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Time domain thermoreflectance 1.0: Fundamentals

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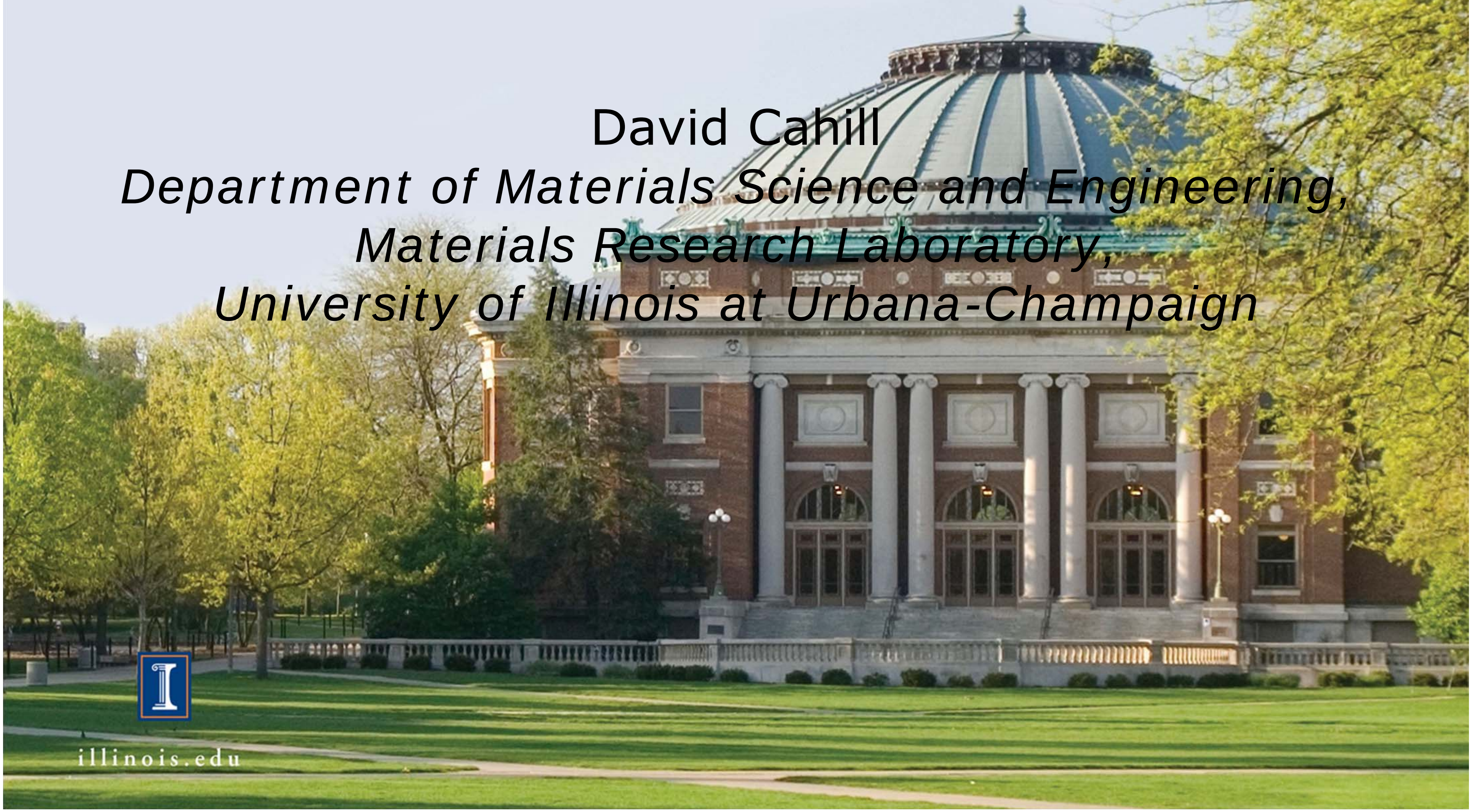

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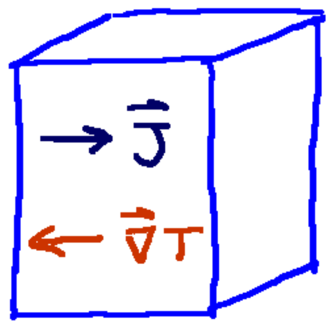
Outline

- Thermal transport coefficients; length and time scales
- Experimental details and data acquisition
- Data analysis
- Validation
- Sensitivities and error propagation
- Examples of high throughput measurements as a function of composition and temperature

Thermal transport coefficients

- Thermal conductivity Λ is a property of the continuum

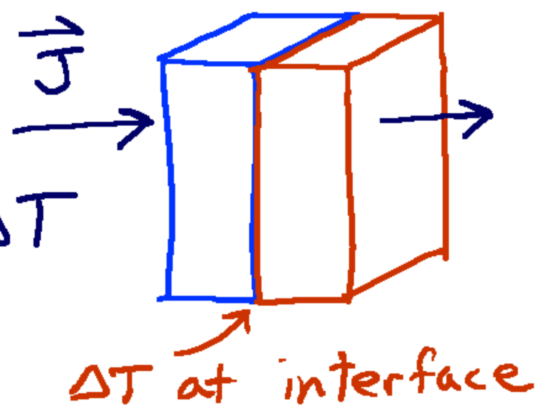
$$\vec{J} = -\Lambda \vec{\nabla} T$$



$$\Lambda = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \vec{j}(t)\cdot\vec{j}(0)\rangle\, dt$$

- Thermal conductance (per unit area) G is a property of an interface

$$J = G\Delta T$$



$$G = \frac{1}{Ak_BT^2}\int_0^\infty \langle q(t)q(0)\rangle\, dt$$

Thermal transport coefficients

- Thermal conductivity Λ appears in the diffusion equation

$$C\frac{dT}{dt} = \Lambda \nabla^2 T$$

C = heat capacity per unit volume

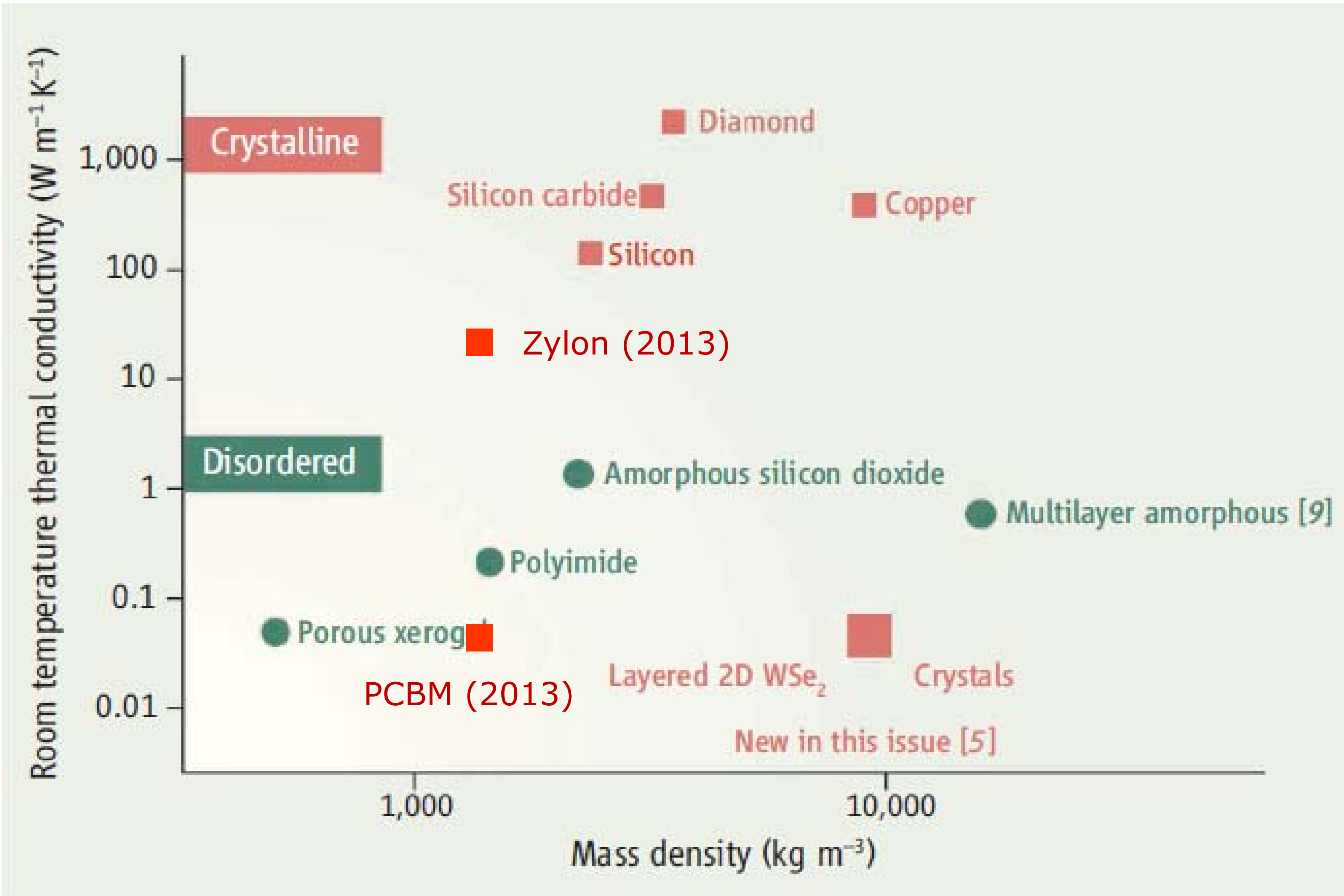
Diffusivity $D = \frac{\Lambda}{C}$ Effusivity $\varepsilon = \sqrt{\Lambda C}$

- Interface thermal conductance G is a radiative boundary condition

$$G\left(T_+ - T_-\right) = \Lambda \left.\frac{dT}{dz}\right|_{z=0}$$

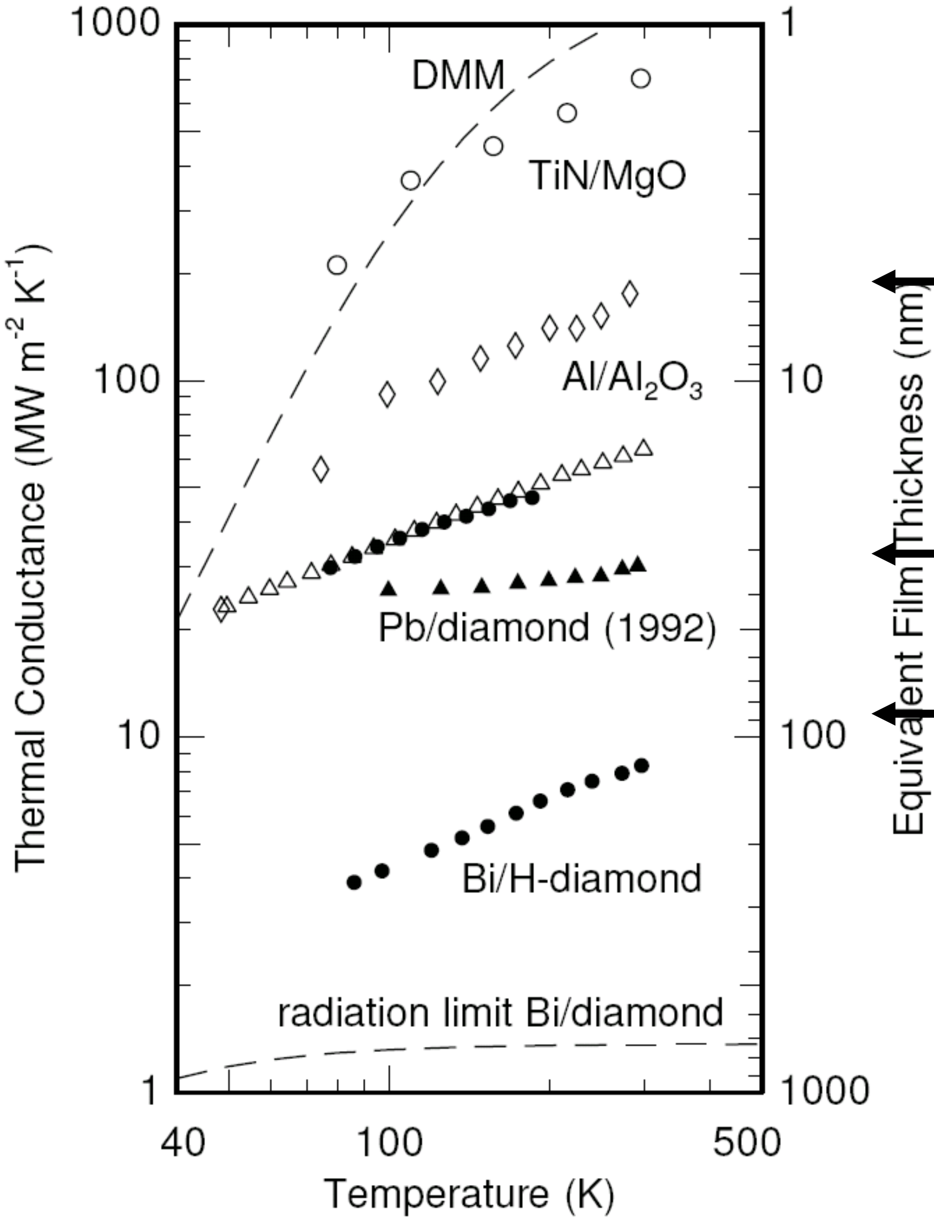
Kapitza length $L_K = \frac{\Lambda}{G}$

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



Adapted from Goodson, *Science* (2007)

Interface condctance spans a factor of 60 range at room temperature



W/Al_2O_3

Au/water

$PMMA/Al_2O_3$

nanotube/alkane

Heat capacity per unit volume of solids spans only a factor of 4 at room temperature

Material	C (J cm^{-3} K^{-1})
water	4.18
Ni	3.95
Al	2.42
Diamond	1.78
Polymer (PMMA)	1.8
PbTe	1.2

Additional length and time scale

- Range of Kaptiza lengths
  - Al/diamond $L_K \sim 10\ \mu m$
  - Al/polymer $L_K \sim 1\ nm$

- Typical thickness for an opaque metal film is h=50 nm.
- Time scales $\tau_D = \dfrac{h^2}{D}$ for heat diffusion over a length scale of 50 nm
  - diamond $\tau_D \approx 25$ ps
  - polymer $\tau_D \approx 25$ ns

Additional length and time scale

- Typical "RC" time-constant for the thermal relaxation of a 50 nm metal film with cooling limited by an interface with G = 100 MW m^{-2} K^{-1}

$$\tau_G = \frac{hC}{G} = 1.5 \text{ ns}$$

Interesting to ask: What thermal conductivity gives

$$\tau_G = \tau_D \text{ , equivalent to } \quad h = L_K$$

$$\Lambda = 5 \text{ W m}^{-1} \text{ K}^{-1}$$

Additional length and time scale

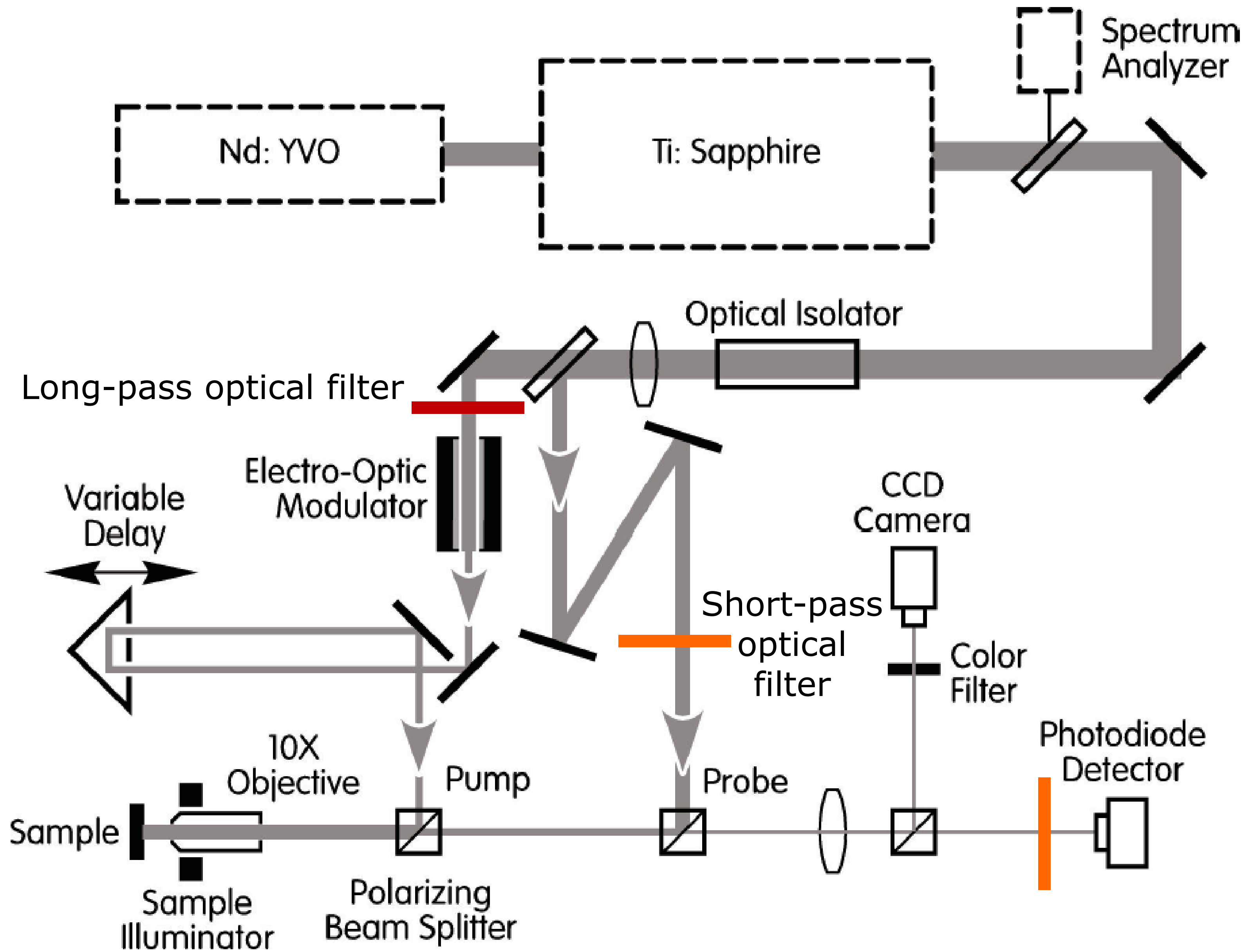
- Bottom line:
  - ✓ to measure G we want to access time scales $\sim\tau_G$, typically ns.
  - ✓ to measure Λ we ideally access time scales $> \tau_D$

- Modulated time-domain thermoreflectance gives us a way to access a wide range of time scales, from ps to

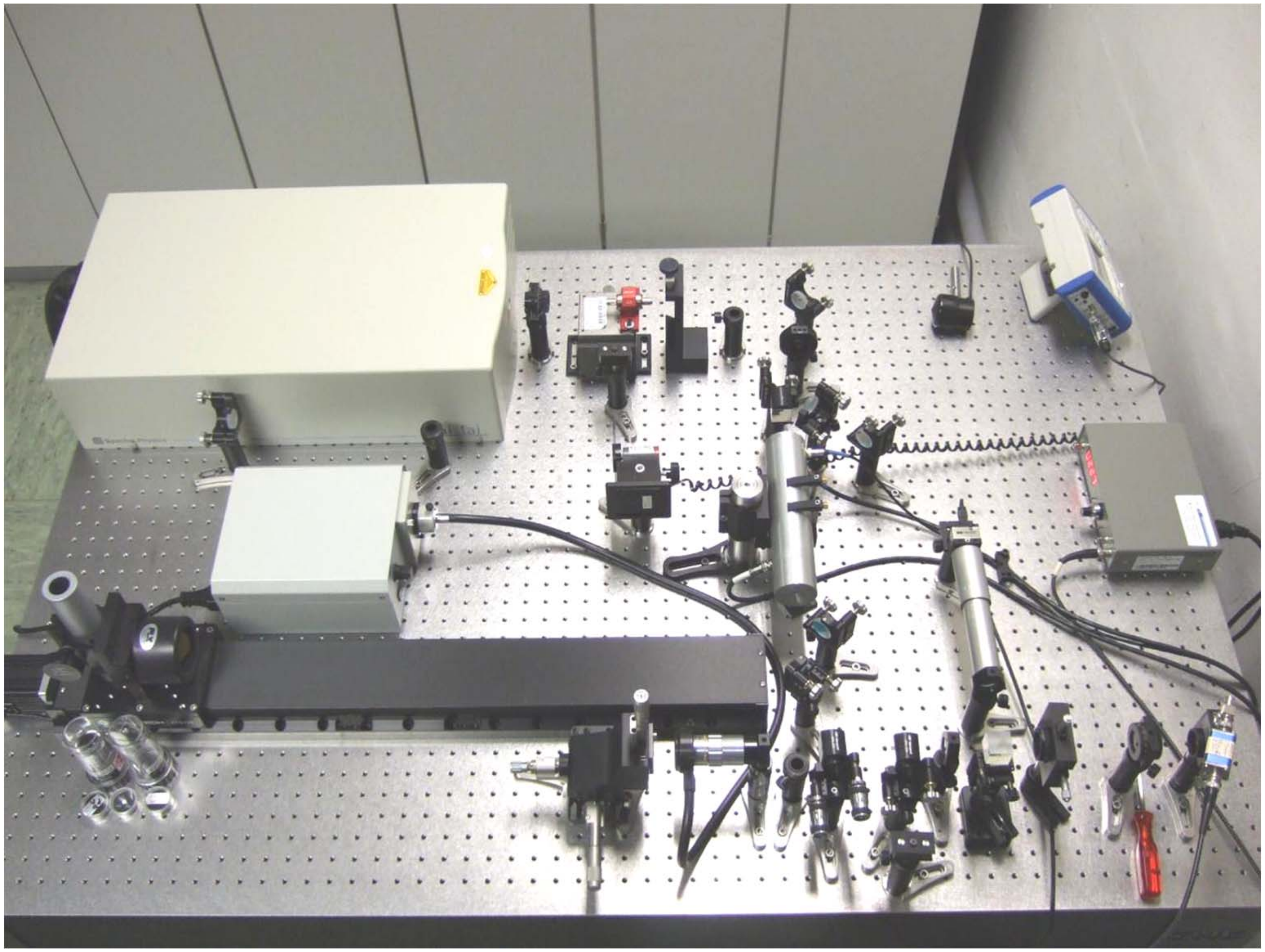
$$\tau_f = \frac{1}{2\pi f}\ , \ \text{where } f \text{ is the modulation frequency}$$

- Typically f=10 MHz, so τ_f = 16 ns

Time-domain thermoreflectance



Time-domain thermoreflectance



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

Digression on signal processing

- We also typically chop the probe beam at 200 Hz.
- Output of the photodiode has a small signal at the pump modulation frequency that turns on and off at 200 Hz.
- We use a series of lockins, the first rf lockin synchronized to the pump modulation frequency followed by two audio frequency lockins synchronized to the two output channels of the rf locking.
- The rf lockin we use has a square wave mixer so odd harmonics of the modulation frequency have to be suppressed using an electrical filter.

Digression on optical design

- Single objective lens focuses the pump and probe, collimates the reflected probe, and forms a dark-field microscopy image on the camera.
  - dark-field microscopy means that specularly reflected illumination light cannot pass through the aperture at the back focal plane of the objective. Perfect surface is dark. Defects, dust are bright.
  - Sample position is determined by focused image on the camera. When the sample is in focus, the sample is f_{obj} away from the front principal plane of the objective lens.

Digression on optical design

- A lens converts angles at the back focal plane to positions at the front focal plane.

$$\Delta x = f_{obj} \Delta \theta$$

- Convention is to characterize the laser beam radius by w_0, the $1/e^2$ intensity radius.

$$I(r) = I_0 \exp\left(-\frac{2r^2}{w_0^2}\right)$$

- A lens transforms a beam of radius w_b in the back focal plane to a radius w_0 at the front focal plane.

$$w_0 = \frac{\lambda f_{obj}}{\pi w_b}$$

- f_{obj} is (usually) 200 mm divided by the power, e.g., 10x, of the lens.

$$f_{obj} = \frac{200 \text{ mm}}{10} = 20 \text{ mm}$$

- Depth of focus scales quadratically with spot radius.

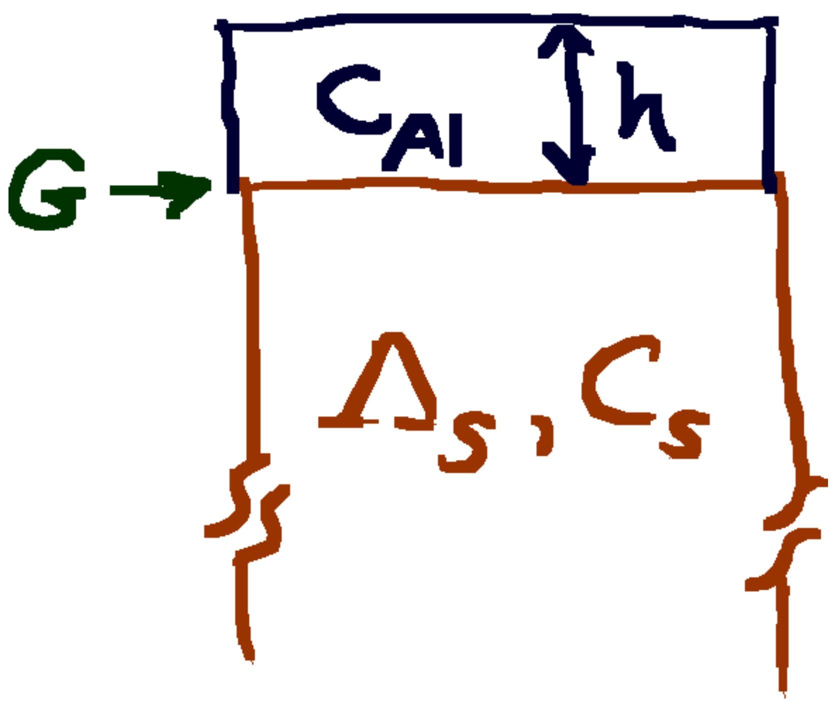
$$\Delta z \propto \frac{w_0^2}{\lambda}$$

Digression on optical design

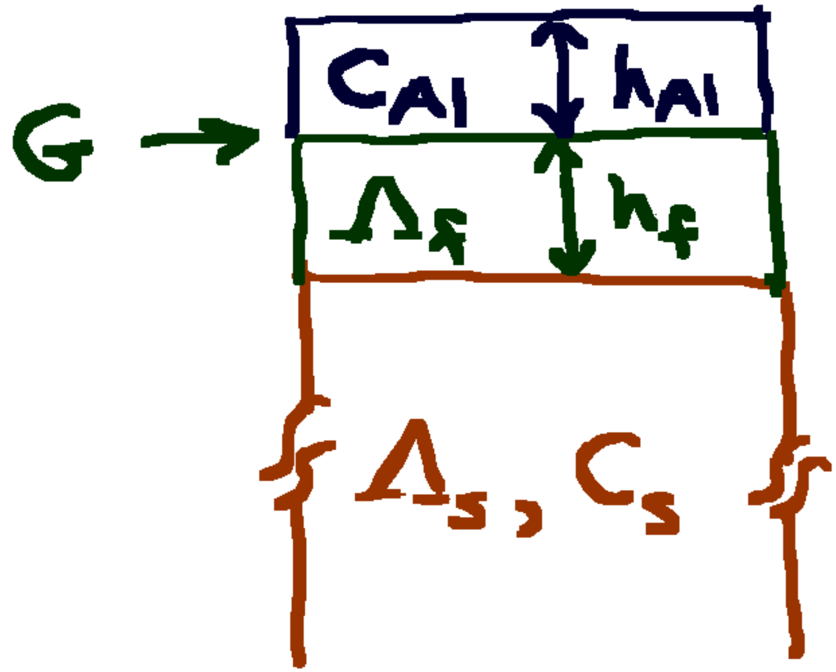
- Crucial that the electric field of reflected probe beam is not clipped by the back focal plane of the aperture or another other obstruction in the beam path to the photodiode.
  - Clipping of the beam can convert phase modulation of the probe due to thermal expansion into amplitude modulation.
  - TDTR depends on the fact that changes in reflected intensity are proportional to temperature of the metal transducer.
  - This limits the minimum w_0 for a given numerical aperture N.A., i.e., the aperture cannot be "filled".
- We used to use an aperture in the reflected probe path but that is no longer needed because of the high quality optical filters and the "two-tint" approach.

Two basic types of experiments

- thermal conductivity of bulk samples and thermal conductance of interfaces

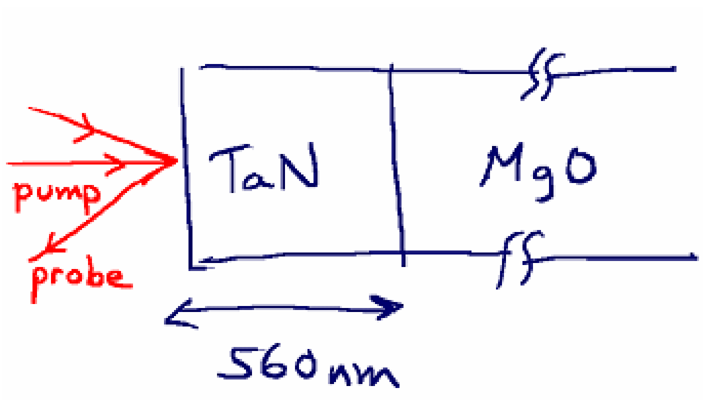


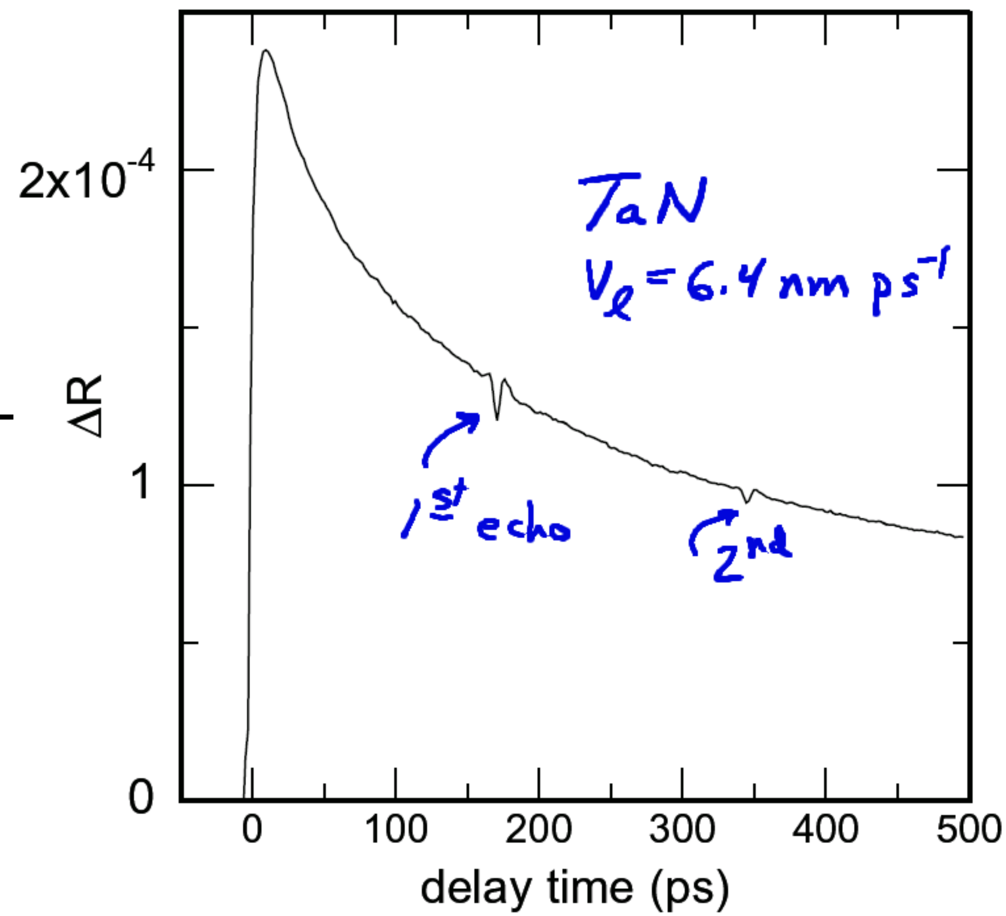
- thermal conductivity of thin films



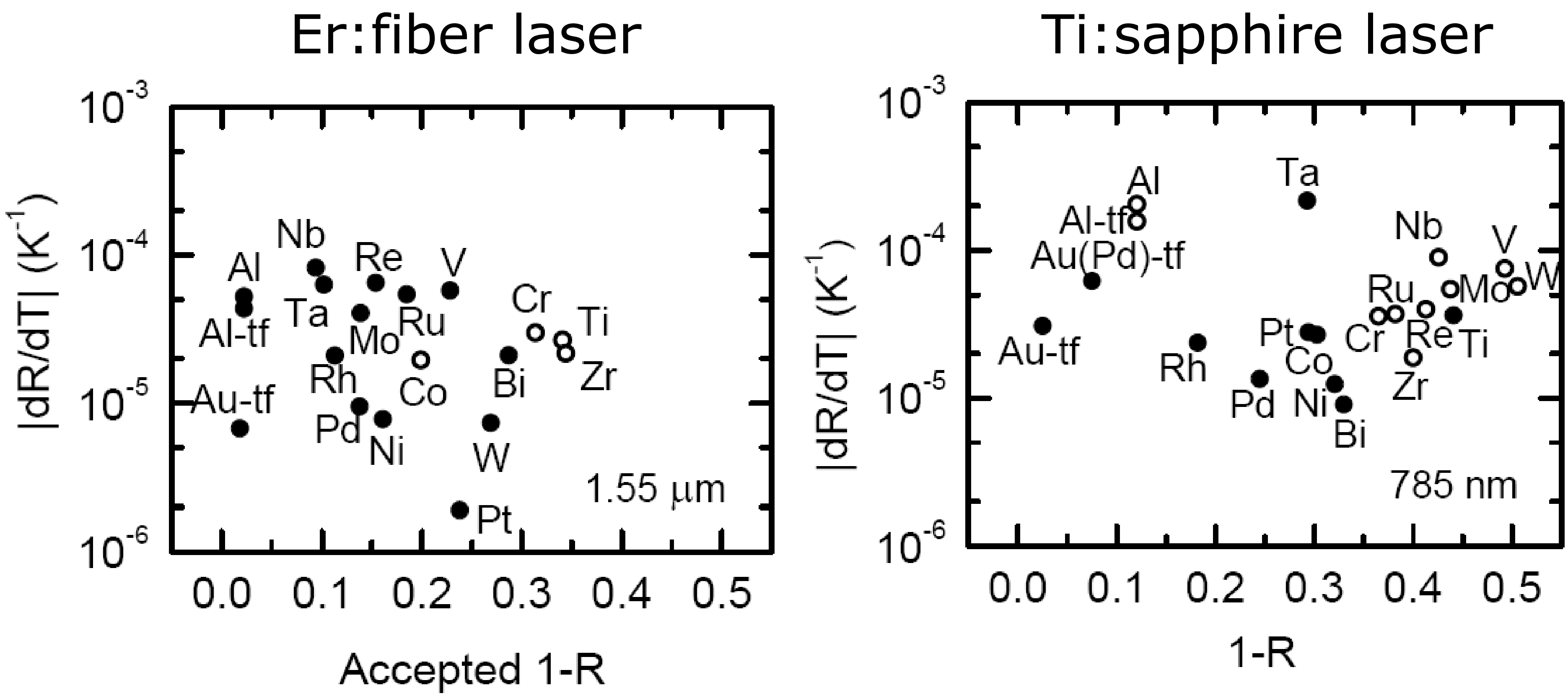
psec acoustics and time-domain thermoreflectance

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





Large dR/dT is desirable but not usually essential

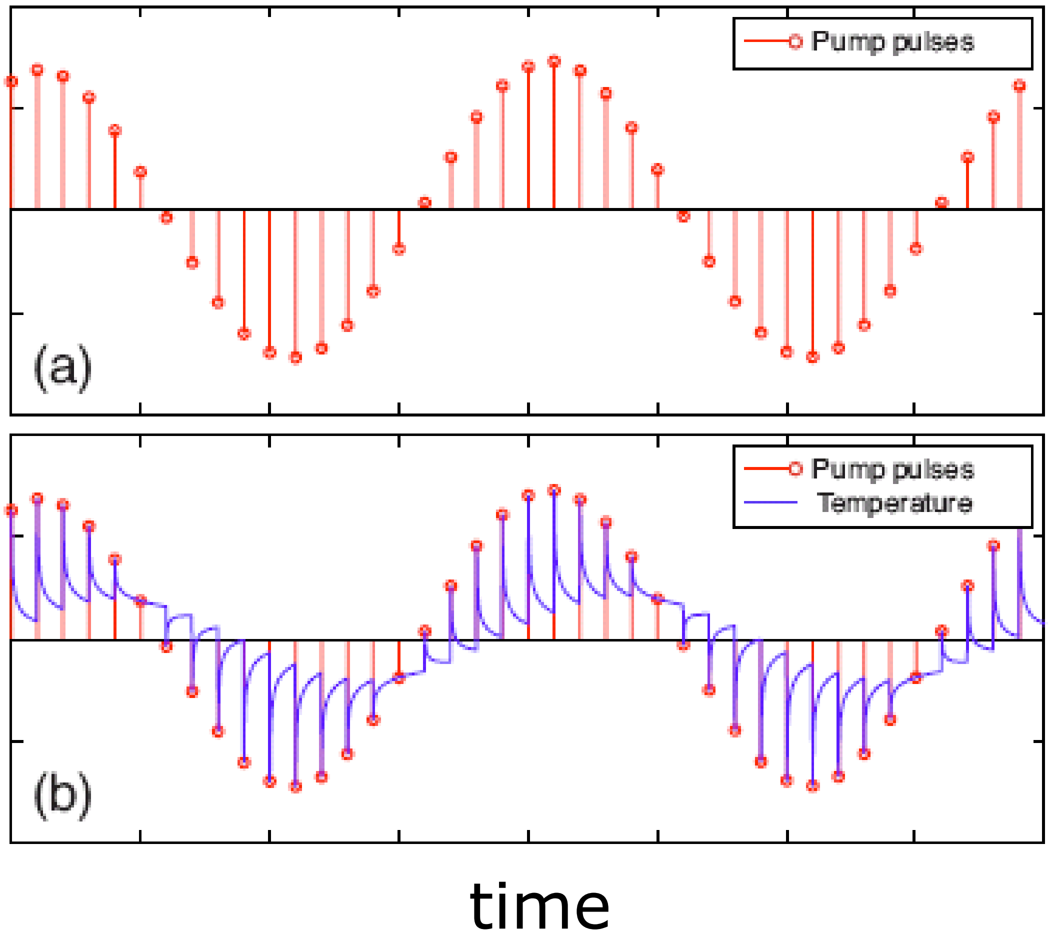


1-R=optical absorption

Wang et al., JAP (2010)

Illustrated by Schmidt et al., RSI 2008

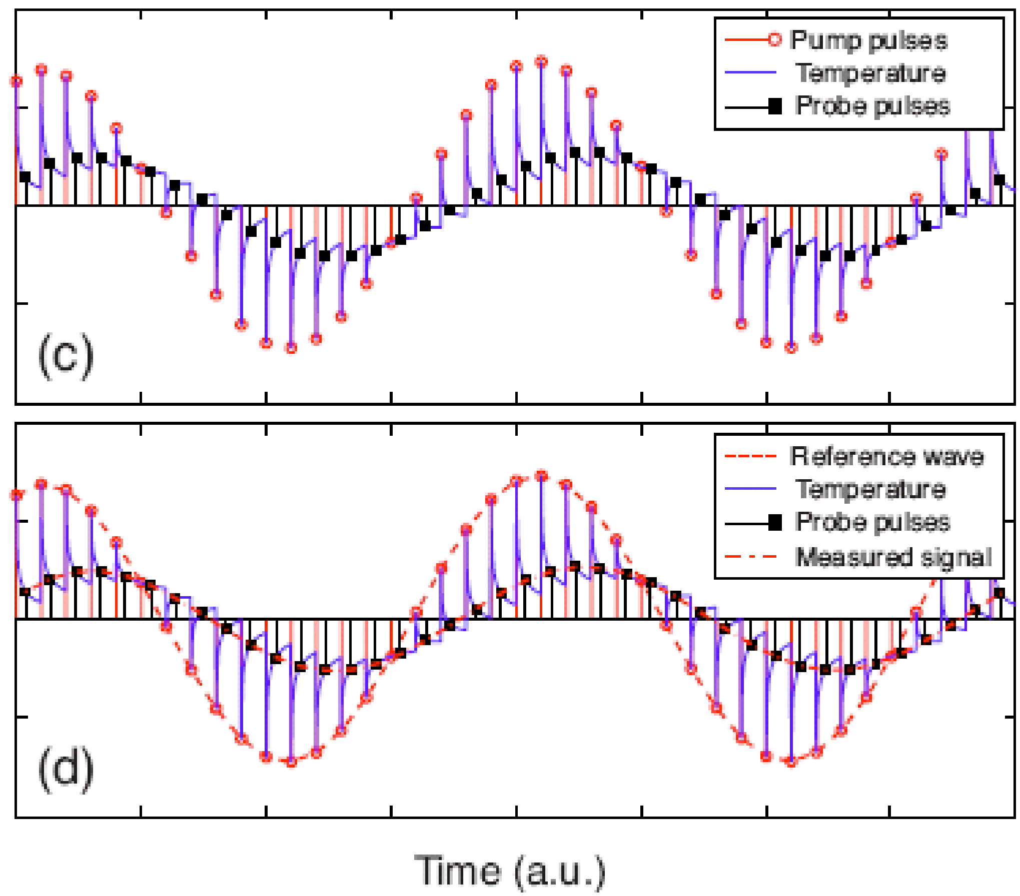
- Heat supplied by modulated pump beam (fundamental Fourier component at frequency *f*)
- Evolution of surface temperature



Illustrated by Schmidt et al., RSI 2008

- Instantaneous temperatures measured by time-delayed probe

- Probe signal as measured by rf lock-in amplifier is a phase-shifted cosine function



Partial differential equations are difficult to solve so transform into an algebraic frequency domain equation in both time and space

- Diffusion equation is a linear equation as long as the temperature excursion are not too large as to create significant changes in Λ, *C*, or *G*.
  - Frequency/spatial-frequency domain solutions contain the same information as time/space solutions.

$$C\frac{dT}{dt} = \Lambda \nabla^2 T \quad \rightarrow$$

$$\tilde{T} = \tilde{T}_0 \exp(i\omega t)\exp(-qz)$$

$$i\omega C\tilde{T} = \Lambda q^2 \tilde{T}$$

$$q = \sqrt{\frac{i\omega}{D}}$$

Analytical solution to 3D heat flow in an infinite half-space, Cahill, RSI (2004)

- spherical thermal wave

$$g(r) = \frac{\exp(-qr)}{2\pi\Lambda r} \quad q^2 = (i\omega/D)$$

- Hankel transform of surface temperature

$$G(k) = \frac{1}{\Lambda(4\pi^2k^2 + q^2)^{1/2}}$$

- Multiply by transform of Gaussian heat source and take inverse transform

$$P(k) = A\exp(-\pi^2k^2w_0^2/2)$$

$$\theta(r) = 2\pi\int_0^\infty P(k)G(k)J_0(2\pi kr)\ k\ dk$$

- Gaussian-weighted surface temperature

$$\Delta T = 2\pi A\int_0^\infty G(k)\exp\left(-\pi^2k^2\left(w_0^2 + w_1^2\right)/2\right)\ k\ dk$$

Analytical solution to 3D heat flow in an infinite half-space, Cahill, RSI (2004)

$$\Delta T = 2\pi A \int_0^\infty G(k) \exp\left(-\pi^2 k^2 \left(w_0^2 + w_1^2\right)/2\right) \; k \; dk$$

- Note the exchange symmetry of the pump and probe radius, w_0 and w_1
- This result is general: the solution must be independent of exchanging the role of heat sources and temperature measurements.
- For any linear problem, the Green's function solution has this symmetry (ρ is a position vector)

$$g(\rho, t; \rho' t') = g(\rho', -t'; \rho, -t)$$

Iterative solution for layered geometries

$$\begin{pmatrix} B^+ \\ B^- \end{pmatrix}_n = \frac{1}{2\gamma_n} \begin{pmatrix} \exp(-u_n L_n) & 0 \\ 0 & \exp(u_n L_n) \end{pmatrix} \times \begin{pmatrix} \gamma_n + \gamma_{n+1} & \gamma_n - \gamma_{n+1} \\ \gamma_n - \gamma_{n+1} & \gamma_n + \gamma_{n+1} \end{pmatrix} \begin{pmatrix} B^+ \\ B^- \end{pmatrix}_{n+1}$$

$$u_n = \left(4\pi^2 k^2 + q_n^2\right)^{1/2} \qquad q_n^2 = \frac{i\omega}{D_n} \qquad \gamma_n = \Lambda_n u_n$$

$$G(k) = \left(\frac{B_1^+ + B_1^-}{B_1^- - B_1^+}\right)\frac{1}{\gamma_1}$$

Note about anisotropy

- Thermal conductivity is the second-rank tensor that relates vector heat flux to a vector temperature gradient. Cubic crystals, glasses and randomly oriented polycrystalline materials are isotropic.

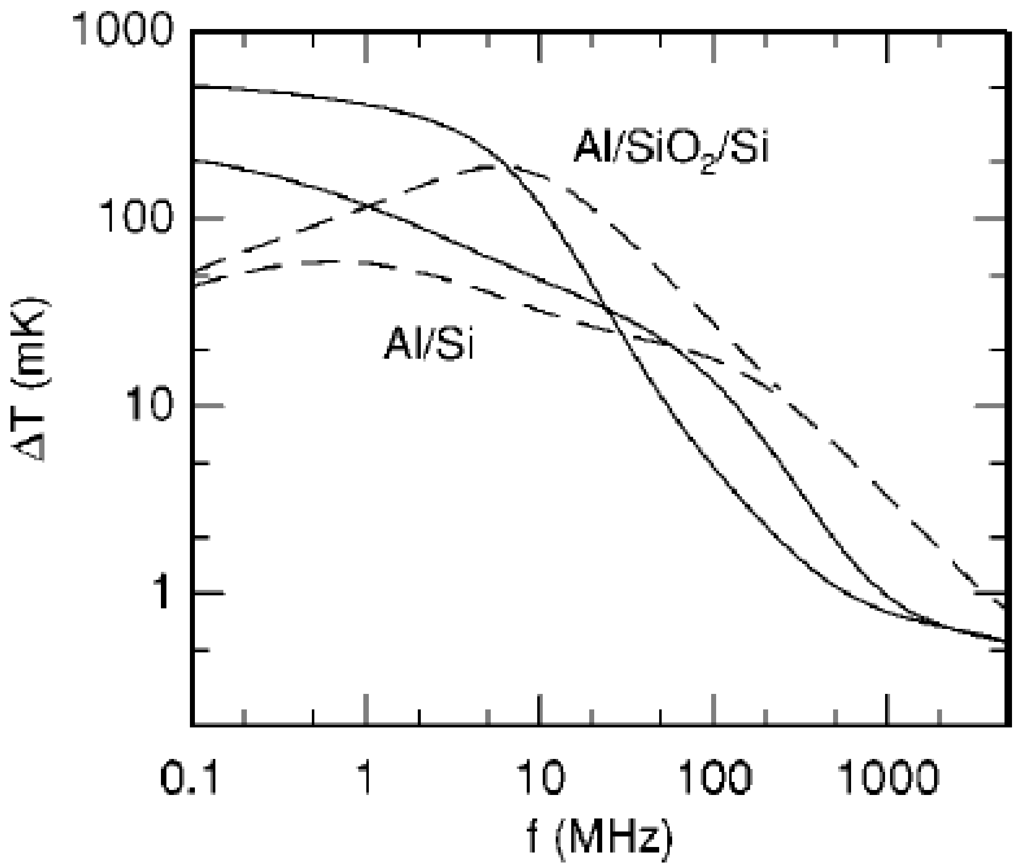
- Simple matter to deal with in-plane vs. through thickness anisotropy: Use in-plane thermal conductivity to calculate the D_n terms.

- Full tensor description is available at Joe Feser's web-site. Need is rare but has come up recently in our studies of the transverse thermal conductivity of polymer fibers and magnon thermal conductivity of cuprates.

Frequency domain solution

- Comparison of Al (100 nm)/SiO2 (100 nm)/Si and Al/Si
- Solid lines are real part; dashed lines are imaginary part

Note the peak in the imaginary part for $Al/SiO_2/Si$ near 10 MHz.



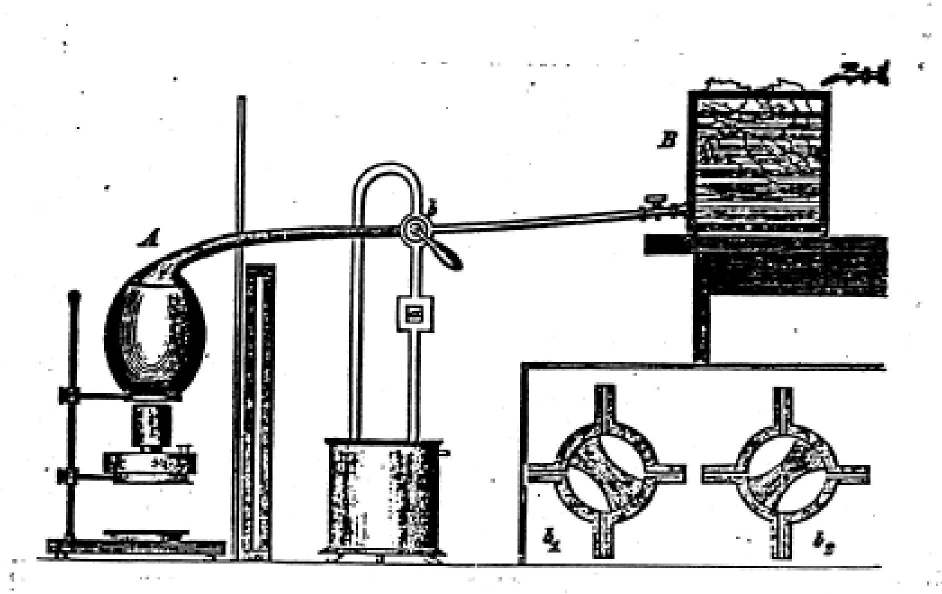
Nothing new—use thermal waves to measure thermal transport—only now down to nanoscale

Ångstöm (1861) used fixed temperature boundary conditions:

$$T(x = 0) = 0°\text{C} \quad \text{for} \quad 0 < t < \Gamma/2$$

$$T(x = 0) = 100°\text{C} \quad \text{for} \quad \Gamma/2 < t < \Gamma$$

where Γ is the period of the temperature oscillations produced by alternating flow of ice water and steam.



Frequency domain solution for 3ω and TDTR are closely related

3ω

- "rectangular" heat source and temperature averaging.
- One-dimensional Fourier transform.
- "known" quantities in the analysis are Joule heating and dR/dT calibration.

TDTR

- Gaussian heat source and temperature averaging.
- Radial symmetric Hankel transform.
- "known" quantity in the analysis is the heat capacity per unit area of the metal film transducer.

Signal analysis for the rf lock-in

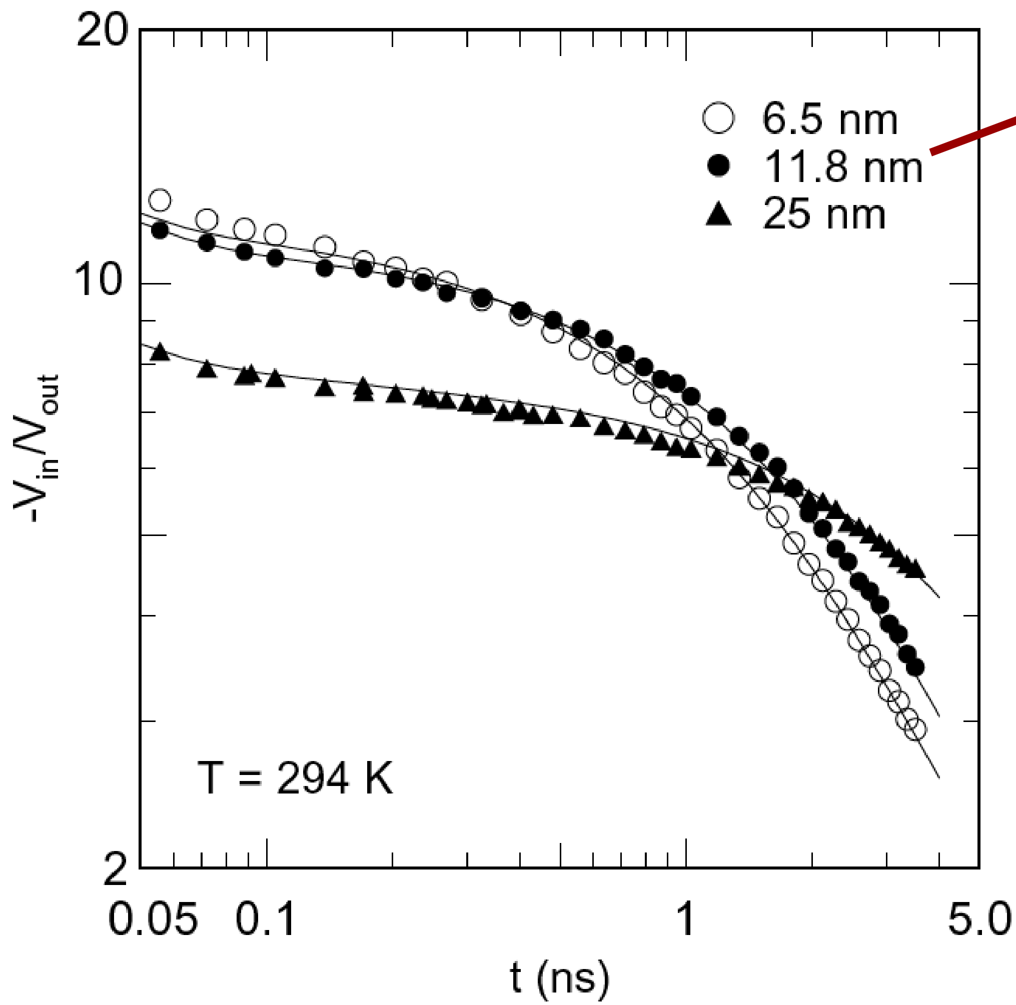
- In-phase and out-of-phase signals by series of sum and difference over sidebands

$$\mathrm{Re}\left[\Delta R_M(t)\right] \;=\; \frac{dR}{dT}\sum_{m=-M}^{M}\left(\Delta\mathcal{T}\left(m/\tau+f\right)+\Delta\mathcal{T}\left(m/\tau-f\right)\right)\exp(i2\pi mt/\tau)$$

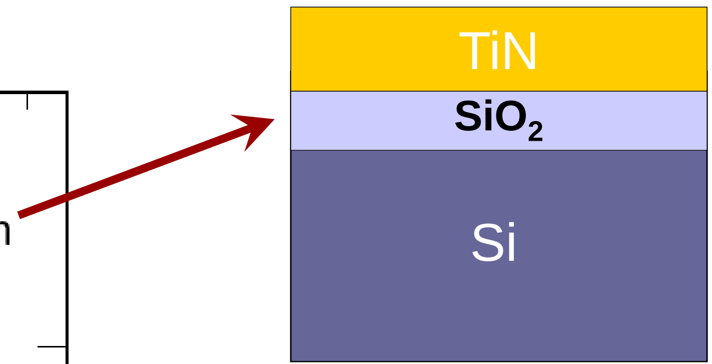
$$\mathrm{Im}\left[\Delta R_M(t)\right] \;=\; -i\frac{dR}{dT}\sum_{m=-M}^{M}\left(\Delta\mathcal{T}\left(m/\tau+f\right)-\Delta\mathcal{T}\left(m/\tau-f\right)\right)\exp(i2\pi mt/\tau)$$

- out-of-phase signal is dominated by the $m=0$ term (frequency response at modulation frequency f)

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

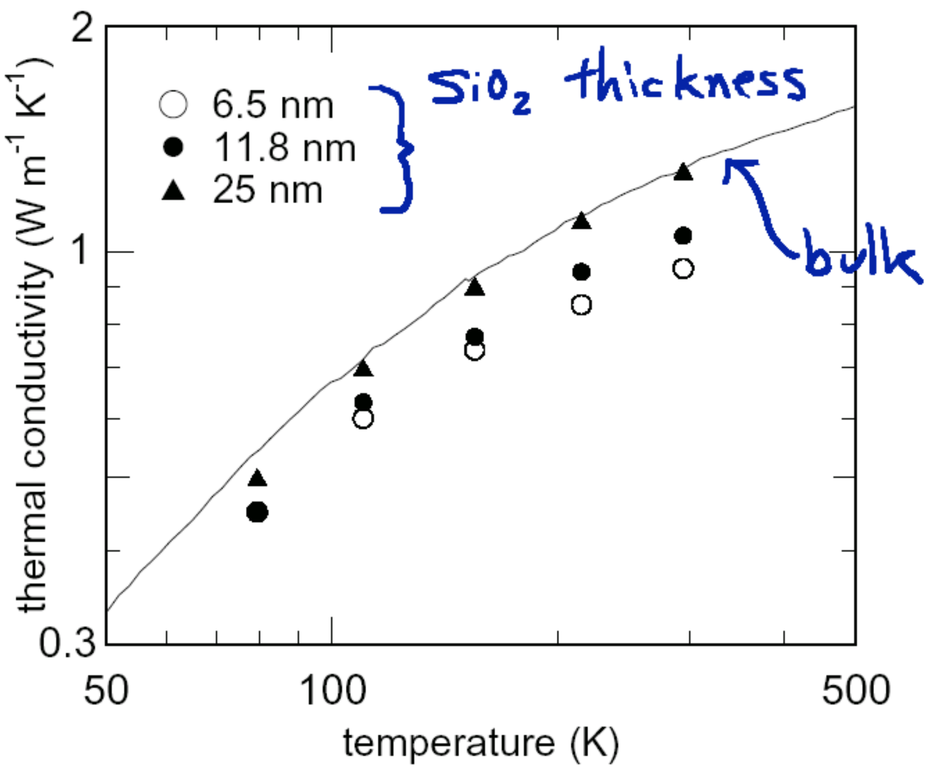


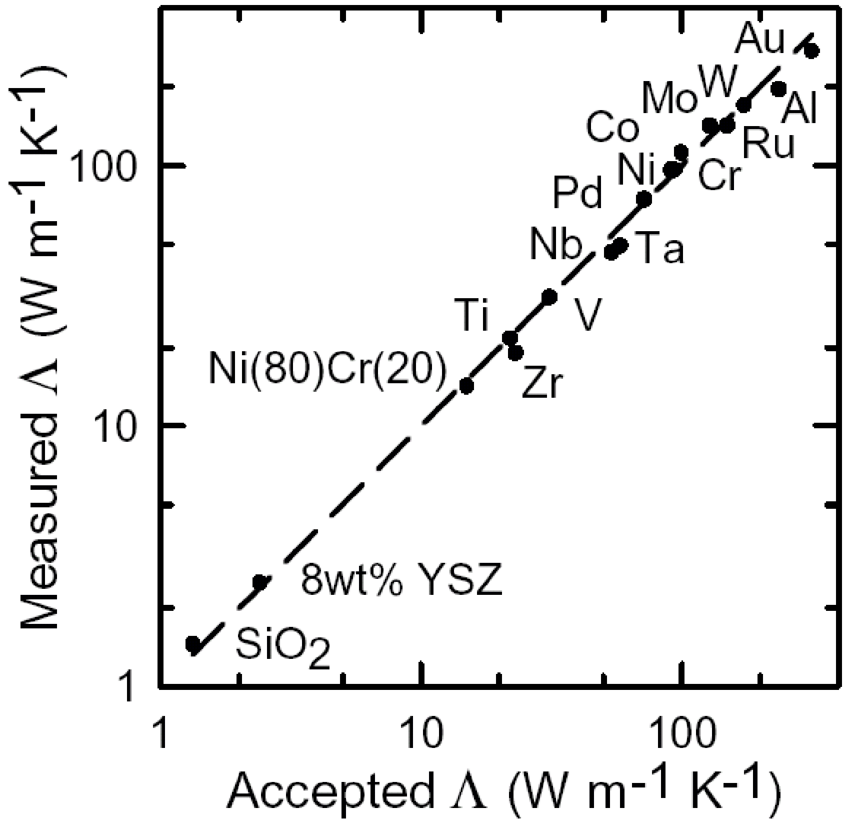
Costescu *et al.*, PRB (2003)



- 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)

Validation experiments for thin films and bulk





Costescu *et al.*, PRB (2003)

Most of the sensitivity to the thermal conductivity of bulk or thin film material comes from the out-of-phase signal

- At delays times long enough for heat to distribute uniformly in the metal film but short enough so that not much heat is lost to the substrate

$$\Delta V_{in} \propto \frac{P\tau_{rep}}{hC_m}$$

- Out-of-phase signal is weakly dependent on delay time

$$V_{out} \propto \frac{P}{\sqrt{f\Lambda C_s}}$$

$$\frac{V_{in}}{V_{out}} \propto \frac{\tau_{rep}\sqrt{f\Lambda C_s}}{hC_m} = \sqrt{\left(\tau_{rep} f\right)\left(\frac{\tau_{rep}\Lambda}{h^2 C_m}\right)\left(\frac{C_s}{C_m}\right)} = \frac{C_s\tau_{rep} f}{C_m}\sqrt{\left(\frac{\Lambda}{fh^2 C_s}\right)}$$

Quantify the sensitivities using the logarithmic derivate of the signal with respect to experimental parameters

- Example of sensitivity to the interface thermal conductance

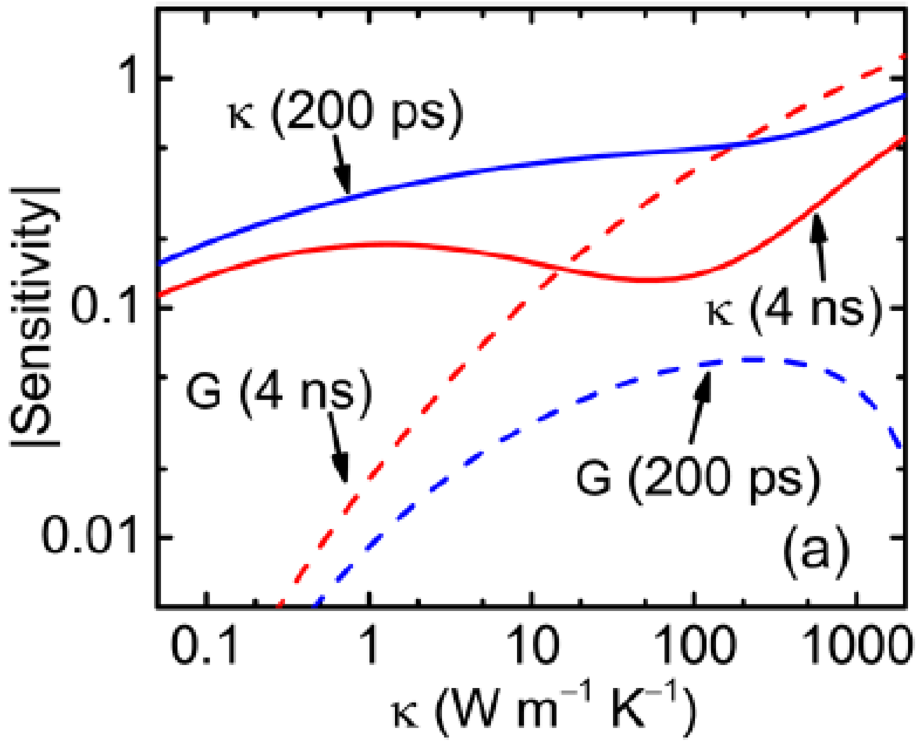
$$\phi(t) = -\frac{V_{in}(t)}{V_{out}(t)}$$

$$S_G(t) = \frac{d\ln\left(\phi(t)\right)}{d\ln G}$$

- If for small changes in *G*, $\phi \propto G^{\beta}$ then $S_G = \beta$

Quantify the sensitivities using the logarithmic derivate of the signal with respect to experimental parameters

- Example of sensitivity to the interface thermal conductance *G* and thermal conductivity (κ in this plot) at two delay times, 200 ps and 4 ns.



w_0=10 μm
G=200 MW m^{-2} K^{-1}

Sensitivities are the key to analyzing uncertainties and error propagation

- Example error propagation from an uncertain in metal film thickness Δh to an uncertainty in thermal conductivity

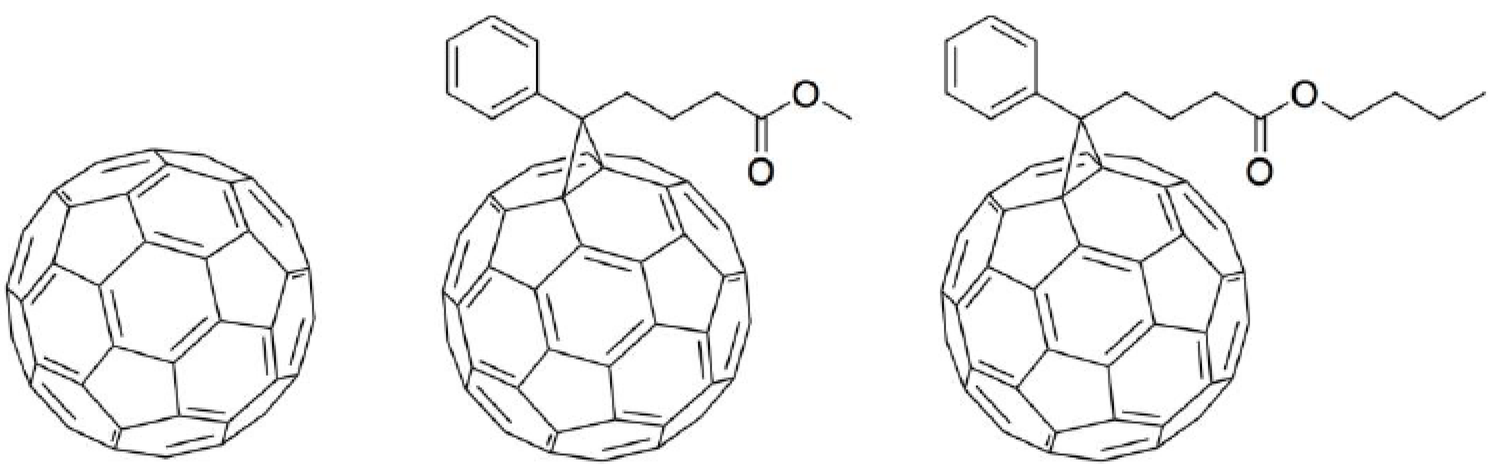
$$\Delta\Lambda = \frac{S_h}{S_\Lambda}\Delta h$$

- Typical numbers,

$S_h \approx 1$; $S_\Lambda \approx 0.5$; $\Delta h = 5\%$ ➔ $\Delta\Lambda = 10\%$

Fullerene derivatives have "ultralow" thermal conductivity, i.e., conductivity well below the conventional lower-limit

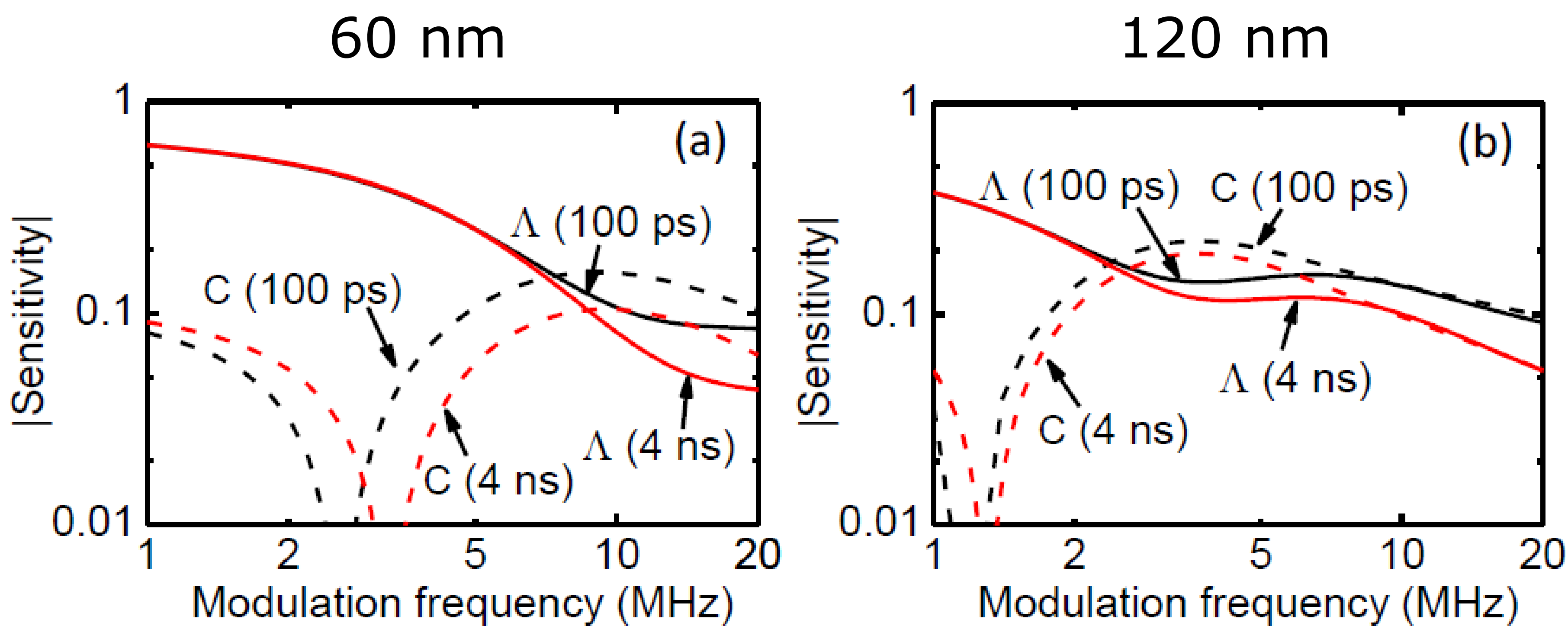
- Duda et al. (2013) reported 0.03 W m^{-1} K^{-1}.
- We find all samples are in the range 0.05 to 0.06 W m^{-1} K^{-1}.



C60 PCBM PCBNB

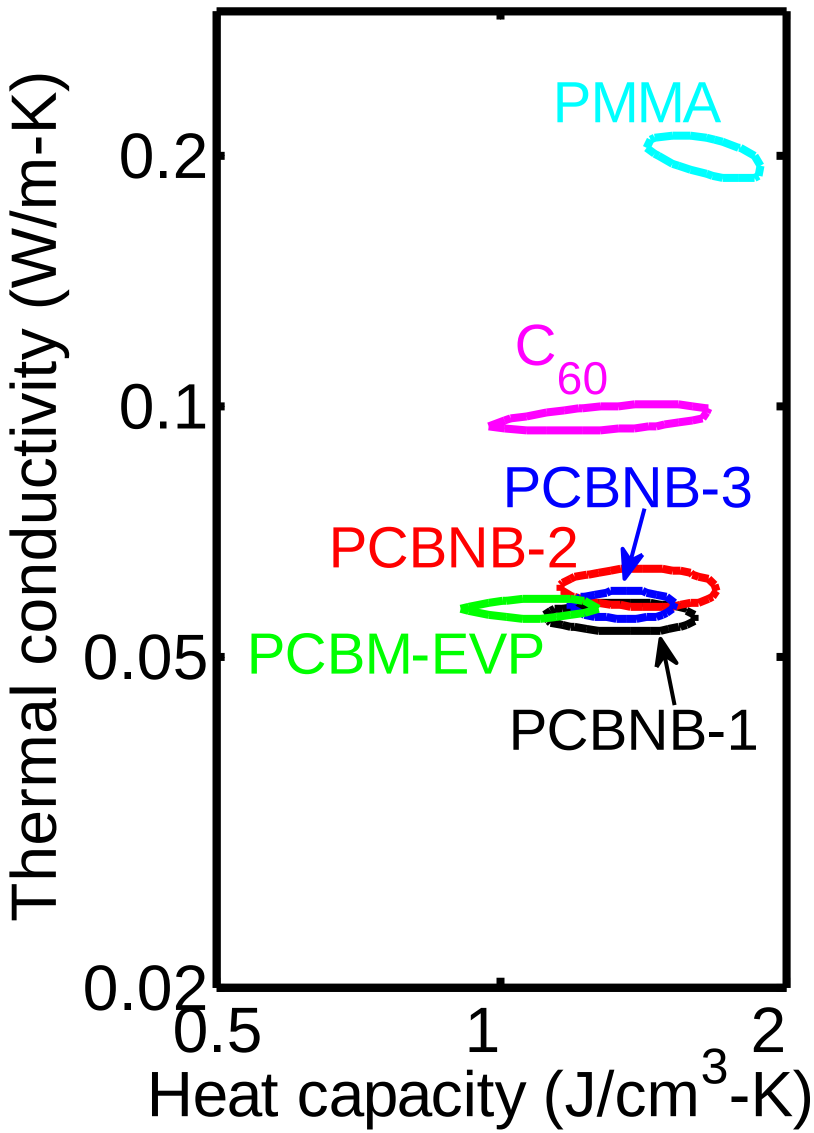
Use thin films (≈60 nm and ≈120 nm thick) and variable modulation frequency to separate thermal conductivity and heat capacity

$$S_\alpha = \frac{d\ln(-V_{in}/V_{out})}{d\ln(\alpha)}$$



Wang *et al.*, PRB, in press.

Fit two parameters (C and Λ) to multiple data sets (modulation frequency, thickness)

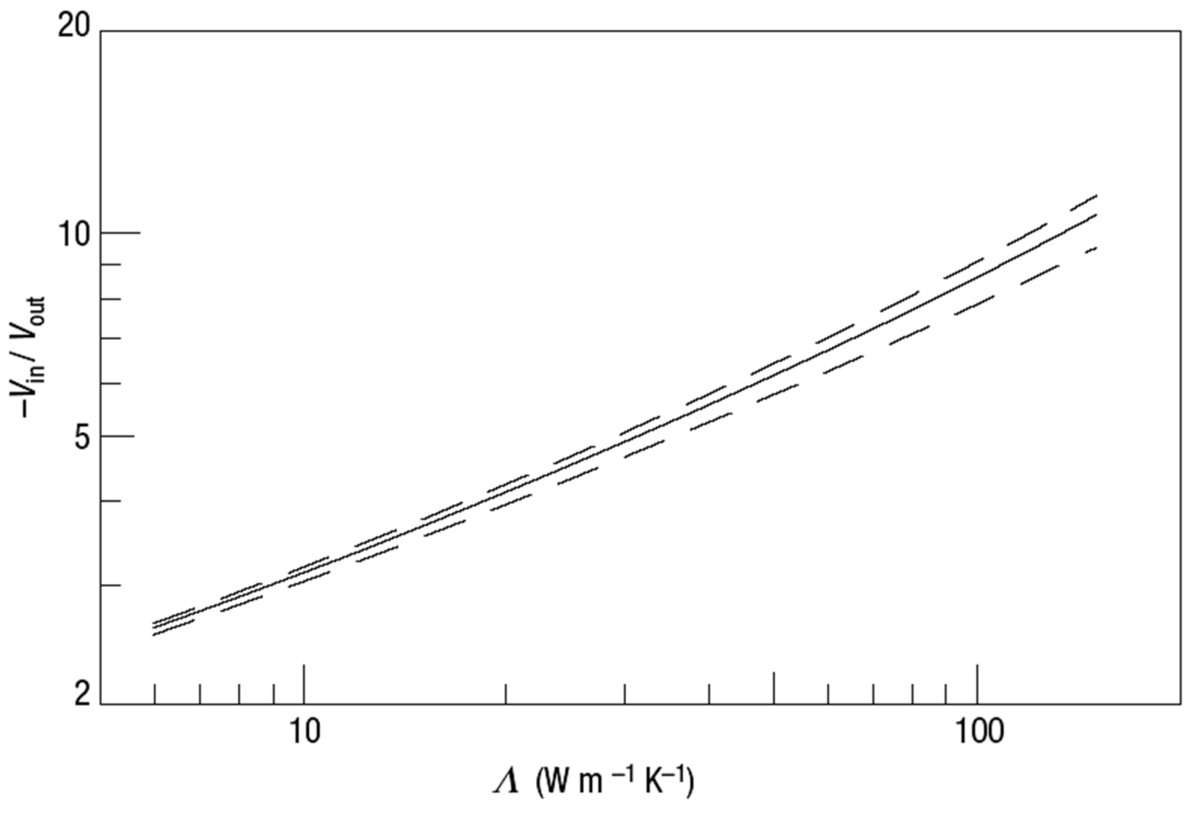


- Assume heat capacity C doesn't depend on thickness but allow thermal conductivity to vary with thickness.
- Contours are 95% confidence limits

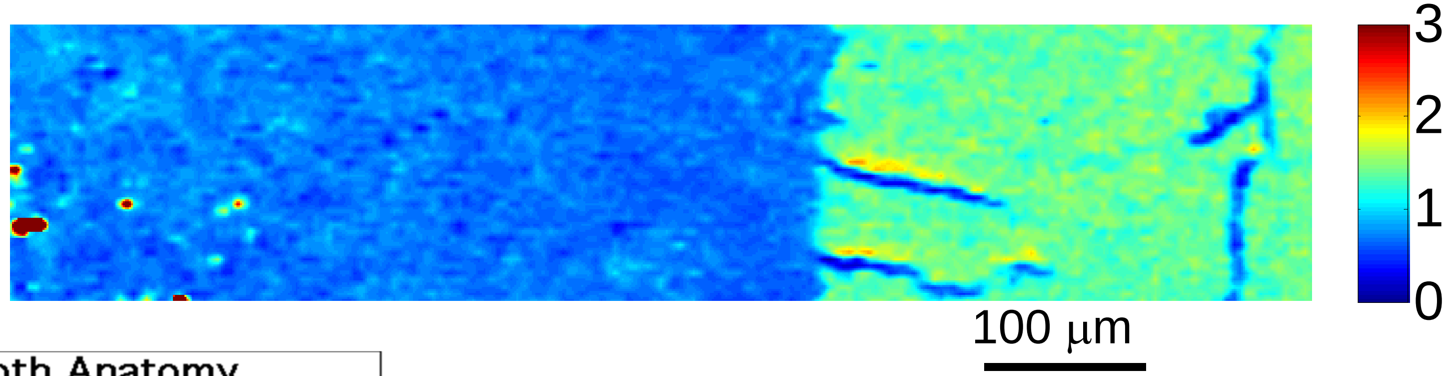
Wang *et al.*, PRB, in press.

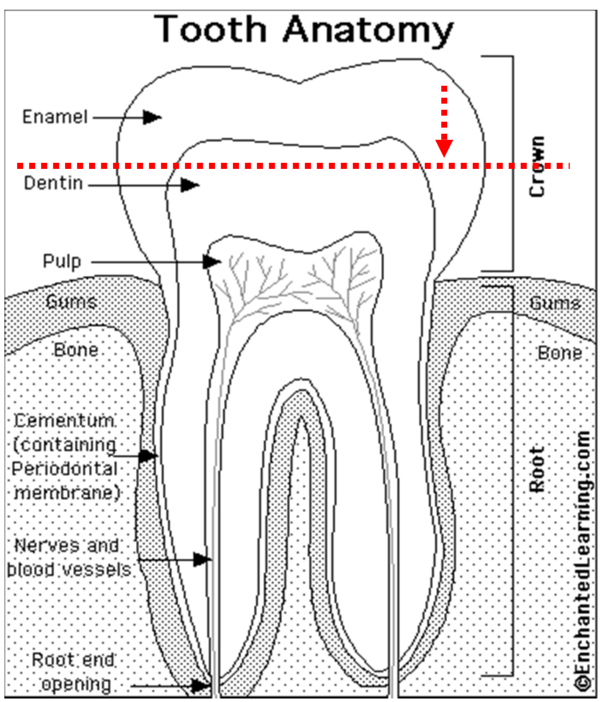
Thermal conductivity mapping: fix delay time and scan position

- At short delay times, t=100 ps,
  - in-phase signal is determined by the heat capacity of the Al film
  - out-of-phase signal is mostly determined by the effusivity $(\Lambda C)^{1/2}$ of the substrate



Thermal conductivity map of a human tooth





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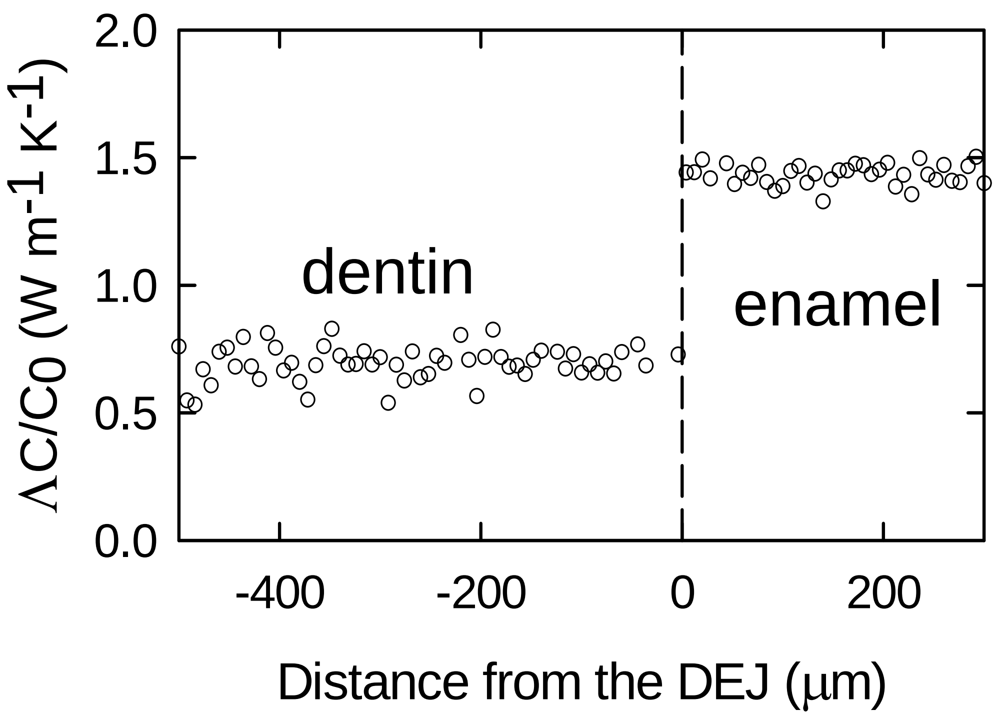
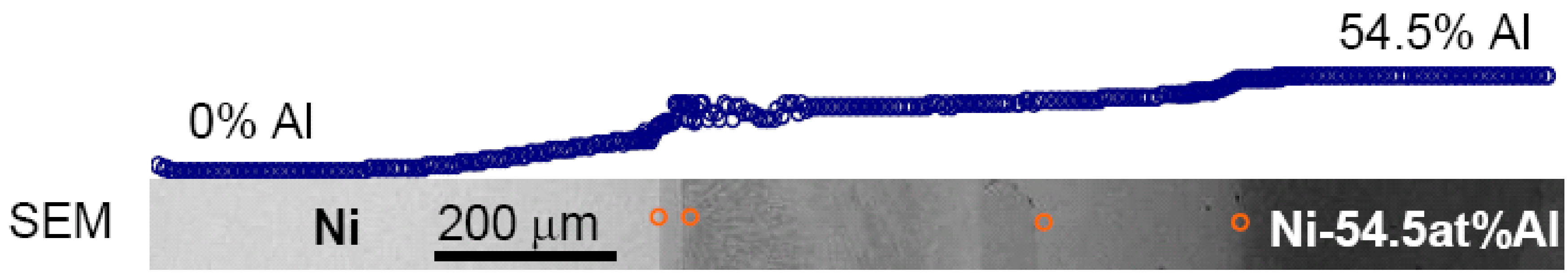
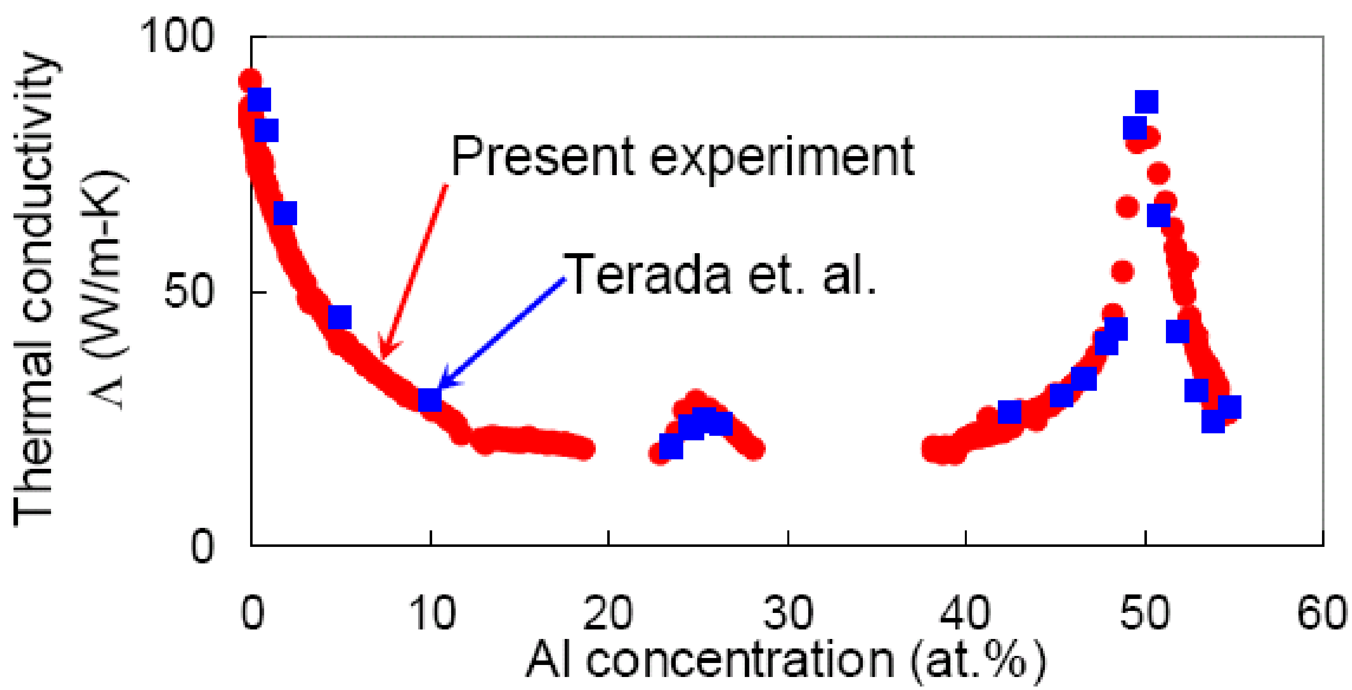


Zheng *et al.*, JAP (2008)

High throughput data using diffusion couples





Zhao *et al.*, Materials Today (2005)

Study phase transformations in materials

- Fix delay time and scan temperature
- As before, for thick specimens TDTR measures effusivity

$$\sqrt{\Lambda C}$$

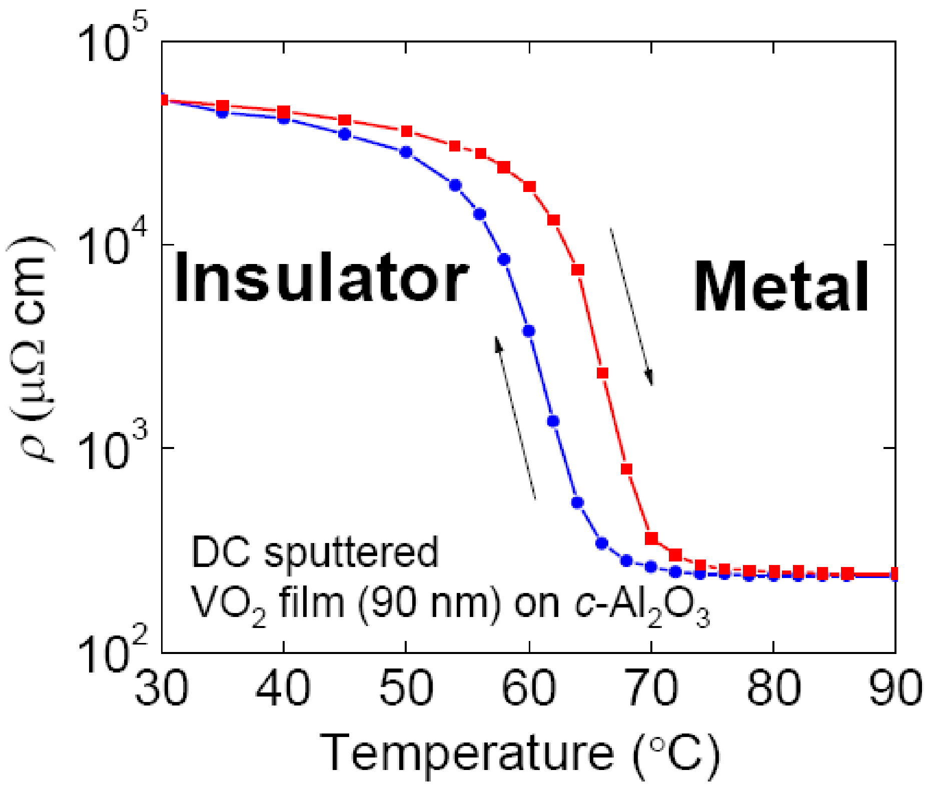
$\Lambda =$ thermal conductivity

C = heat capacity per unit volume

- Modulation frequency is typically 10 MHz; only sensitive to contributions to C that are reversible on a time scale of $\sim$30 nsec.

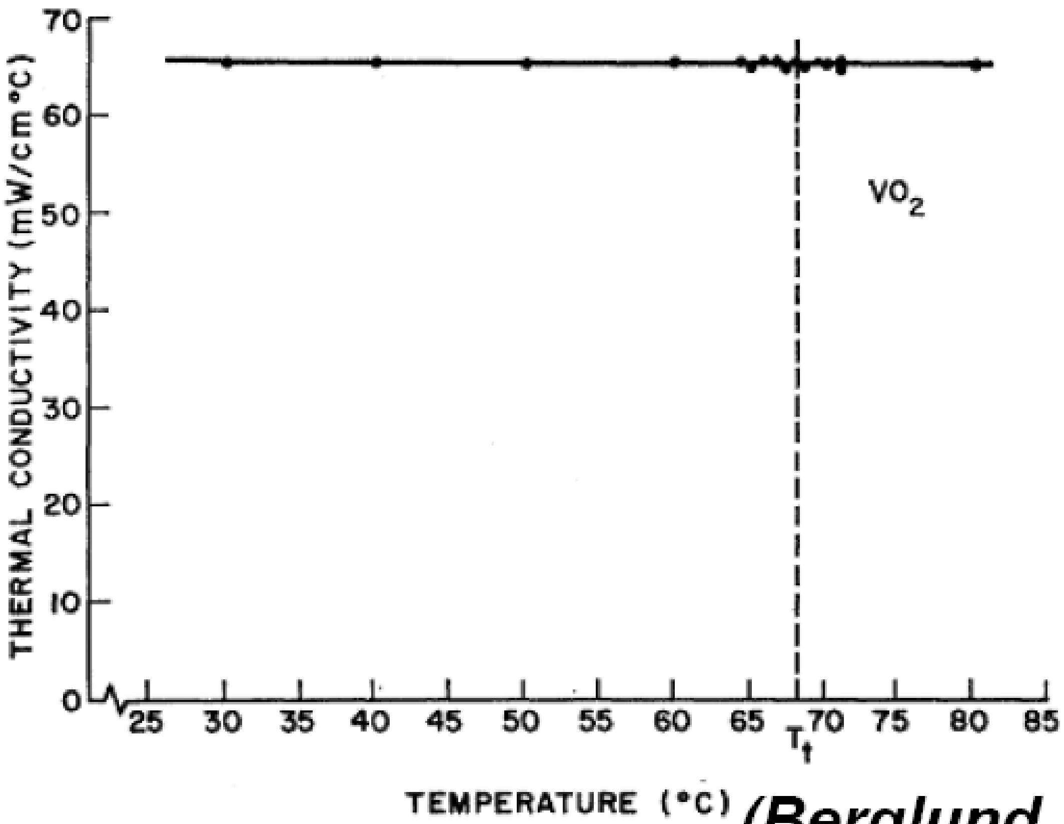
VO_2 is a model material for phase transformation in materials

- Crystalline structure changes from monoclinic (I) to tetragonal (M) (ΔH=51.5 J/g)
- Hysteresis behavior (width ~ 5 °C)
- ρ_{el} ~ 300 $\mu\Omega$ cm corresponds to ~ 3 W/mK but…



VO_2 is a model material for phase transformation in materials

- No change in thermal conductivity of single crystals was observed at the metal-to-insulator transition.
- Change in lattice thermal conductivity perfectly compensates for change in electronic thermal conductivity ???

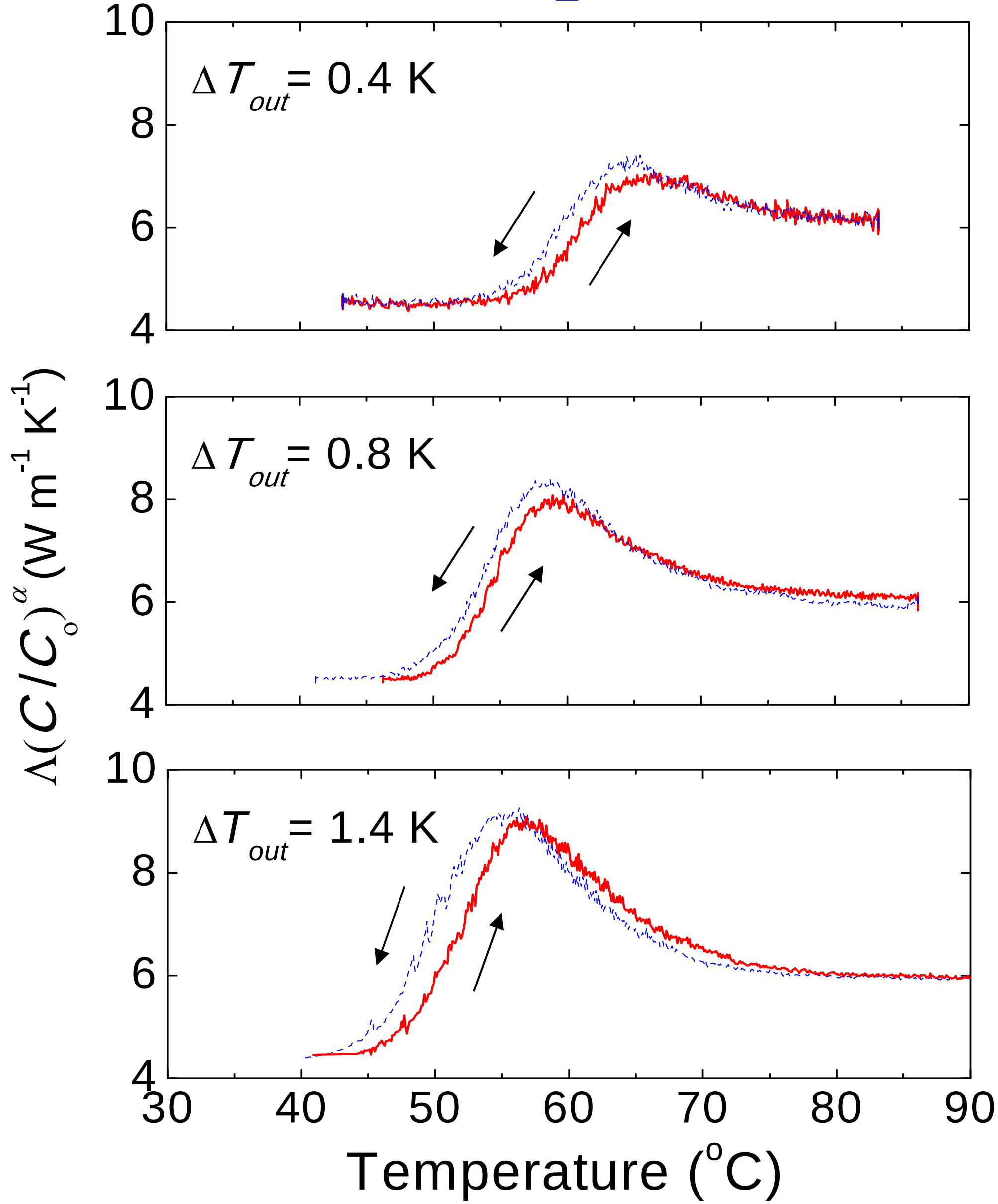


(Berglund, 1969)

Our first steps in a search for a solid-state heat switch…

- Change is observed presumably due to point defects that scatter phonons
- Large 10 MHz temperature oscillations in the TDTR experiment activate latent heat contributions to the heat capacity
- Contrast in thermal conductivity is only 50%. Need larger contrast between "off" and "on"

Epitaxial VO_2/sapphire



Oh *et al.*, APL (2010)

Summary

- Time domain thermoreflectance (TDTR) is a robust and routine method for measuring the thermal conductivity of almost anything (that has a smooth surface).
- Data—and uncertainties in the data—can be analyzed rigorously as long as the diffusion equation is a valid description of the heat conduction.
- Enables rapid data collection across composition, temperature, pressure, or magnetic field.