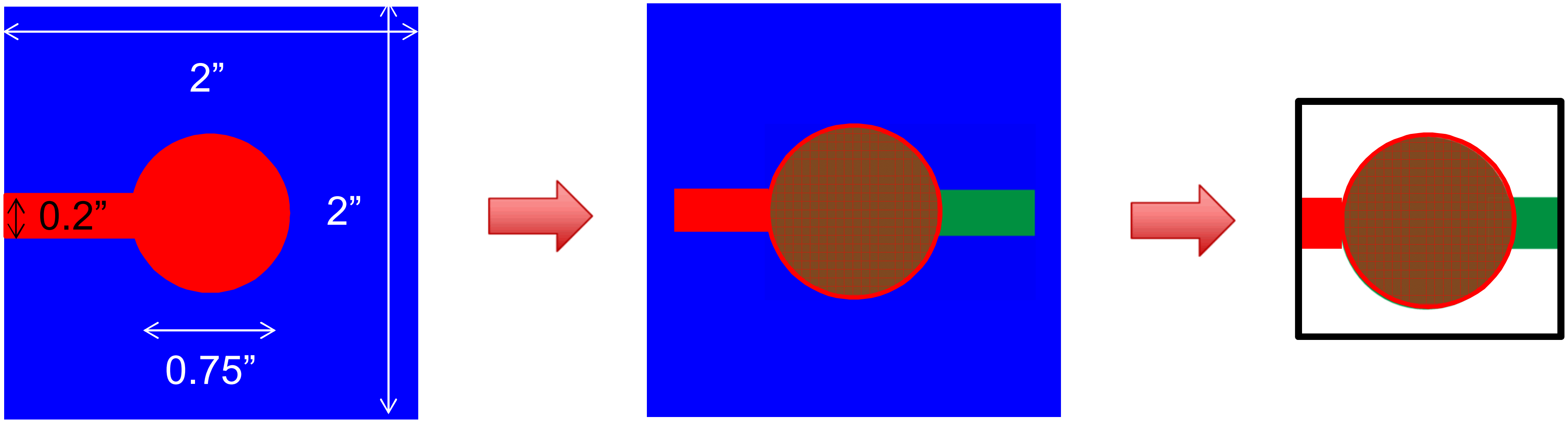


Fabrication of Multi-layer Glass Capacitor



- Pattern 0.75” diameter electrode with edge tab
  - Al electrode deposition top and bottom – rotated 180°
- Laser cut glass to form individual capacitor layer
  - 5.5 nF for 10 µm thick glass
  - Edge margin is 0.125” (~10 kV hold off voltage)

Thinning of Glass - Process

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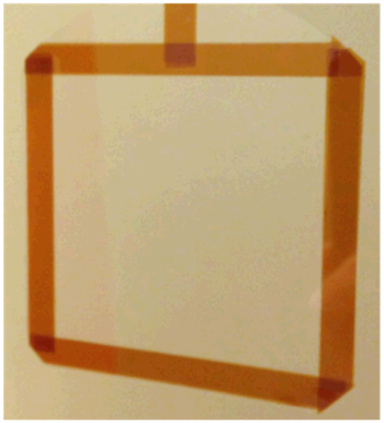
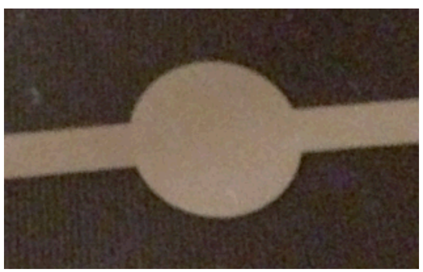
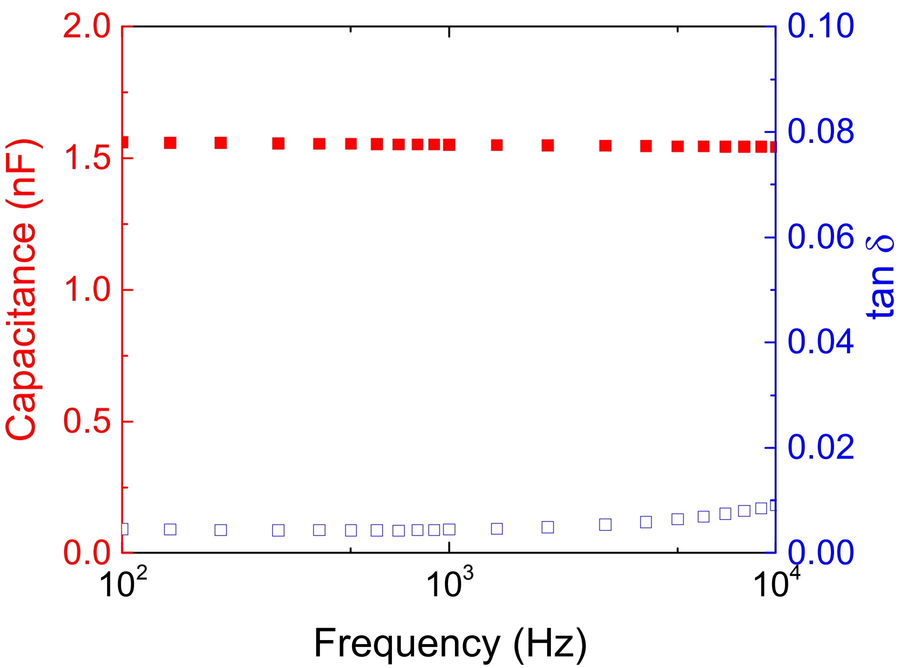
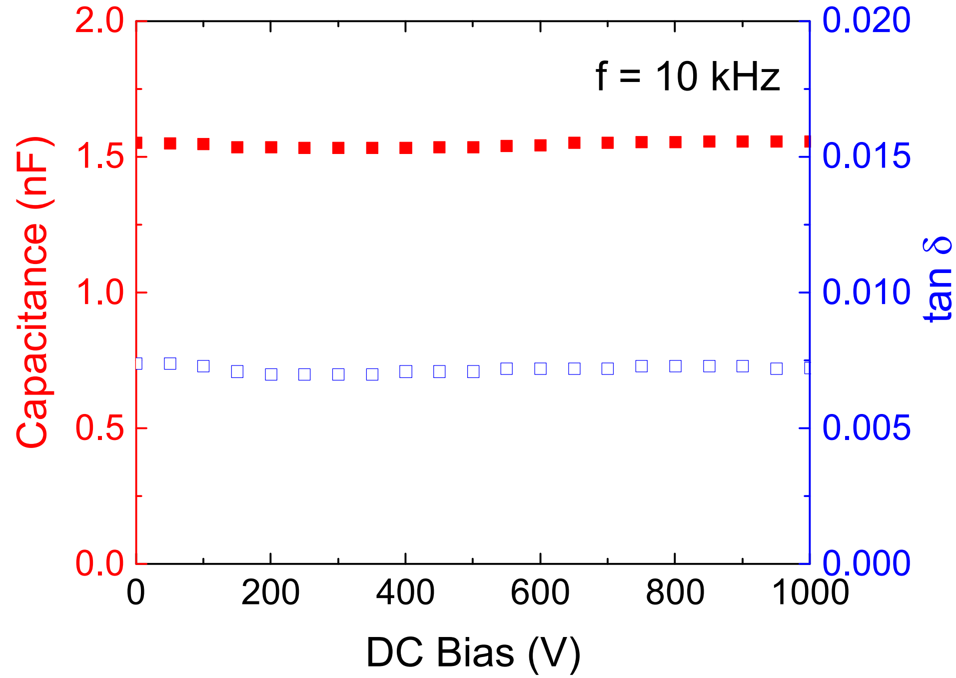




- Glass is masked on edges – provide mechanical structure for thinned samples
- Etched in 2.5% HF solution (0.01 $^{\mu m}/_{s}$)
- Al contacts evaporated in Semicore e-beam evaporator

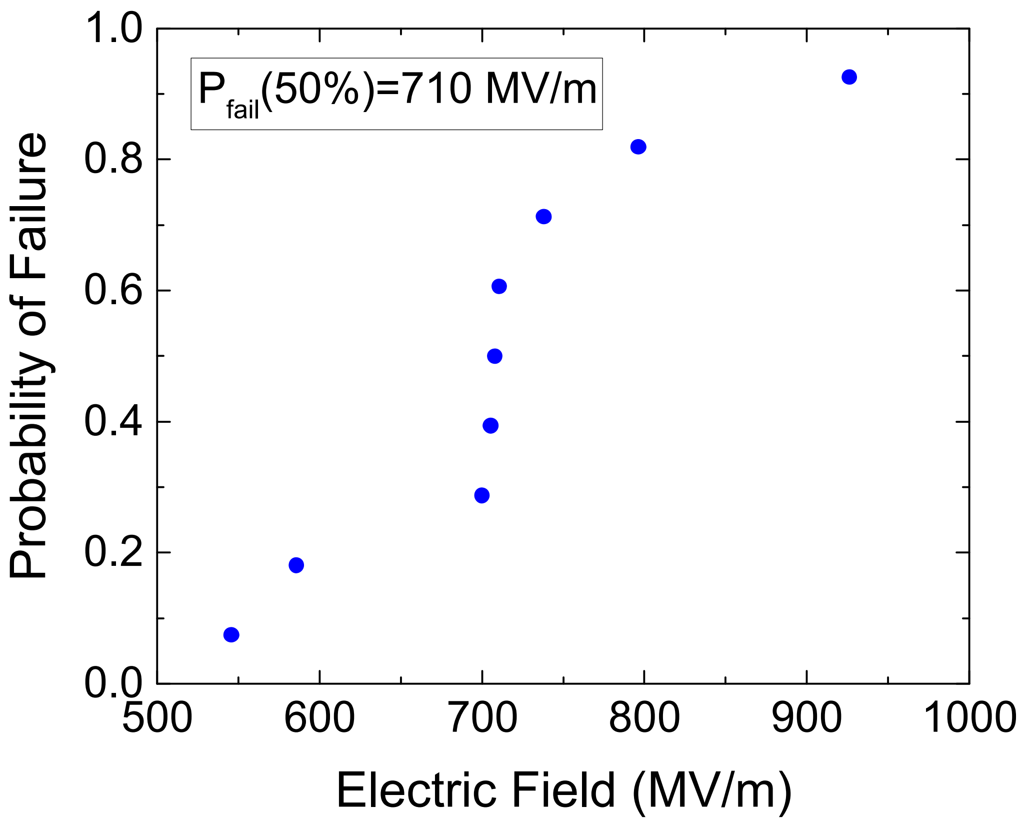
Electrical Properties of nF Sized "Bulk" Capacitors





- Corning Willow thinned to ~ 15 µm thickness
- Electrode diameter = 1 inch (5.07 cm^2)
- Flat frequency response with no tunability at 1 kV
- $\rho > 10^{15}\ \Omega$*cm

Breakdown Characteristics of Thinned Corning Willow Glass



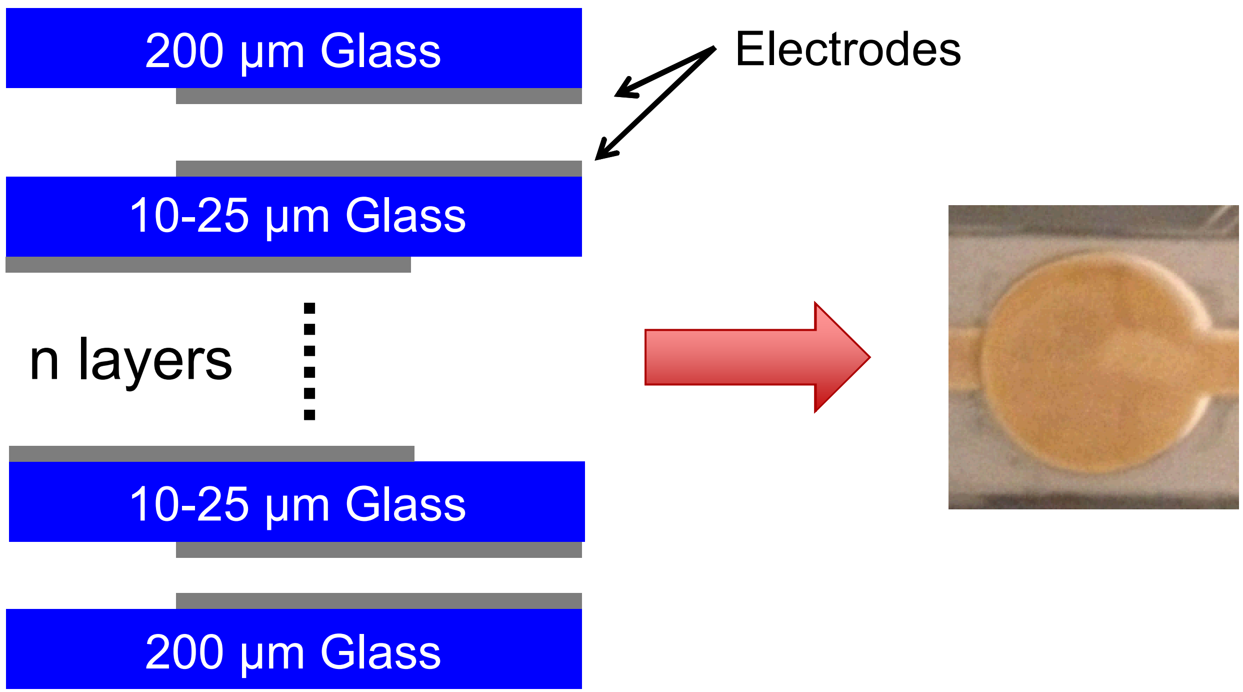
- t~19 µm (estimated from capacitance)
- A~9.6 mm^2

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

- Breakdown strength scales with area (greater probability of sampling defects)
- Weibull Statistics prediction of E_b of AF45 = 800 MV/m

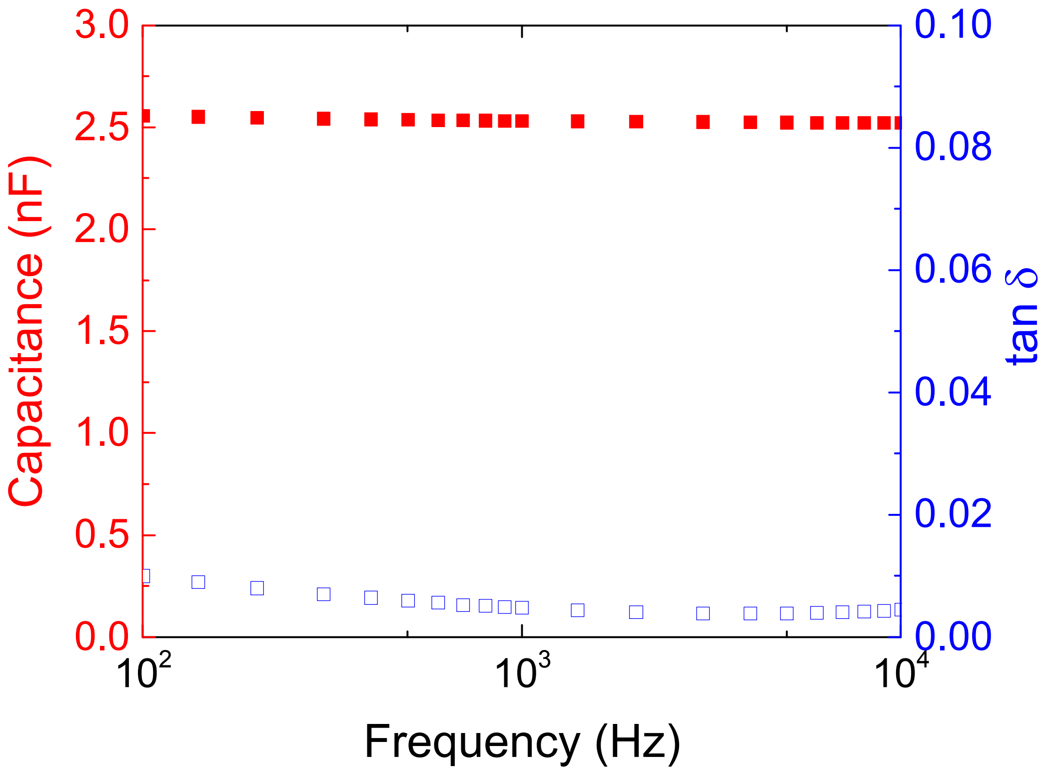
Lee et al. JACS 2010

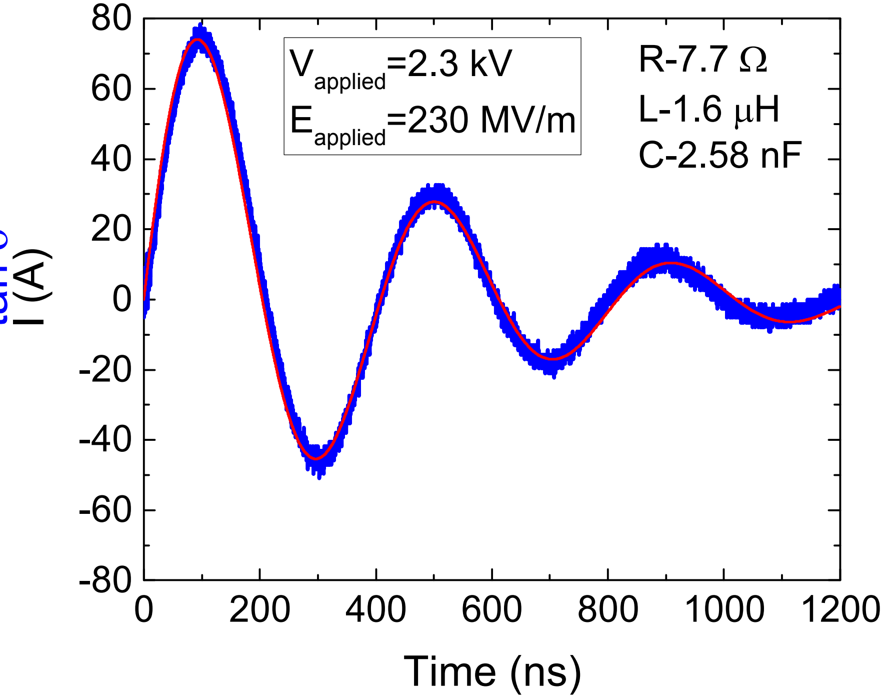
Thermal Bonding Multi-Layer Glass Capacitor



- Heat above annealing point ($\eta < 10^{13}$ poises at 722 °C) $\Rightarrow$ 850-900 °C
- Allow softened glass layers to react
- Ti/Pt electrodes used as high temp replacement for Al (T_m~650 °C)
  - Cu/Ni base metal electrodes possible if fired at low PO_2

Properties of 2 layer Glass Capacitor





- C (1 kHz) = 2.5 nF, tan δ=0.005
- R=310 GΩ ⇒ $\rho > 10^{18}$ Ω*cm
- Underdamped RLC discharge – $U_{dielectric}$~1.3 J/CC, $U_{capacitor}$~60 mJ/cc
  - Can increase $U_{capacitor}$ 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
    - $E_b > 1$ GV/m
    - U ~ 35 J/cc
    - tan $\delta < 0.01$ at 200 °C
    - Alkali content is crucial for high energy density and temperature stability
  - Challenging to make and handle!
    - Our approach – thin and build multi-layer capacitor through laser cutting and thermal bonding
      - Have process for thinning to 10 μm (1-2 nF per layer)
      - Bond layers at 850-900 °C
    - Industrially – might be able to make wound capacitors if companies build infrastructure to thin glasses sufficiently