Electrochemical control of thermal conductivity in thin films

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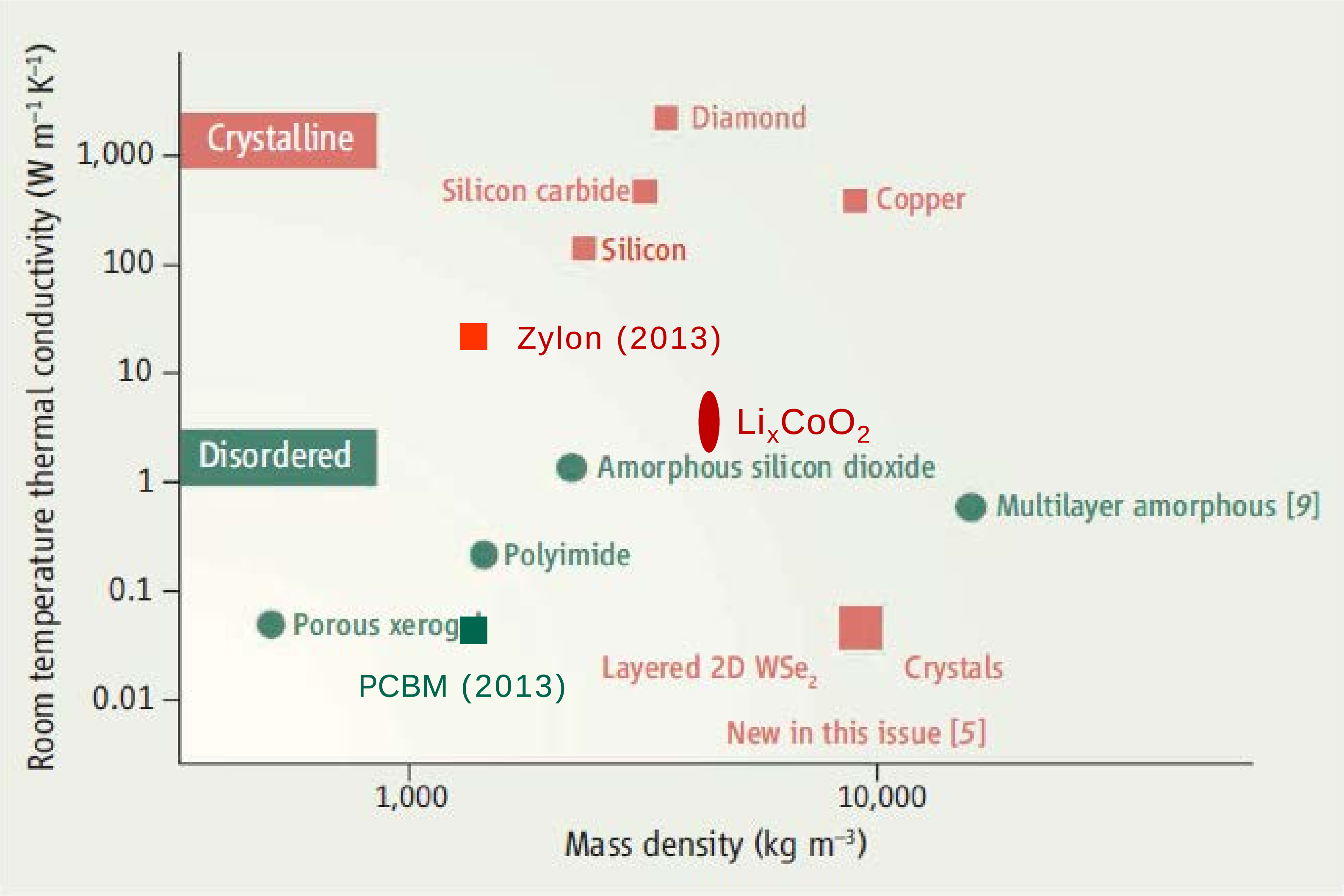
Outline

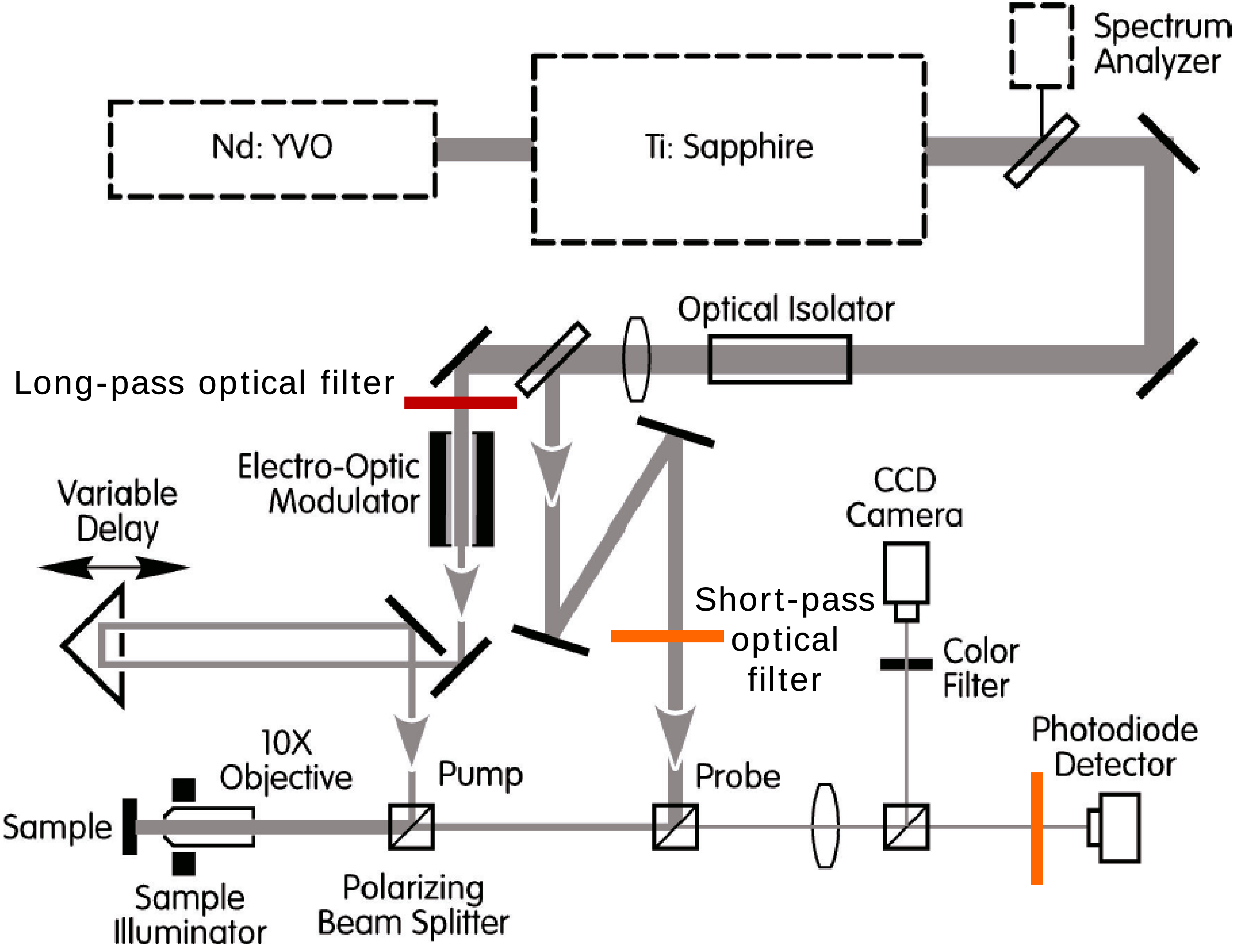
- Thermal conductivity and measurement by time-domain thermoreflectance (TDTR)
- Big picture goals of our work:
  - Understand and push the limits of thermal conductivity in various classes of materials
  - enhance thermal function in materials, e.g., abrupt changes in conductivity, actively controlled conduction, more efficient heat pumping.
- Electrochemical modulation of the thermal conductivity of Li_xCoO_2
  - Materials science and phenomenology
  - Materials physics

Thermal conductivities of dense solids span a range of 40,000 at room temperature

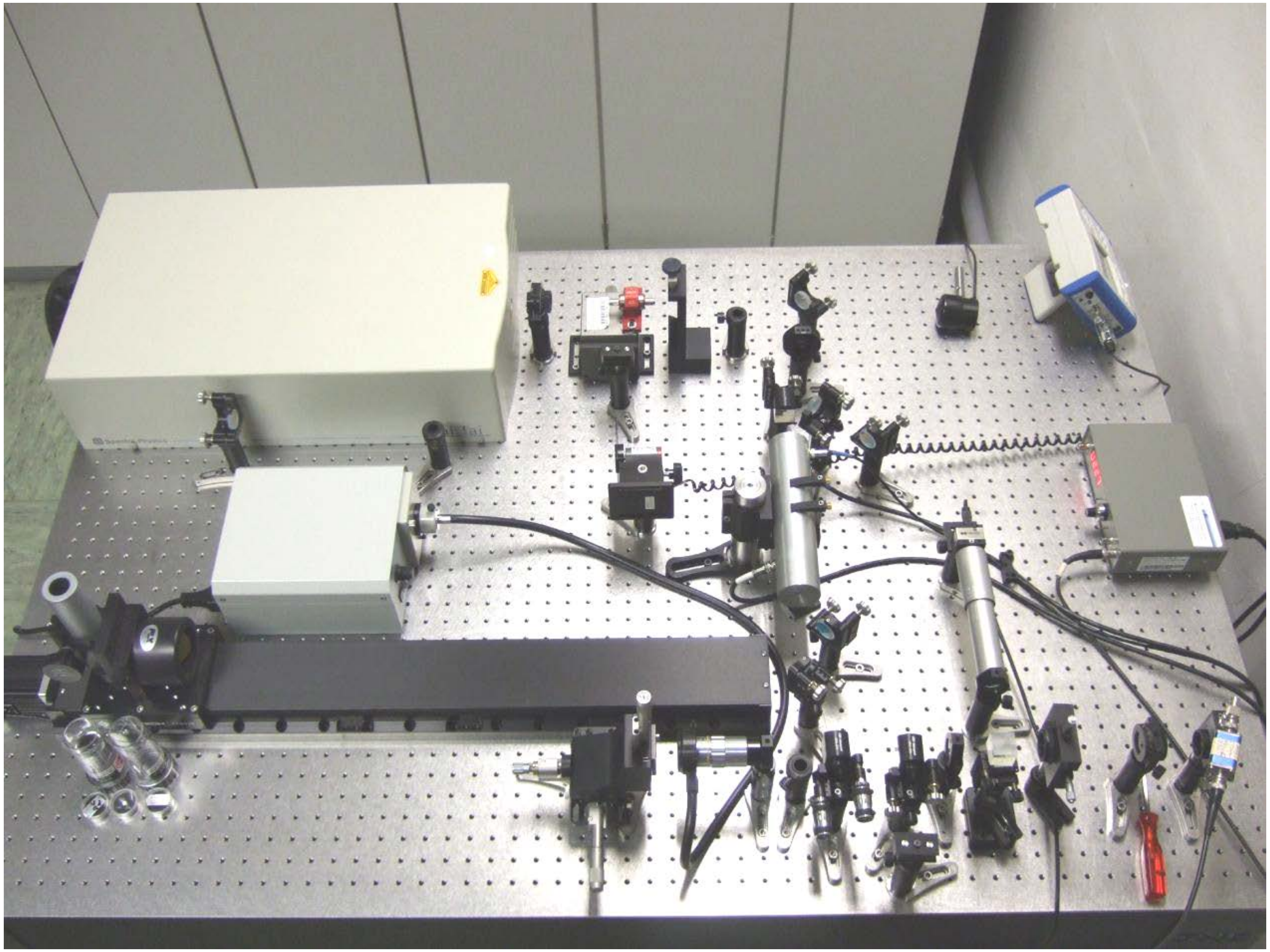


Adapted from Goodson, *Science* (2007)

Time-domain thermoreflectance



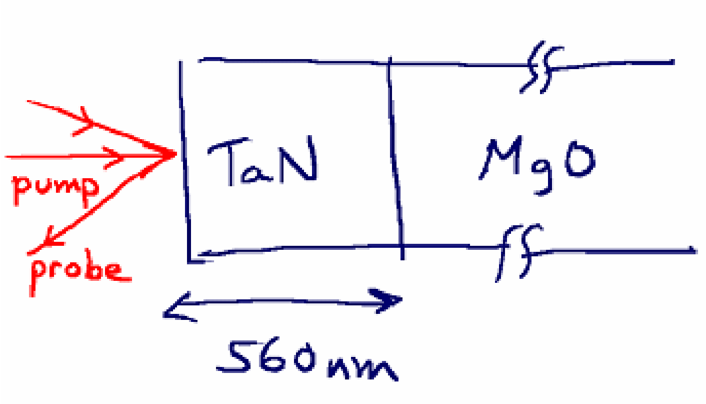
Time-domain thermoreflectance

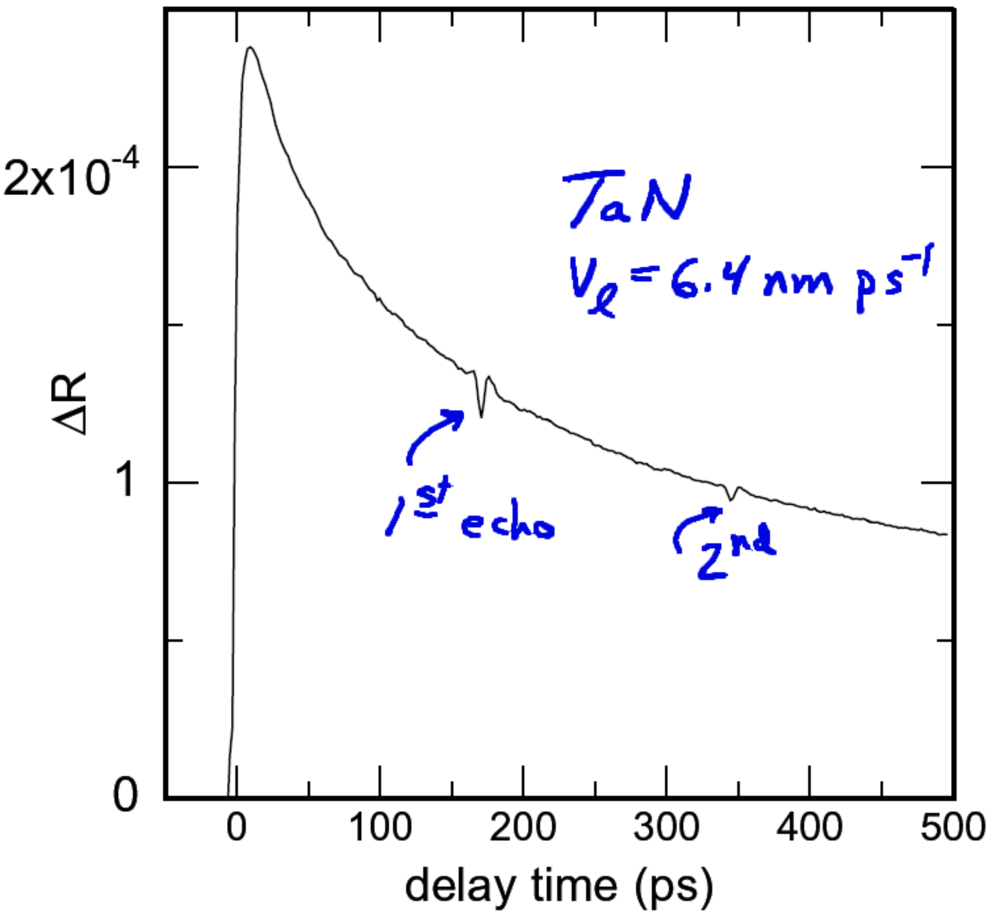


Clone built at Fraunhofer Institute for
Physical Measurement, Jan. 7-8 2008

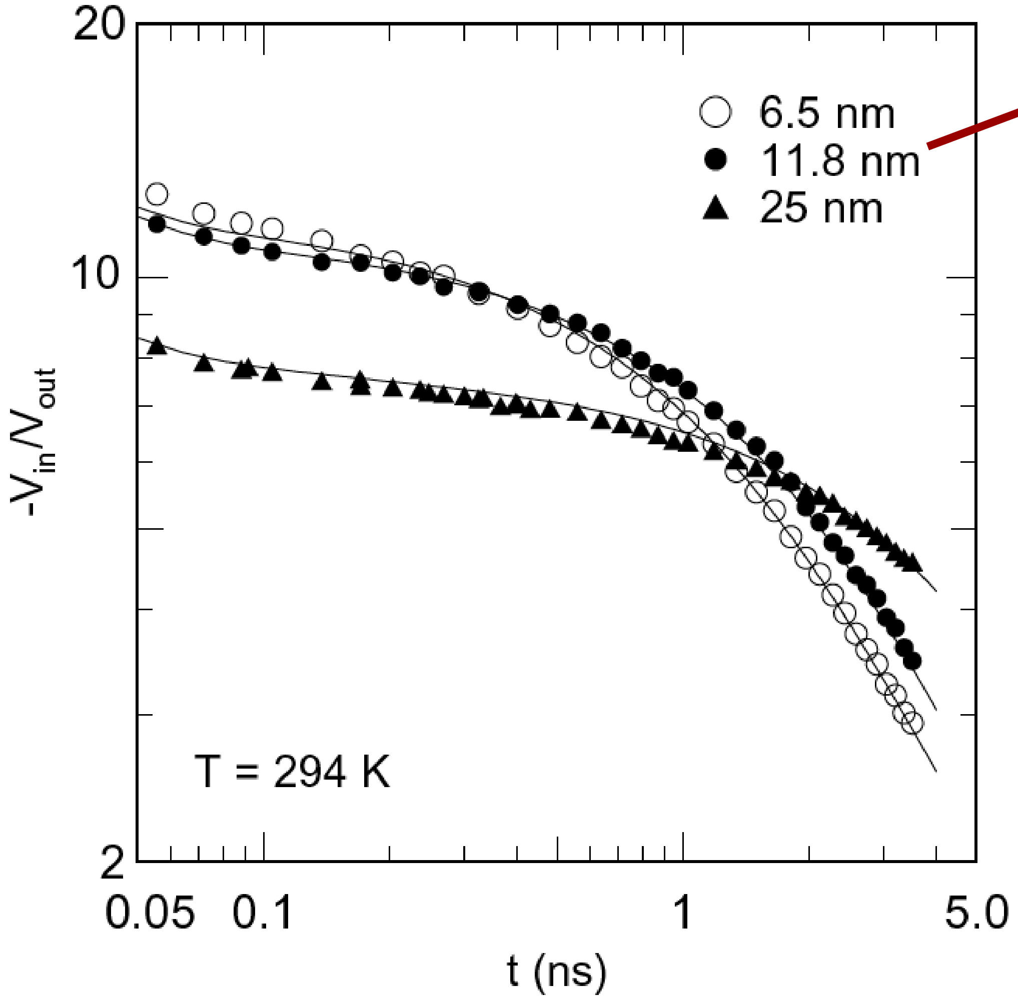
psec acoustics and time-domain thermoreflectance

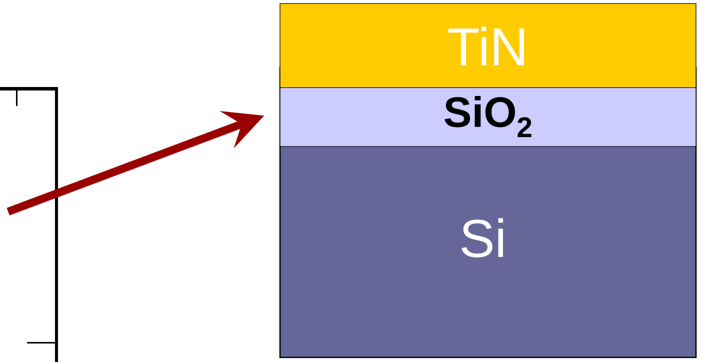
- Optical constants and reflectivity depend on strain and temperature
- Strain echoes give acoustic properties or film thickness
- Thermoreflectance dR/dT gives thermal properties





Time-domain Thermoreflectance (TDTR) data for $TiN/SiO_2/Si$

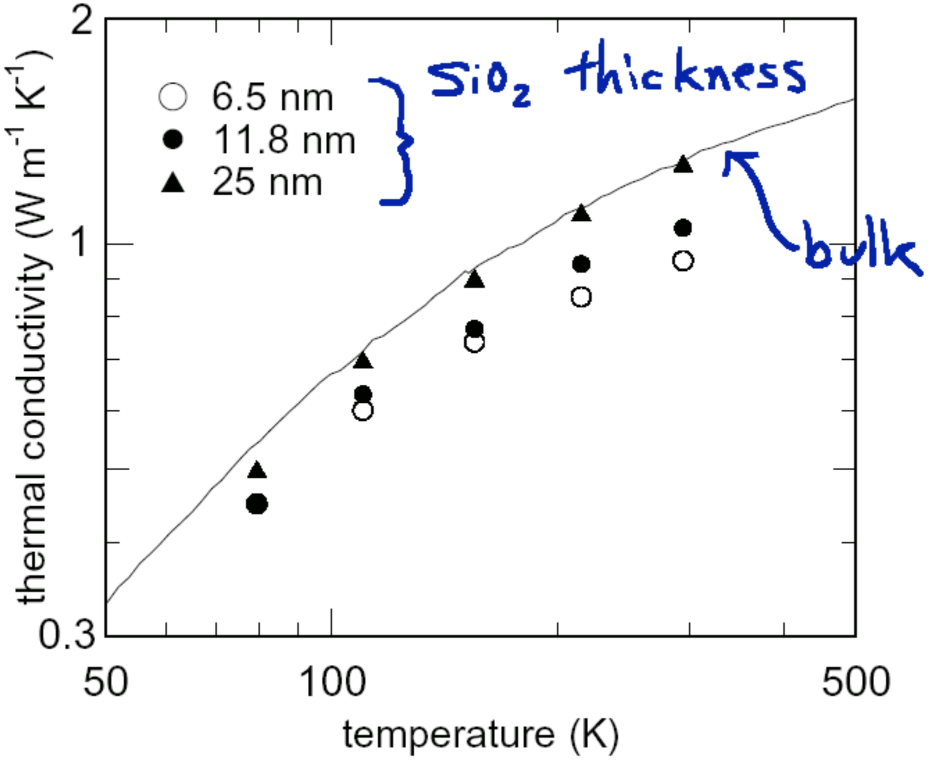


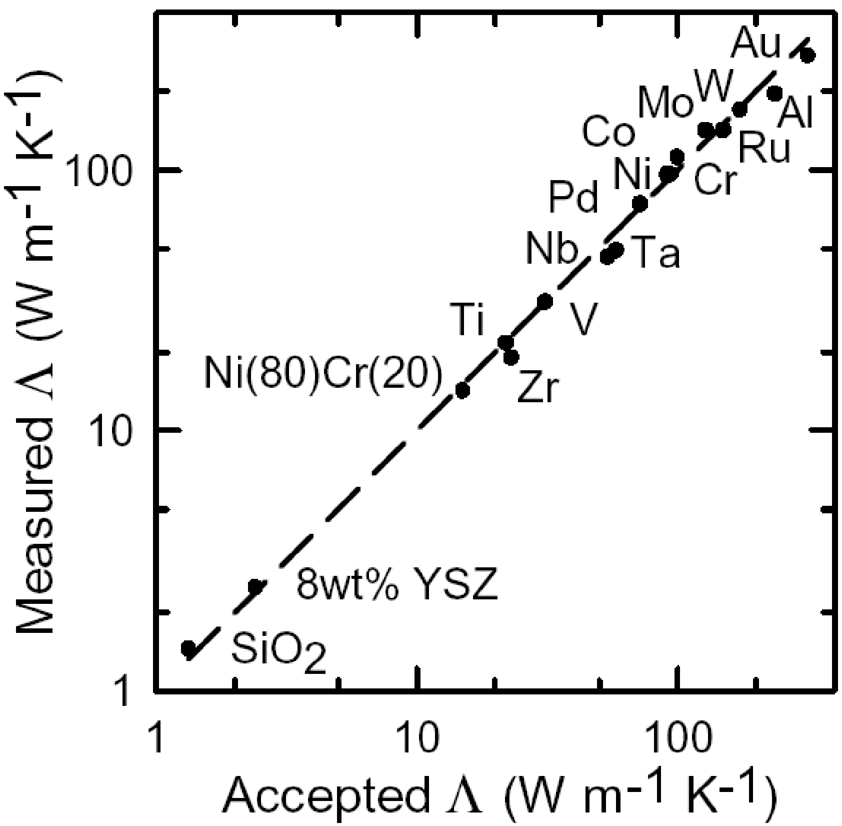


- reflectivity of a metal depends on temperature
- one free parameter: the “effective” thermal conductivity of the thermally grown SiO_2 layer (interfaces not modeled separately)

Costescu *et al*., PRB (2003)

TDTR: validation experiments

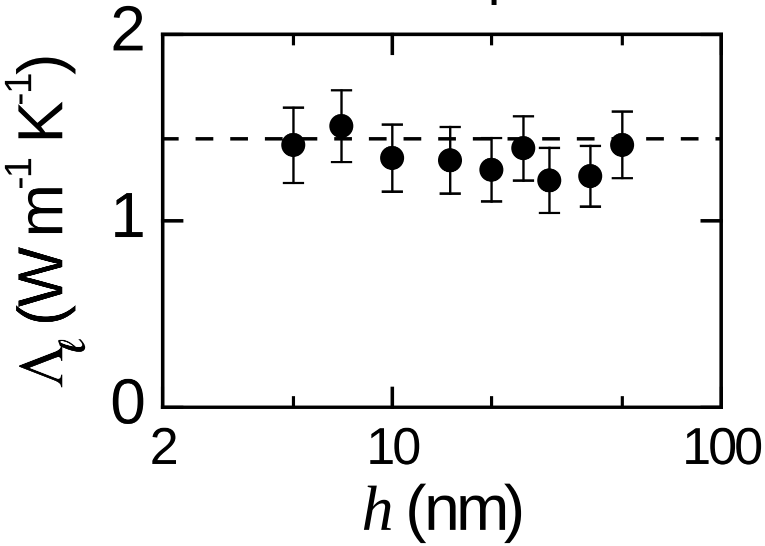




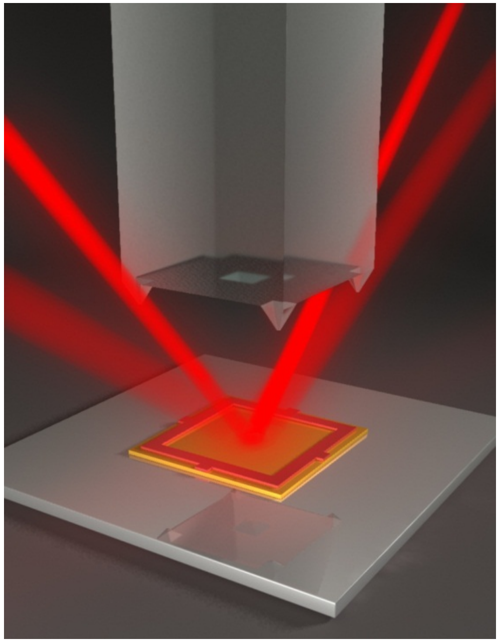
Costescu *et al*., PRB (2003)

TDTR: Flexible, convenient, and accurate

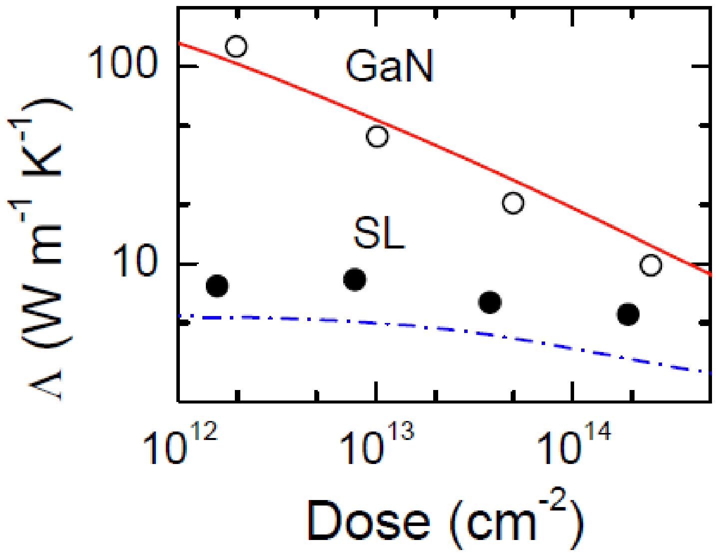
PbTe/PbSe superlattices



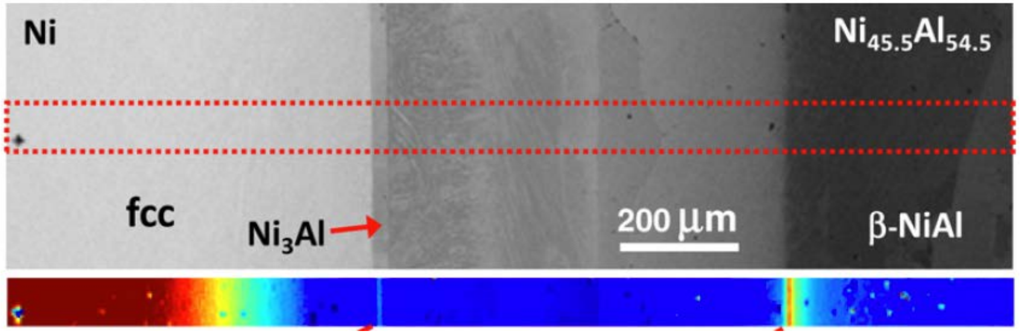
Transfer-printed interfaces



Radiation damage

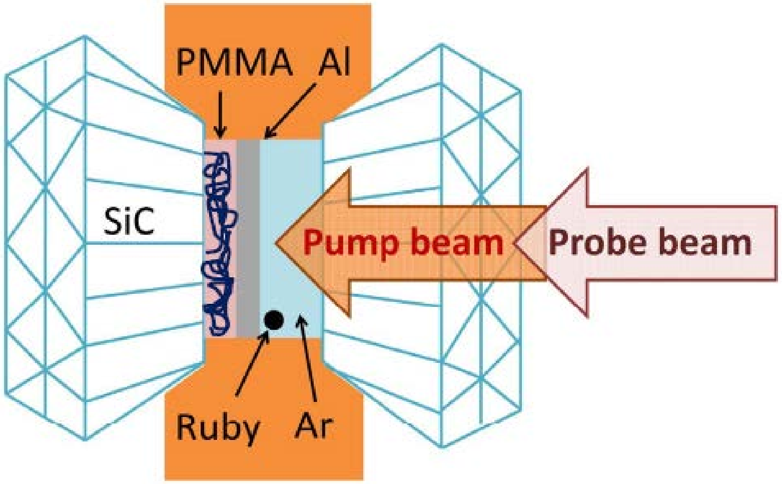


High resolution mapping

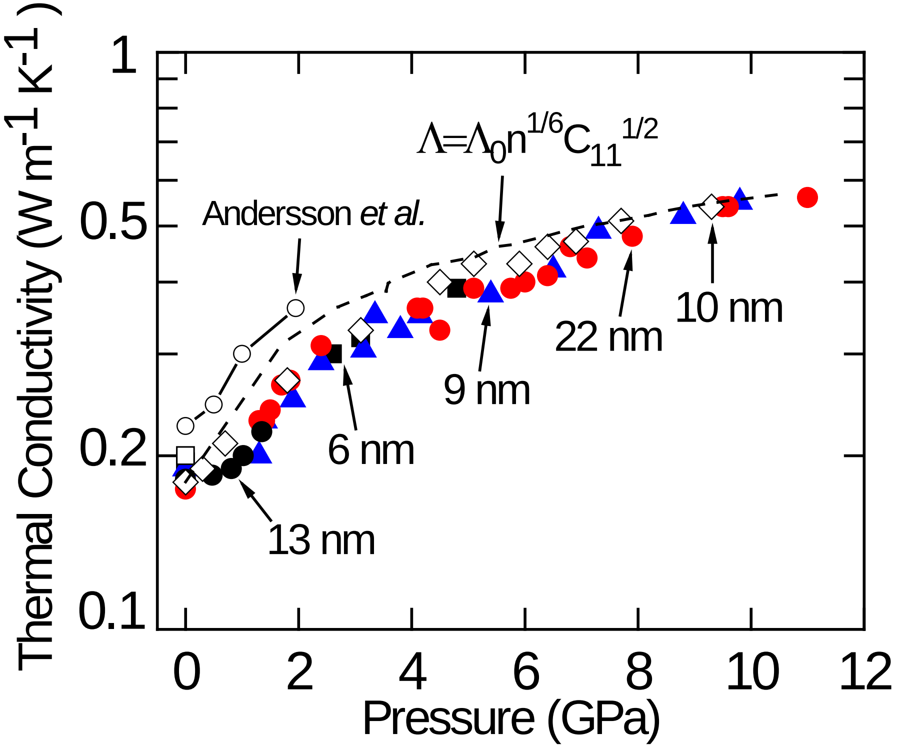


TDTR is all optical method: adaptable to "extreme" environments such as high pressure

Diamond anvil cell

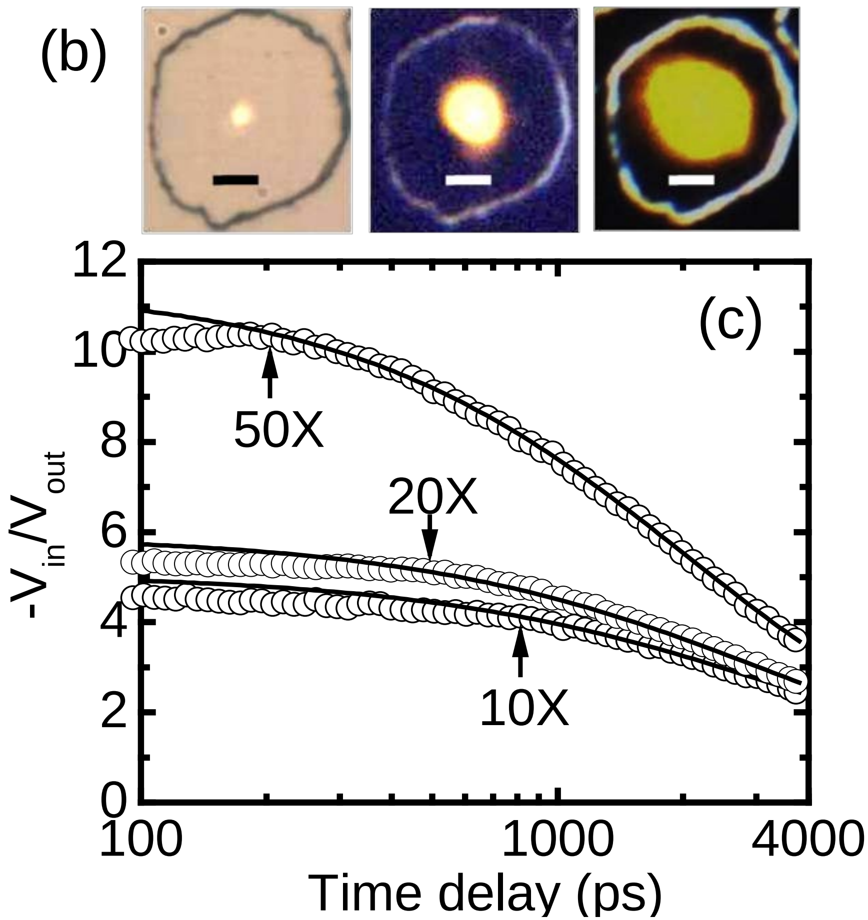


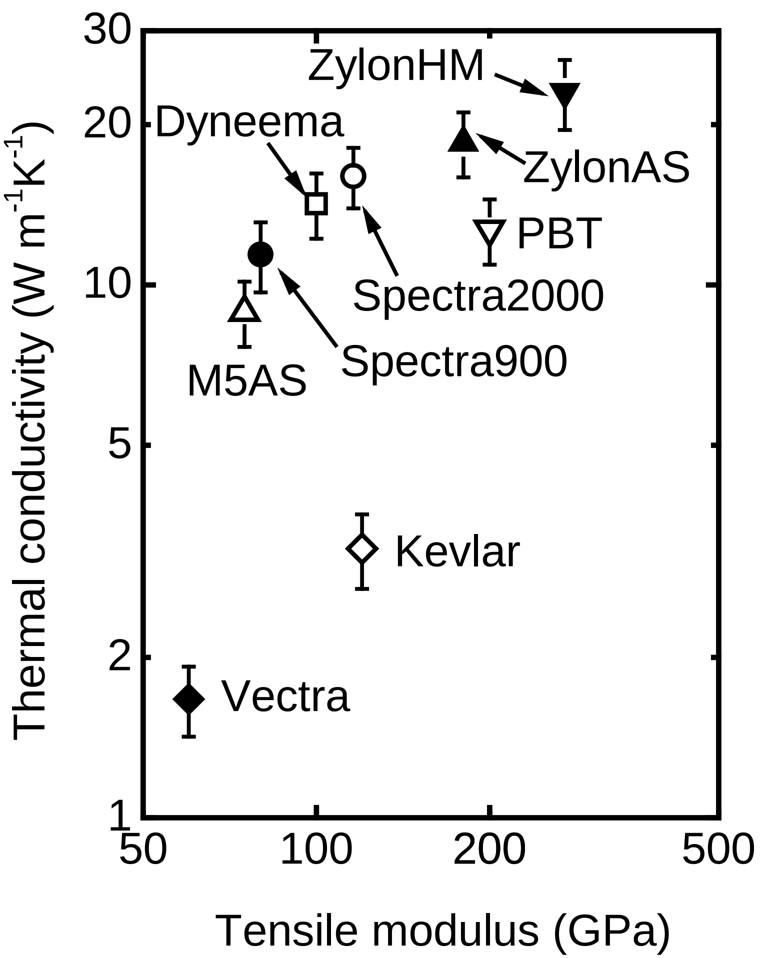
Thermal conductivity of PMMA is independent of thickness and agrees well with the predicted scaling with $(C_{11})^{1/2}$



Hsieh *et al.*, PRB (2011)

High throughput measurements of polymer fibers by time-domain thermoreflectance

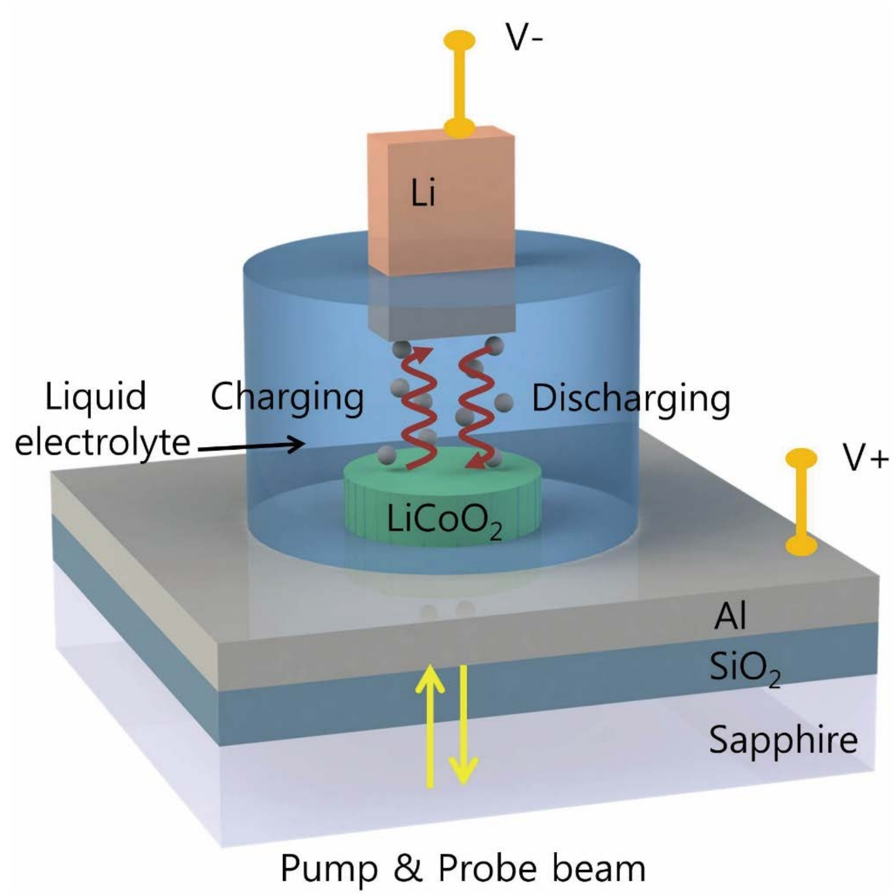




Wang *et al*., Macromolecules (2013)

Electrochemical modulation of thermal conductivity of Li_xCoO_2

- Polycrystalline thin film prepared by sputter deposition and annealing
- Real-time measurement by TDTR and picosecond acoustics.
  - ✓ Thermal conductivity 3.6→5.4 W m^{-1} K^{-1}
  - ✓ Elastic modulus 220→300 GPa
  - ✓ Ex-situ thermal conductivity contrast as large as a factor of 2.7

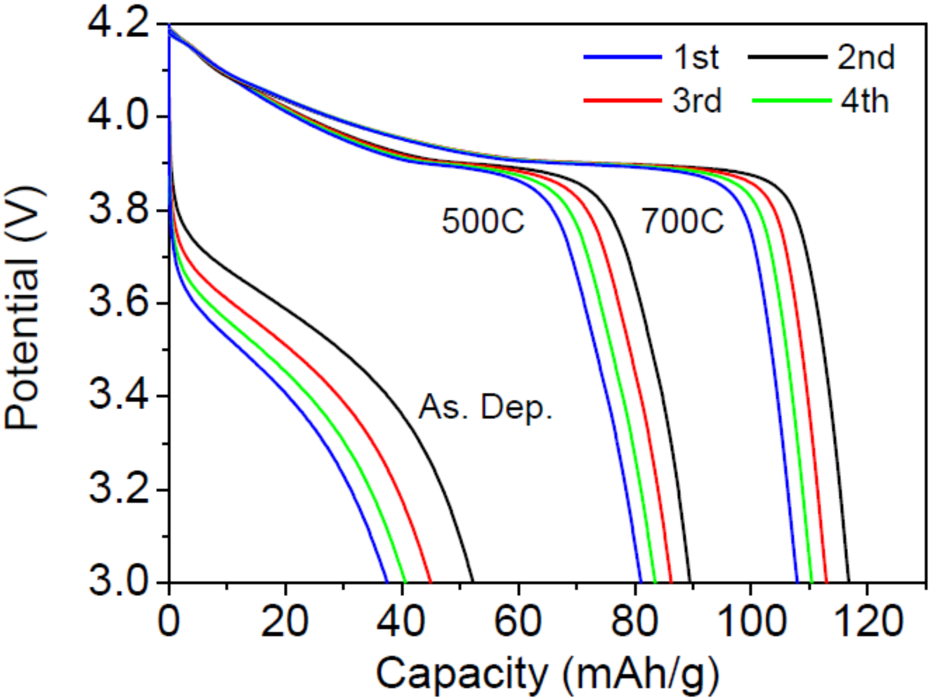


Cho *et al*., Nat. Commun. (2014)

Sputter deposit LixCo2 and anneal in air

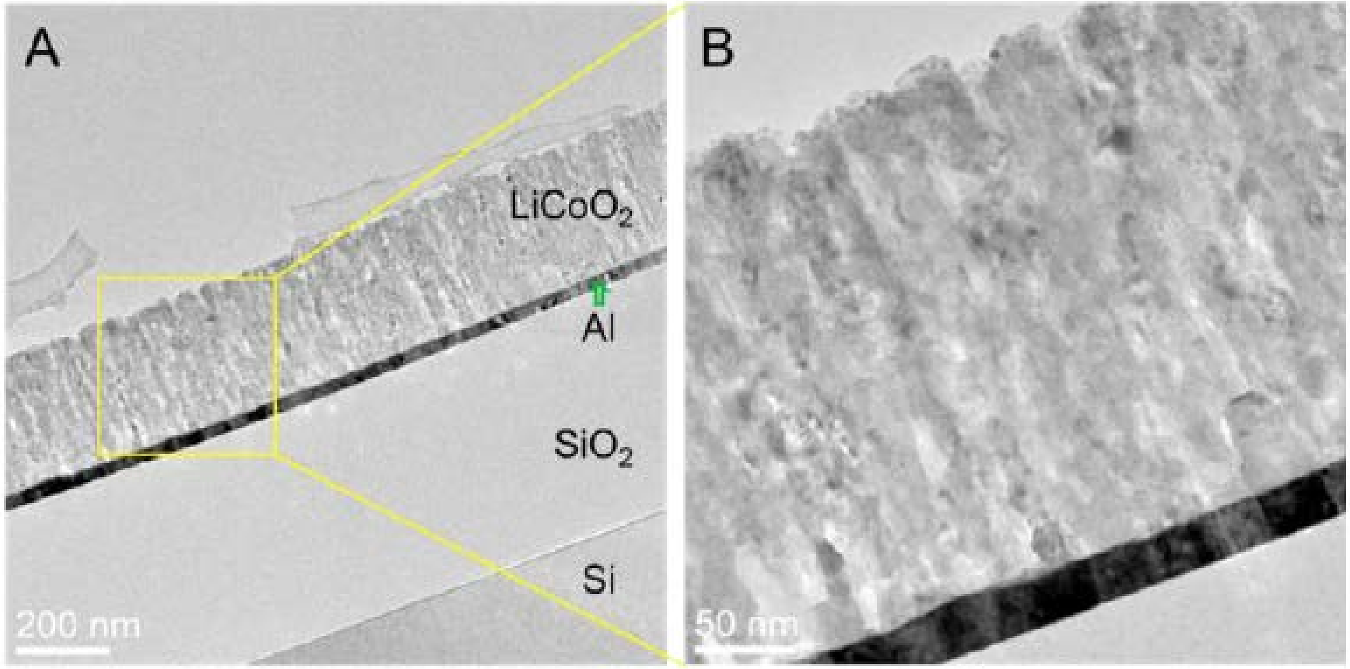
- TDTR works best with Al transducer.
  - —Limit annealing temperature of samples for in-situ studies to 500°C

500 nm Li_xCoO_2; 0.3C rate



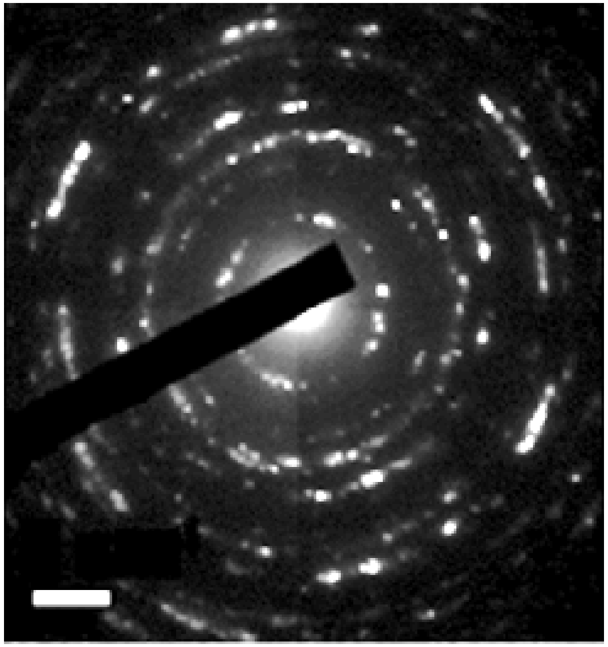
Characterize microstructure by electron microscopy

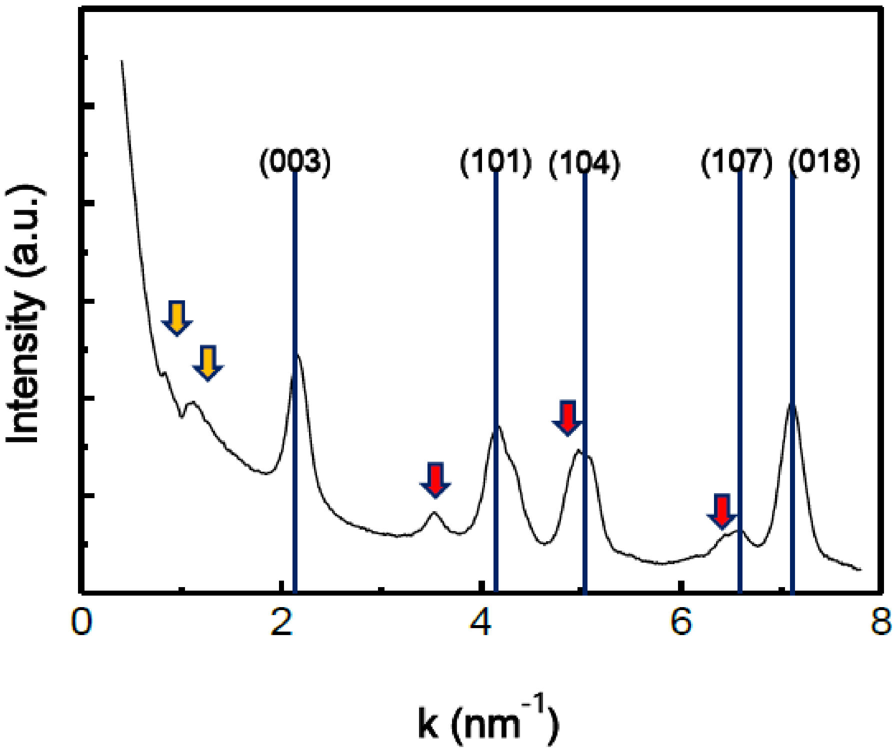
- After annealing at 500C in air
- Nanocrystalline, dense microstructure



Characterize microstructure by electron diffraction

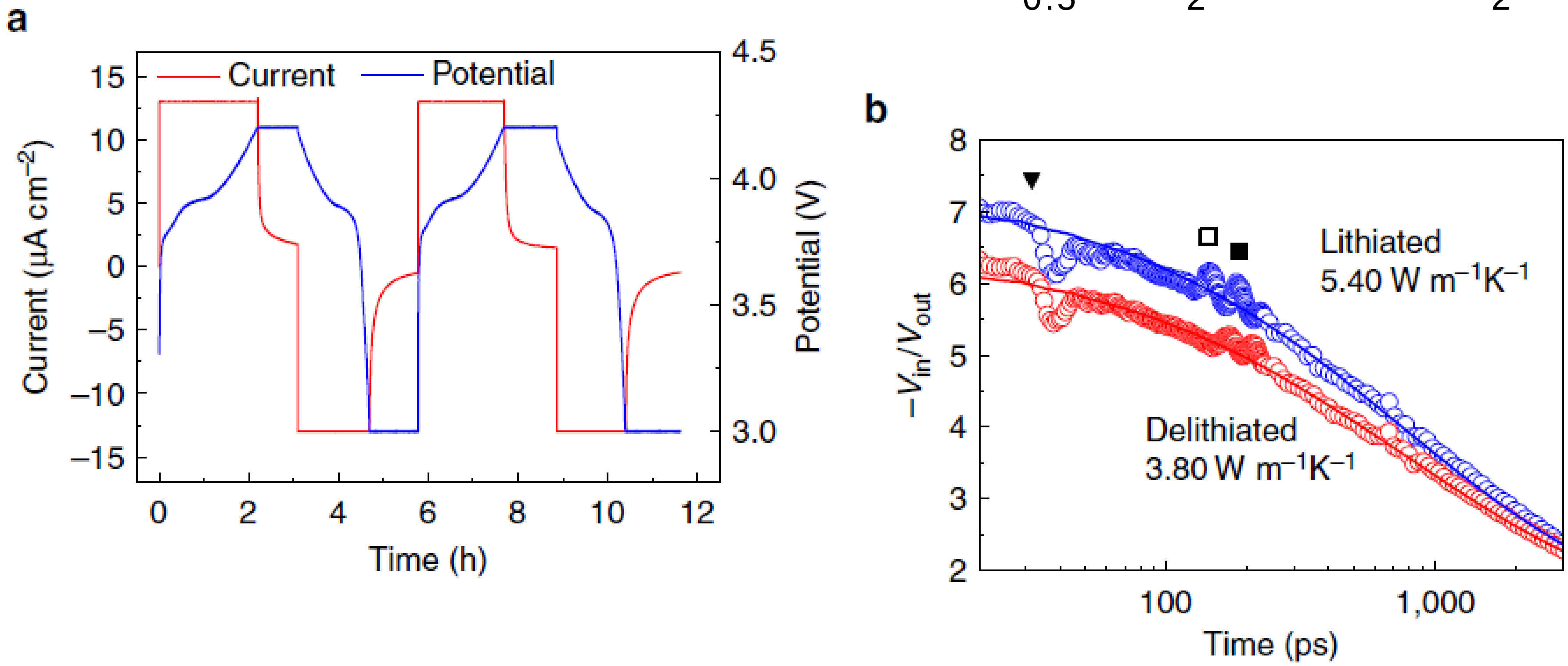
- No strong texture; would eventually like to study textured films





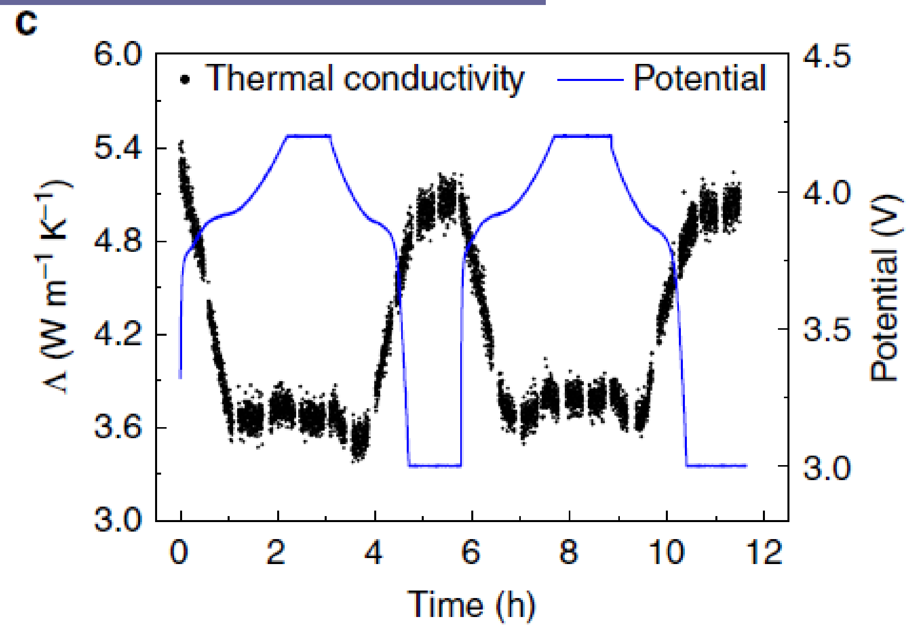
In-situ measurements of thermal conductivity and elastic constants

- Full delay time scans of $Li_{0.5}CoO_2$ and $LiCoO_2$

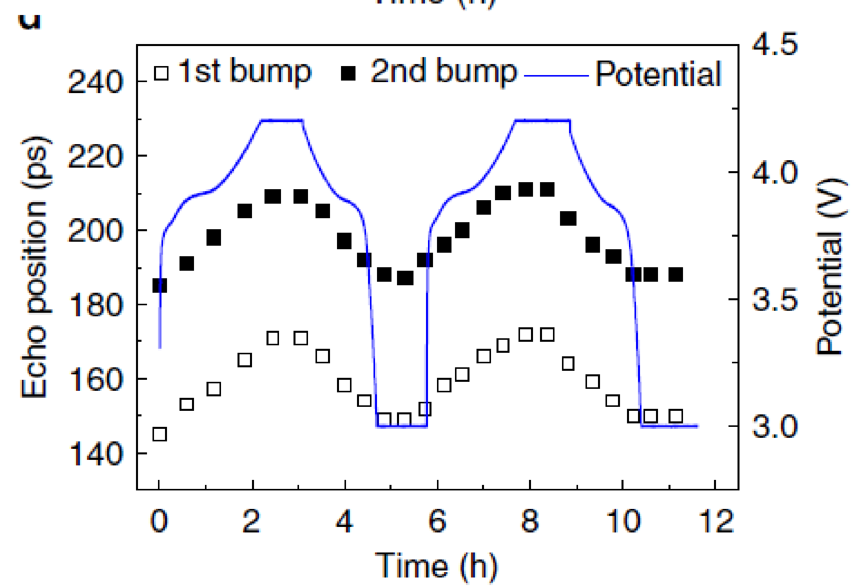


Continuous real-time measurements during electrochemical cycling

- With delay time set to a fixed value, ratio can be measured continuously and converted to thermal conductivity.

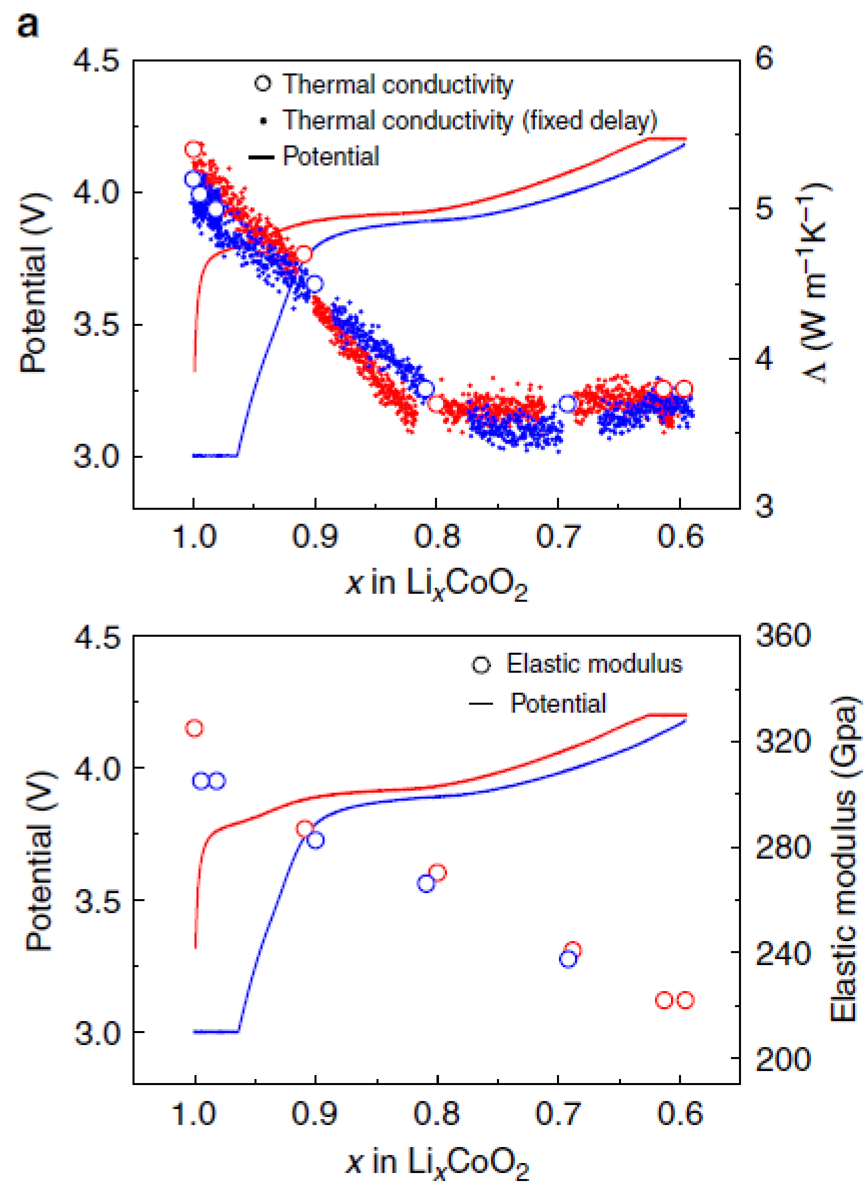


- Position of acoustic echo requires a scan over a limited range of delay times. Peak volume change is only 1.3% so changes in thickness are negligible.



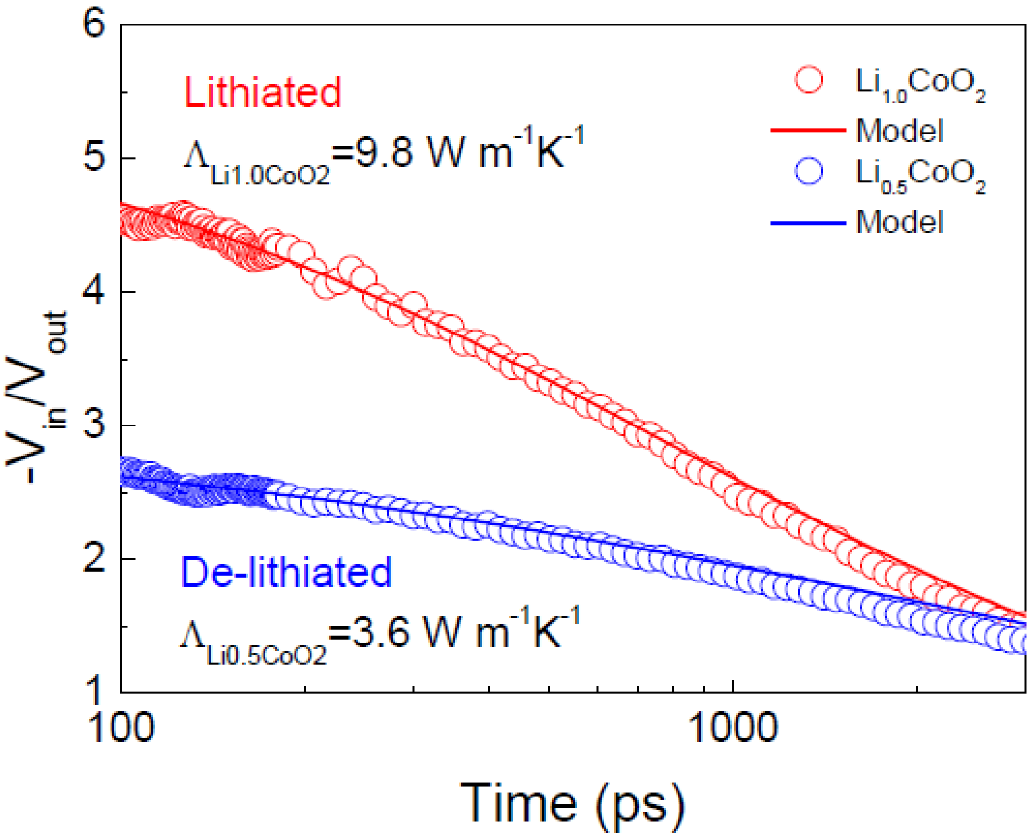
Continuous real-time measurements during electrochemical cycling

- Convert time-axis to composition. (We assume irreversible capacity loss occurs only during the lithiation cycle.)
- Thermal conductivity is not a linear function of x; plateau for 0.5<x<0.8
- Longitudinal elastic modulus is a linear function of x.



Ex-situ measurements of film annealed at 700°C shows higher conductivity in fully lithiated state.

- Not yet sure of the mechanism.
    - Different texture?
    - Larger grain size?
    - Fewer point defects?



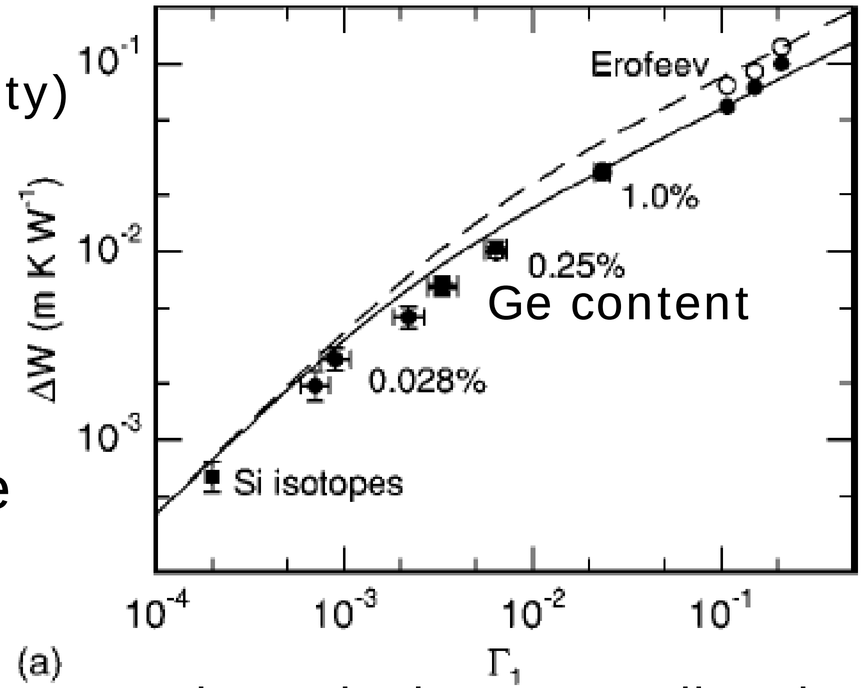
Do Li vacancies scatter phonons?

- Classic example of point defect scattering is mass disorder created by isoelectronic substitution, e.g., SiGe alloy

dilute SiGe alloys

Change in thermal resistivity
(Reciprocal of thermal conductivity)

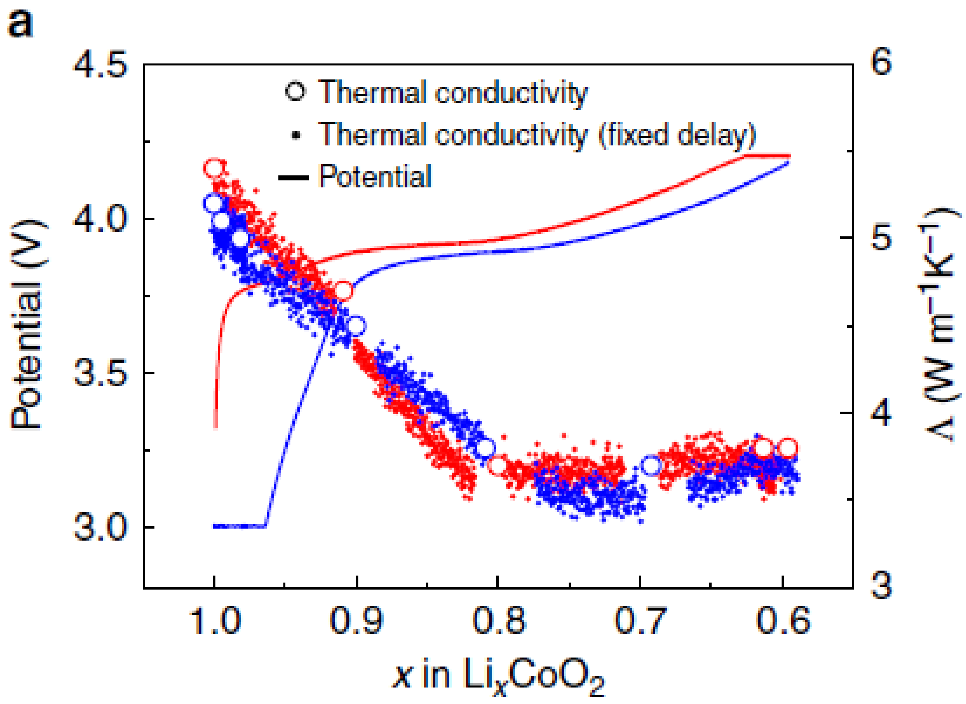
- Unlikely that random Li vacancies alone can explain the dependence of thermal conductivity on *x*.



Dimensionless mass disorder

Mixture of Li rich and Li poor nanoscale phases?

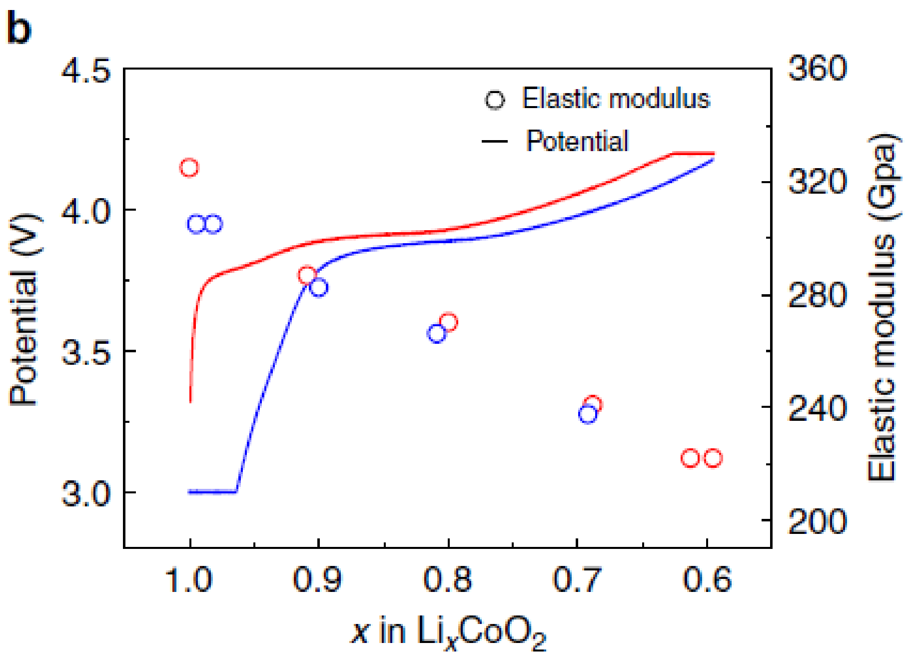
- Evidence in the literature (Reimer *et al.*, JES (1992)) for a two-phase region $0.75<x<0.93$.
- This possibility makes the situation exceedingly complicated to predict the effect on thermal conductivity: disorder and characteristic size of each phase could vary with the average lithium content.

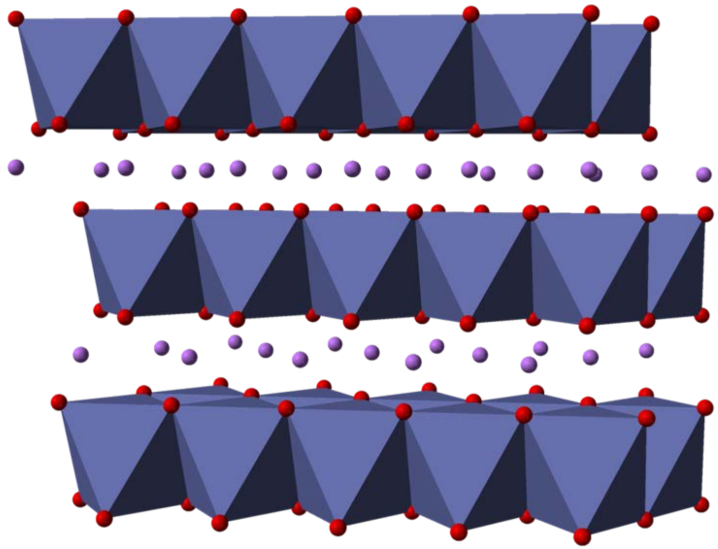


Li content has a strong influence on stiffness of bonds in the CoO_2 sheets

- Our samples are not textured so the change in longitudinal modulus is most due to C_{11} (stretch/compress along *a*-*b* plane)

- Higher Li content → greater electron density in the CoO_2 sheets → increased bond strengths (?)





Summary

- Time-domain thermoreflectance and picosecond acoustics enable real-time measurements of thermal conductivity and elastic constants of electrode materials.
- Contrast between low and high thermal conductivity states of Li_xCoO_2 up to a factor of 2.7.
- Working on getting full set of elastic constants: by experiment (surface-acoustic waves; orientation dependence) and theory (DFT by Prof. Elif Ertekin).
- Changes in longitudinal elastic modulus are linear in *x*; i.e., virtual crystal or effective medium seems to apply.
- Changes in thermal conductivity are not linear in *x* and show a plateau for $0.5 < x < 0.8$.
  - Speculate that this is caused by changing mixture of phases.