Electrochemical control of thermal conductivity in thin films

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• 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 $\text{Li}_x\text{CoO}_2$
  – 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

Nd: YVO → Ti: Sapphire

Long-pass optical filter

Variable Delay

Electro-Optic Modulator

10X Objective

Sample Illuminator

Pump

Sample

Polarizing Beam Splitter

Short-pass optical filter

Optical Isolator

CCD Camera

Color Filter

Probe

Photodiode Detector

Spectrum Analyzer
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)
Costescu et al., PRB (2003)
TDTR: Flexible, convenient, and accurate

PbTe/PbSe superlattices

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

Transfer-printed interfaces

Radiation damage

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

High resolution mapping
TDTR is an all-optical method adaptable to “extreme” environments such as high pressure.

Thermal conductivity of PMMA is independent of thickness and agrees well with the predicted scaling with $(C_{11})^{1/2}$.
High throughput measurements of polymer fibers by time-domain thermoreflectance

(b) [Images of fiber samples]

(c) [Graph showing thermal conductivity and tensile modulus]

- $-V_{in}/V_{out}$ vs. time delay (ps)
- Thermal conductivity (W m$^{-1}$K$^{-1}$) vs. tensile modulus (GPa)

Wang et al., Macromolecules (2013)
Electrochemical modulation of thermal conductivity of Li$_x$CoO$_2$

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

Sputter deposit \( \text{Li}_x\text{CoO}_2 \) and anneal in air

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

500 nm \( \text{Li}_x\text{CoO}_2 \); 0.3C rate
Characterize microstructure by electron microscopy

- After annealing at 500°C 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

Change in thermal resistivity (Reciprocal of thermal conductivity)

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

![Graph showing the change in thermal resistivity as a function of Ge content in dilute SiGe alloys.](image)
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 $\rightarrow$ greater electron density in the CoO$_2$ sheets $\rightarrow$ 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$_x$CoO$_2$ 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.