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Thermal conductivity and elastic constants of PEDOT:PSS

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Outline

- Introduction and background
- Thermal conductivity of PEDOT:PSS, thin and thick, through-thickness and in-plane
- Elastic constants by picosecond acoustics and surface acoustic waves
- Conclusions
  - Thermal conductivity of ~30 μm thick, cast layers of PEDOT:PSS have strongly anisotropic thermal conductivity.
  - Data are consistent with the Sommerfeld value of the Lorenz number.

A suppressed value of the Lorenz number enhances *ZT*

- Electronic thermal conductivity = Lorenz number × electrical conductivity × temperature

$$\Lambda_{el} = L\sigma T$$

- Sommerfeld (1929) degenerate electron gas and elastic scattering

$$L = L_0 = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$$

- Non-degenerate with power law scattering exponent *r*

$$L = \left(\frac{5}{2} + r\right)\left(\frac{k_B}{e}\right)^2$$

A suppressed value of the Lorenz number enhances *ZT*

- If we can't make L small, Λ_{el} has to be large

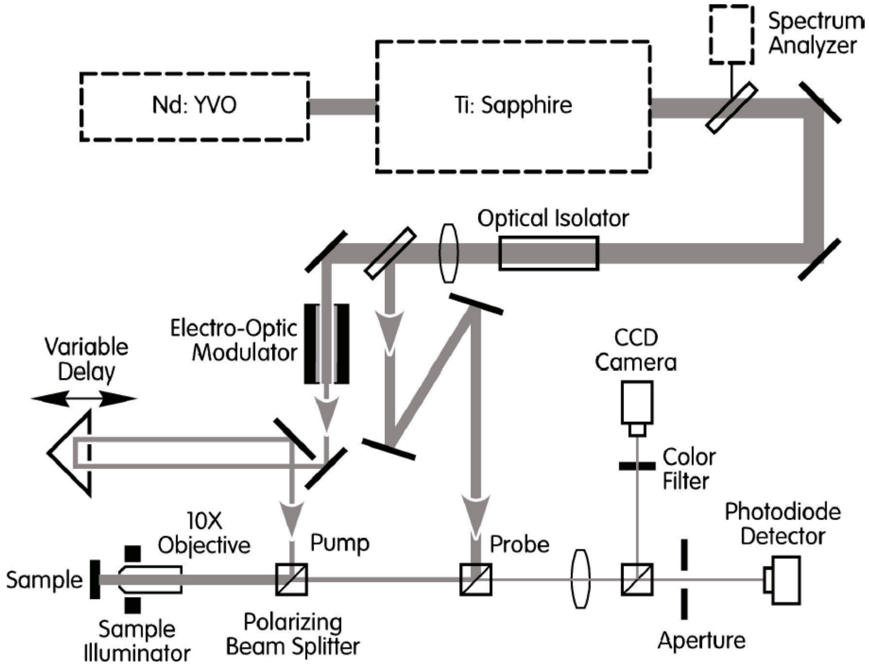
$$ZT = \frac{S^2 \sigma T}{\Lambda_{el} + \Lambda_{ph}} = \left(\frac{S^2}{L}\right)\left(\frac{\Lambda_{el}}{\Lambda_{el} + \Lambda_{ph}}\right)$$

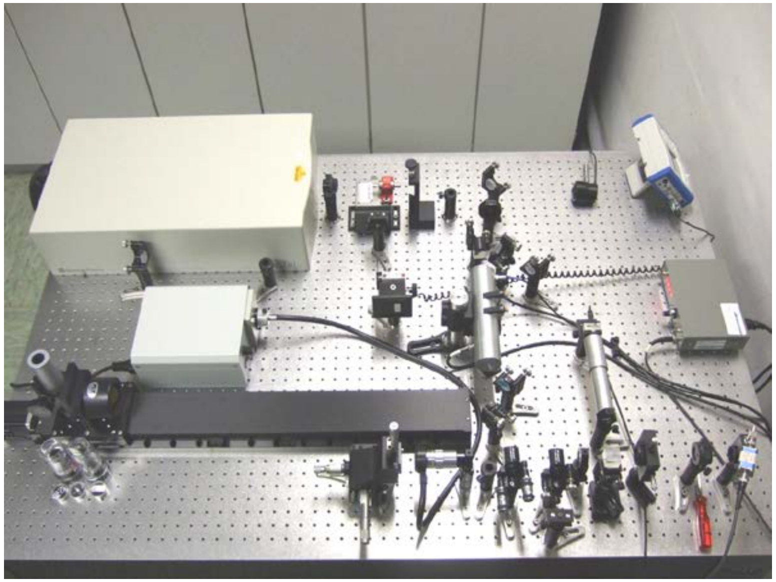
- For conventional good thermoelectrics near room temperature

$$ZT = \left(\frac{S^2}{L}\right)\left(\frac{\Lambda_{el}}{\Lambda_{el} + \Lambda_{ph}}\right) \approx (4)\left(\frac{0.5}{2}\right) \approx 1$$

Time domain thermoreflectance since 2003

- Improved optical design
- Normalization by out-of-phase signal eliminates artifacts, increases dynamic range and improves sensitivity
- Exact analytical model for Gaussian beams and arbitrary layered geometries
- One-laser/two-color approach tolerates diffuse scattering

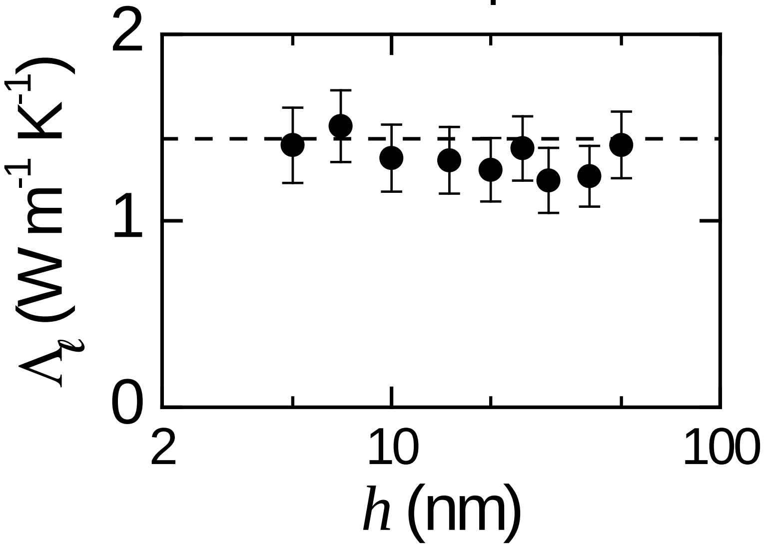




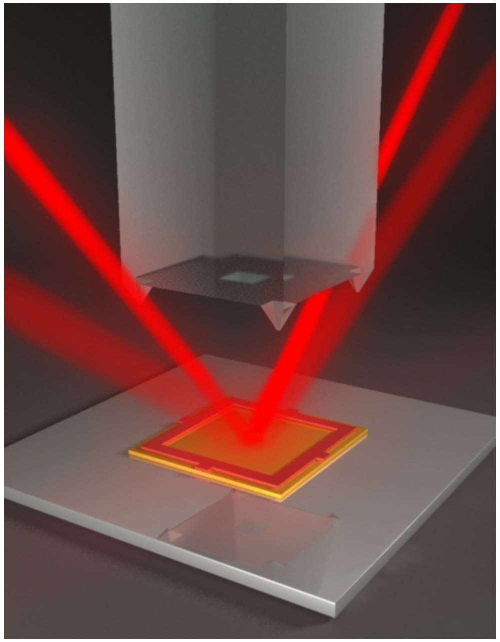
Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008

TDTR: Flexible, convenient, and accurate

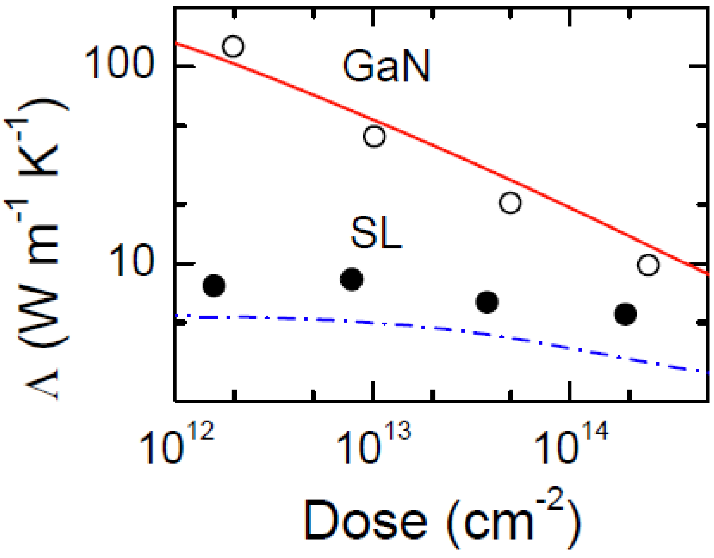
PbTe/PbSe superlattices



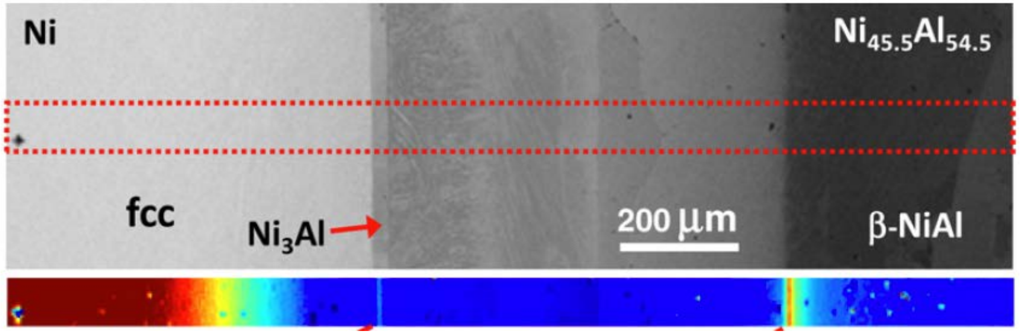
Transfer-printed interfaces



Radiation damage



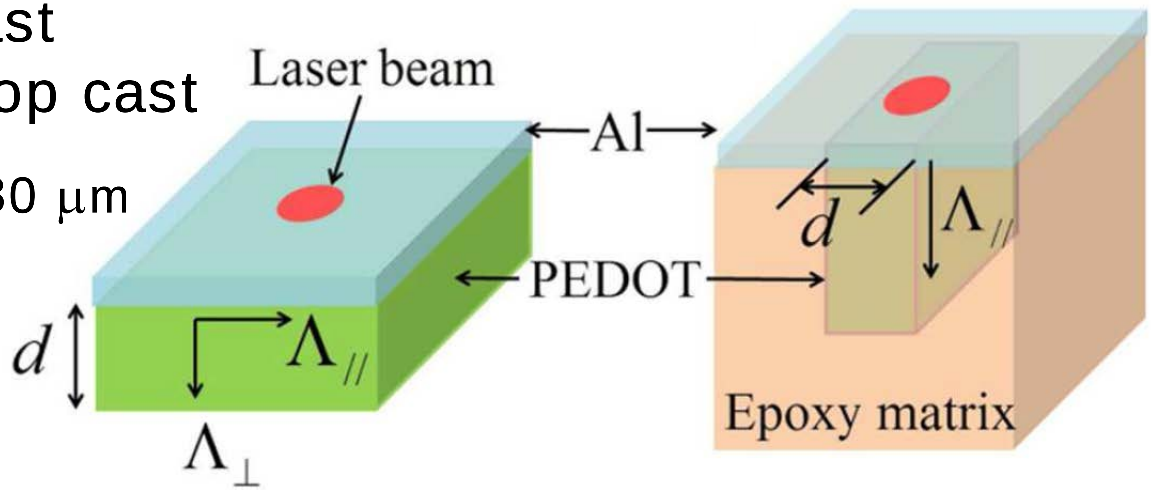
High spatial resolution mapping



Samples prepared from aqueous dispersions of PEDOT:PSS

spin cast
and drop cast

$d \approx 65$ nm to 30 μm

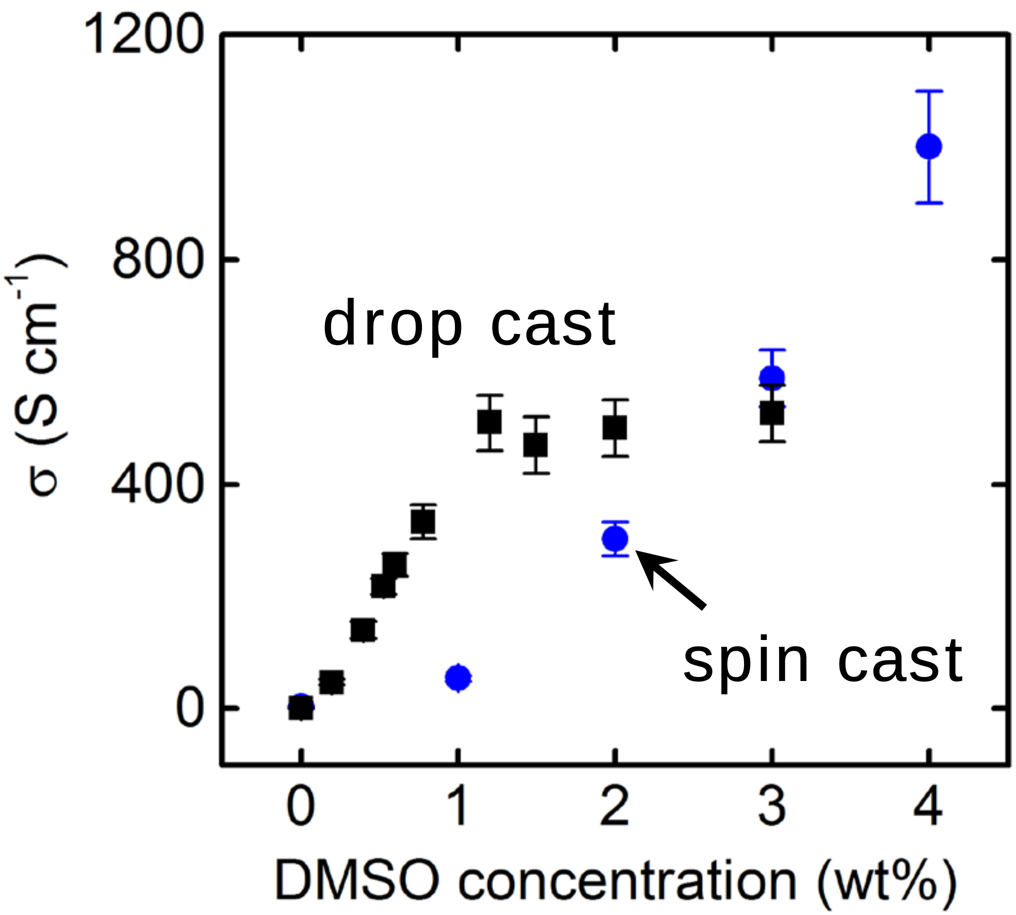


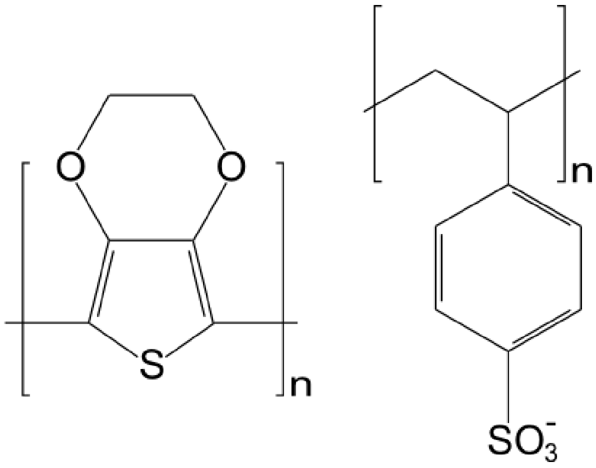
drop cast

$d \approx 30$ μm

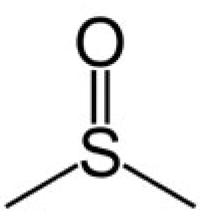
- 1% by weight solids; Clevious™ PH1000
- Particle size from dynamic light scattering
- Density by Rutherford backscattering spectrometry (in progress)
- Spin cast samples: bake at 130°C for 15 min
- Drop cast: bake at 70°C for 3 h

Electrical conductivity of PEDOT:PSS varied concentration of DMSO co-solvent





carbon.physics.ncsu.edu

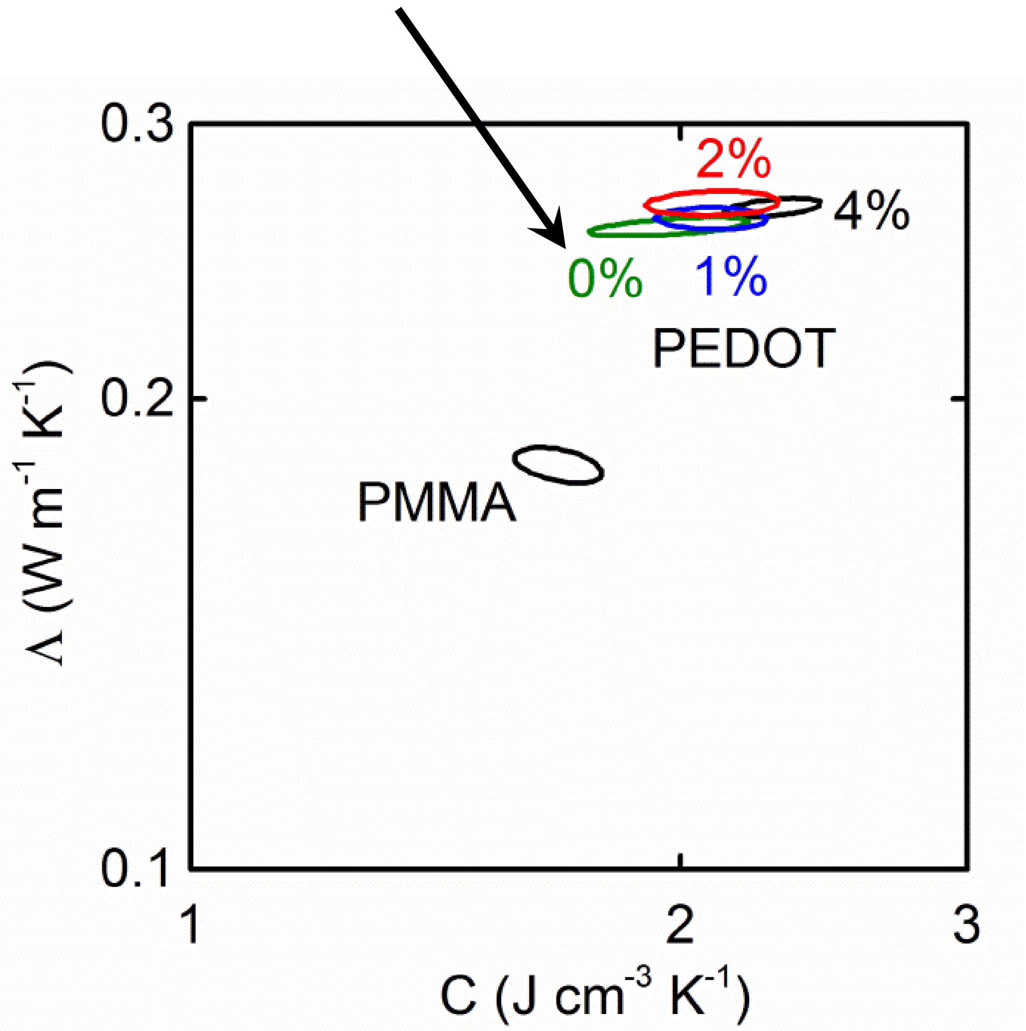


Digression: what is the mechanism by which the DMSO co-solvent changes the electrical conductivity

- Changes to the polymer morphology that produce more conductive pathways through the sample?
- DMSO has low vapor pressure compared to water; therefore, DMSO becomes more concentrated as drying proceeds and final steps of drying are delayed significantly.
- Acts as a coalescent. Before evaporating, DMSO lowers Tg of the polymers so that the particles can better weld together.
- Where does the anisotropy come from? Surface tension forces during drying?

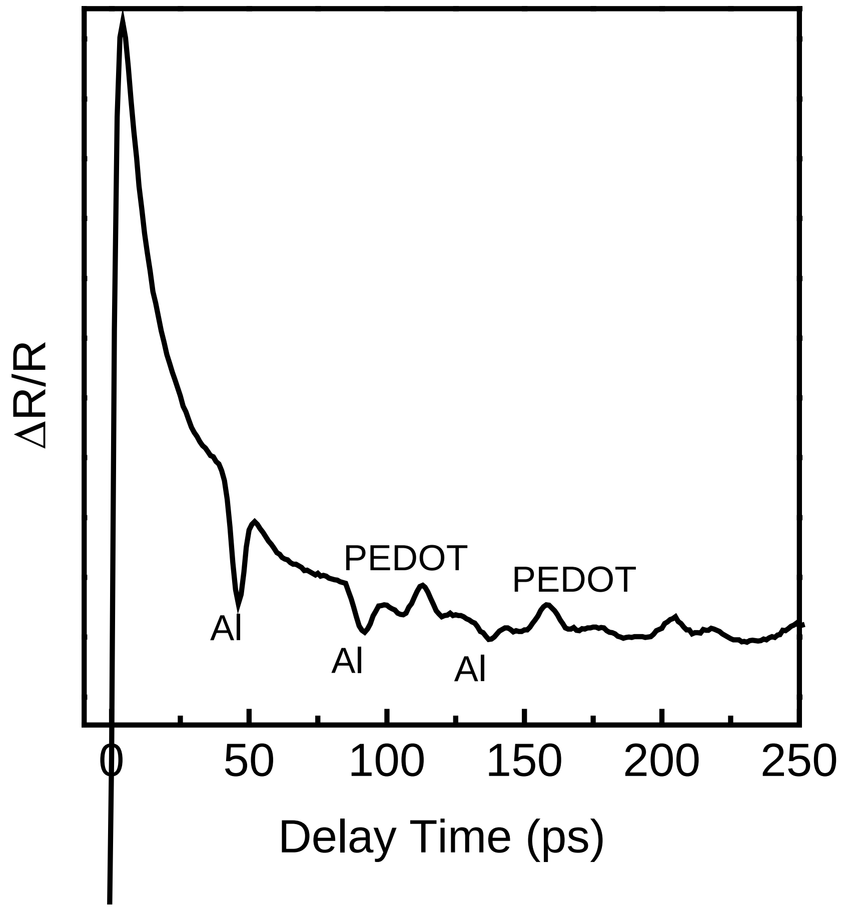
Spin cast samples (65 nm): Vary modulation frequency to separately measure thermal conductivity and heat capacity

DMSO co-solvent concentration

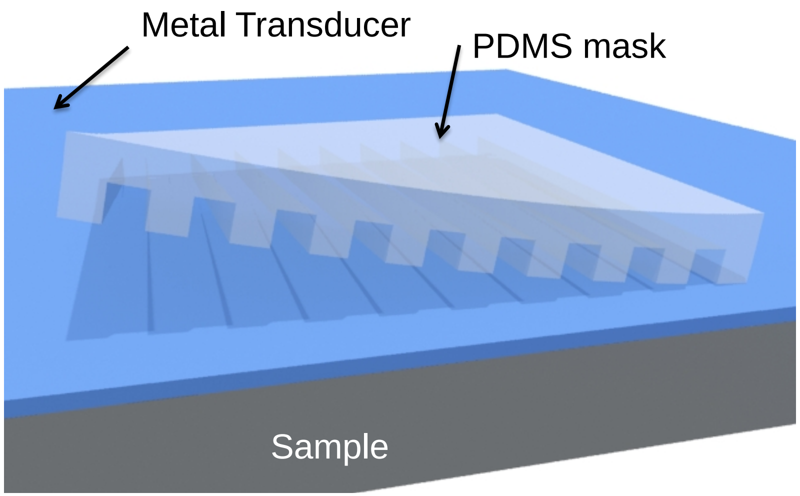


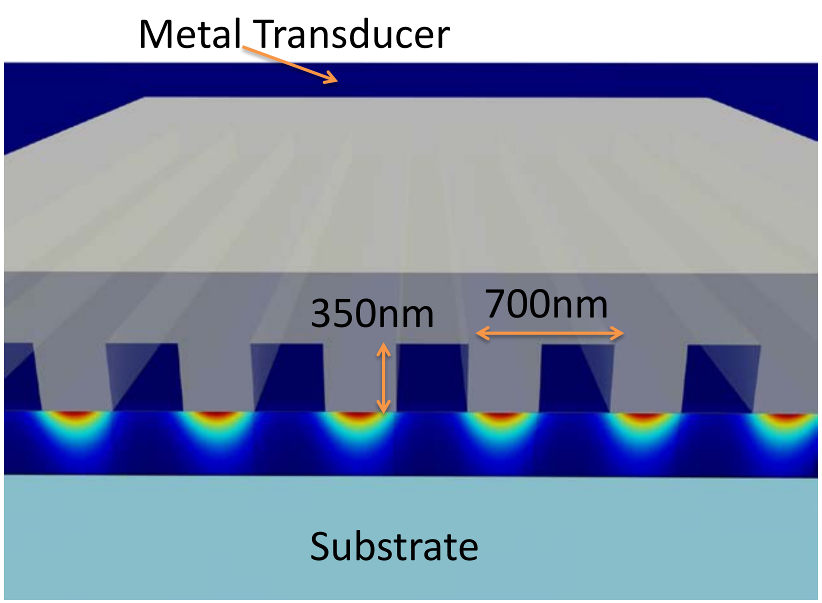
- Through thickness thermal conductivity is independent of DMSO concentration and therefore independent of in-plane electrical conductivity.

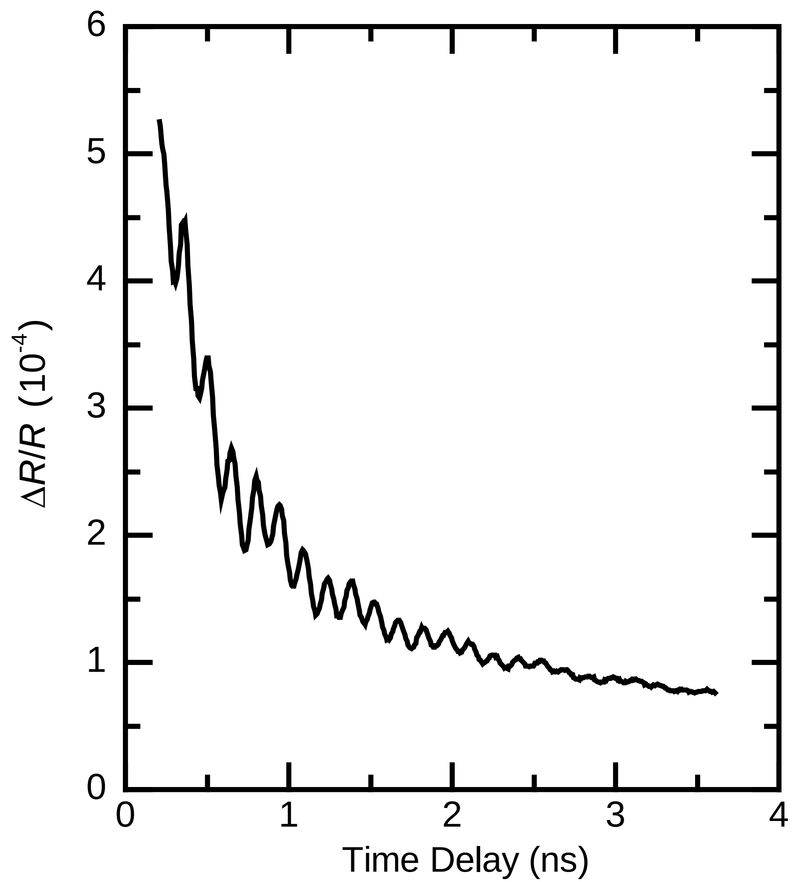
Measure longitudinal sound velocity using picosecond acoustics



Measure surface acoustic wave velocity using elastomeric phase shift mask







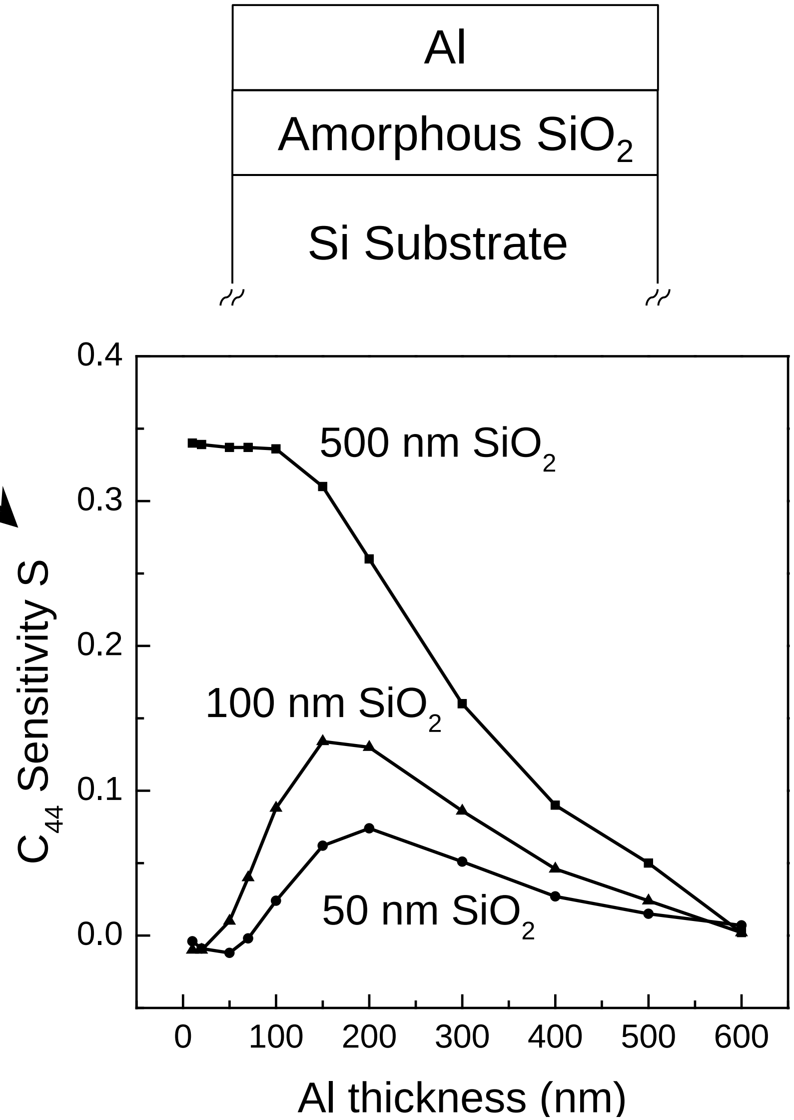
Experimental details: need to optimize thickness of sample and metal transducer

- Example sensitivity calculations for Al/SiO_2/Si

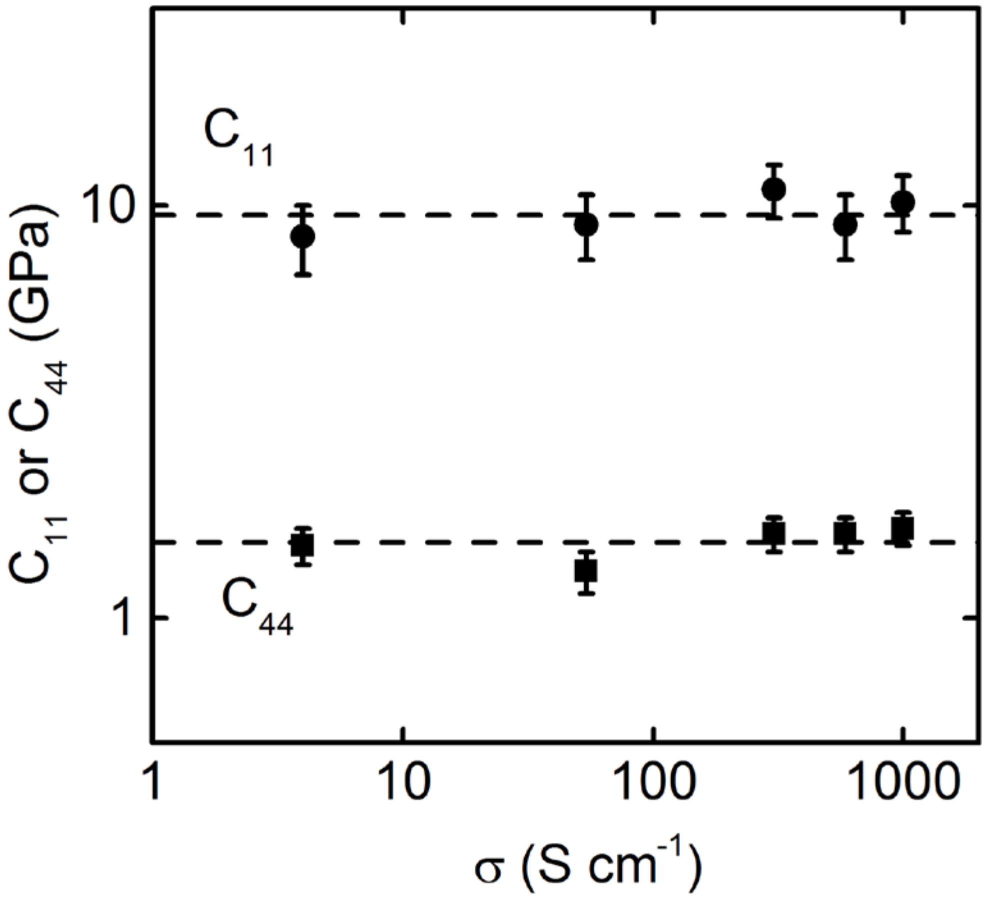
$$S = \frac{c_{44}}{v_{SAW}} \frac{\partial v_{SAW}}{\partial c_{44}}$$

- Approach fails for thick layers of polymeric materials.
- S=0.12 using

Al(160 nm)/PEDOT:PSS(140 nm)



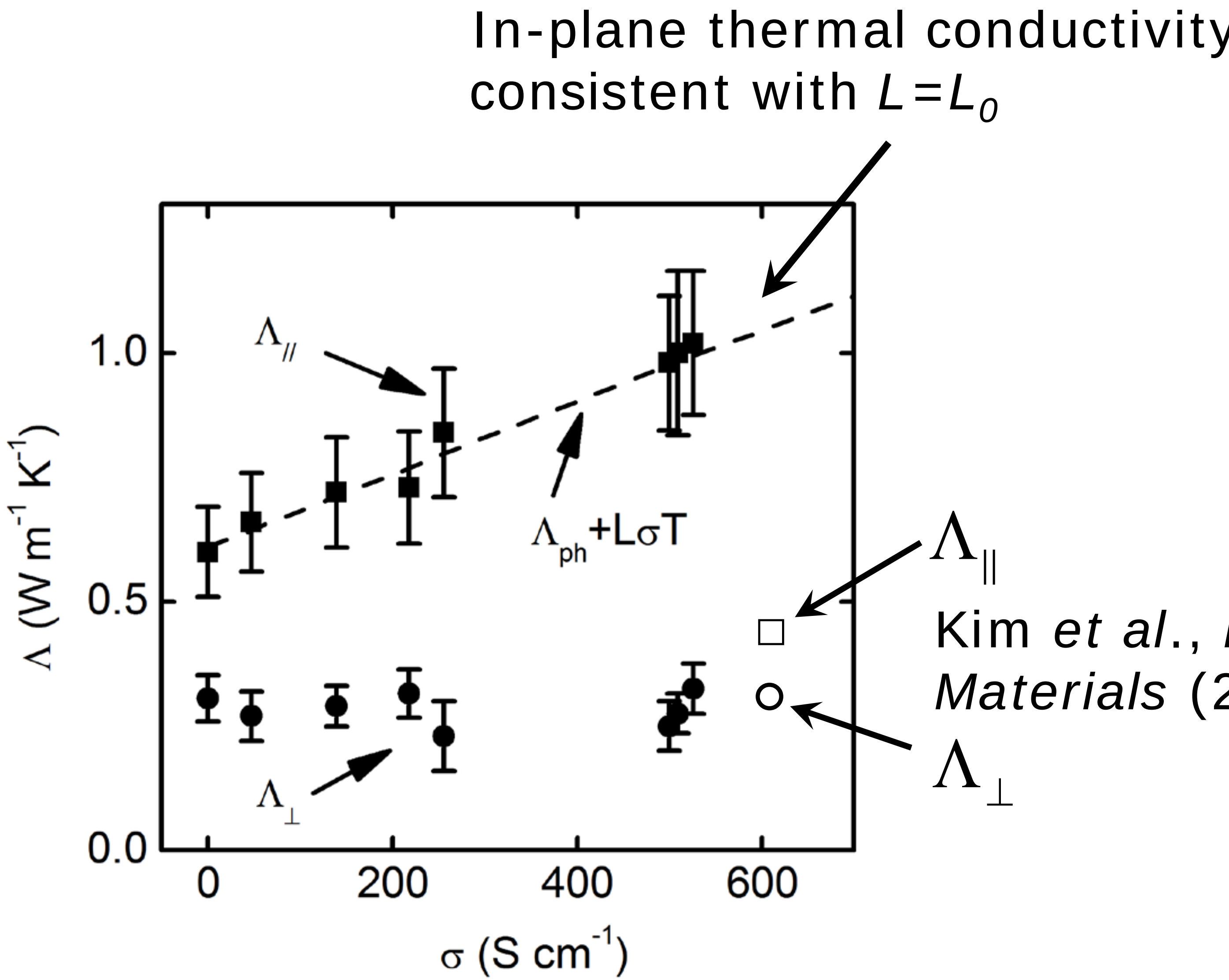
Elastic constants of PEDOT:PSS are independent of DMSO concentration



picosecond acoustics assuming $\rho = 1$ g cm^{-3}

SAW measurements and knowledge of c_{11}

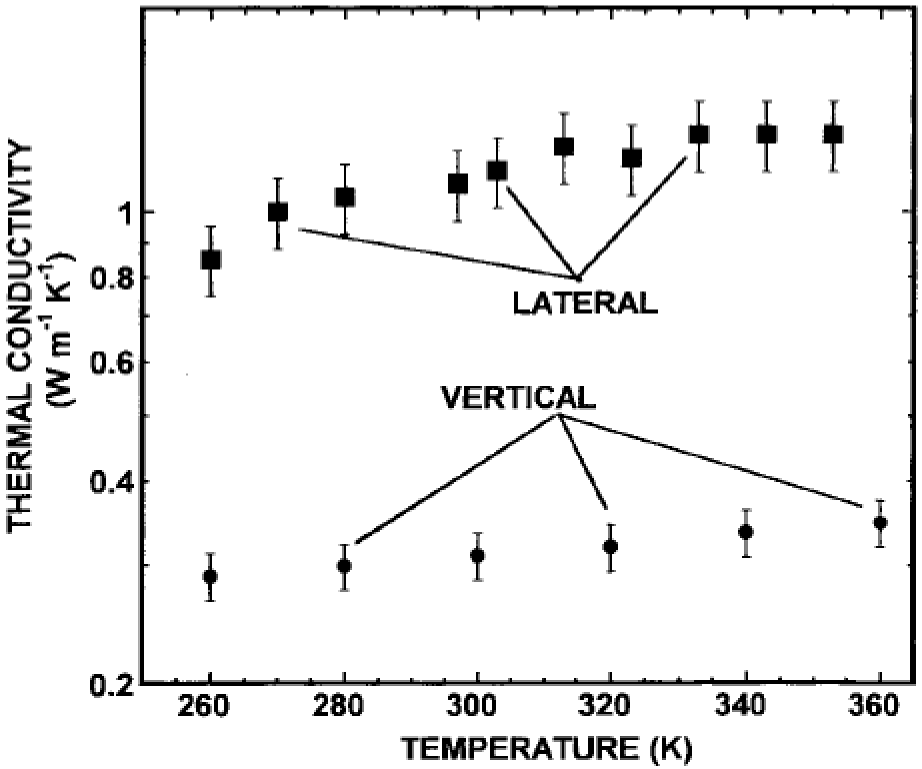
Drop cast layers are thermally anisotropic



Kim *et al.*, *Nature Materials* (2013)

Spin-coated polyimide for comparison

Kurabayashi (1999)



2.25 μm Du Pont PI 2556, BTDA-ODA-MPD

Conclusions

- Thermal conductivity of drop cast PEDOT:PSS is consistent with the Sommerfeld value of the Lorenz number, $L \approx L_0$
  - Assumption that vibrational thermal conductivity is independent of DMSO concentration used in processing is supported by the fact that the elastic constants are independent of DMSO concentration
- We cannot directly test the anisotropy of thin spin cast layers.
  - Could Lorenz number be different in spin cast vs. drop cast layers? Possible but seems unlikely…
- If we combine $L=L_0$, our measurement of the in-plane vibrational thermal conductivity, and power factor measurements from Kim *et al*.:

$$ZT_{max}=0.11 \text{ at room temperature.}$$