Thermal conductivity and elastic constants of PEDOT:PSS

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• 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 \( \sim 30 \ \mu m \) 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 $= \text{Lorenz number} \times \text{electrical conductivity} \times \text{temperature}$

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

- 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, $\Lambda_{el}$ 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

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

\[ \Lambda (W \text{ m}^{-1} \text{ K}^{-1}) \]

\( h \) (nm)

Transfer-printed interfaces

Radiation damage

\[ \Delta (W \text{ m}^{-1} \text{ K}^{-1}) \]

Dose (cm\(^{-2}\))

High spatial resolution mapping
Samples prepared from aqueous dispersions of PEDOT:PSS

- 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

\( d \approx 65 \text{ nm} \) to 30 \( \mu \text{m} \)
Electrical conductivity of PEDOT:PSS varied with concentration of DMSO co-solvent.

- **Drop cast**
- **Spin cast**

![Graph showing the relationship between DMSO concentration and electrical conductivity](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

- 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

Substrate

Metal Transducer

PDMS mask

Sample

Metal Transducer

350nm 700nm

$\Delta R/R (10^4)$

Time Delay (ns)

$\Delta R/R$
Experimental details: need to optimize thickness of sample and metal transducer

- Example sensitivity calculations for Al/SiO₂/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 assuming $\rho = 1 \text{ g cm}^{-3}$.

picosecond acoustics
SAW measurements and knowledge of $c_{11}$
Drop cast layers are thermally anisotropic

In-plane thermal conductivity consistent with $L = L_0$

Spin-coated polyimide for comparison

Kurabayashi (1999)

2.25 \( \mu \text{m} \) 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.:

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