

Measurement of thermal conductivity

David G. Cahill

*Department of Materials Science
University of Illinois at Urbana-Champaign*

Part A:

- Thermal conductance methods and radiation errors
- Thermal diffusivity methods
- 3ω method
- Thermoreflectance methods

Part B:

- Time domain thermoreflectance

$N \gg 1$ methods for measuring thermal conductivity – focus on the use of periodic heat sources and temperature profiles.

- solutions to the diffusion equation are simpler.
- lockin amplifiers are powerful instruments (and cheap).
- radiation errors are minimized relative to static methods.

See also: (Taylor, 1995) for a general review; (Graebner, 1993) for diamond films; (Goodson, 1994) for dielectric films.

Thermal Conductance Methods and Radiation Errors

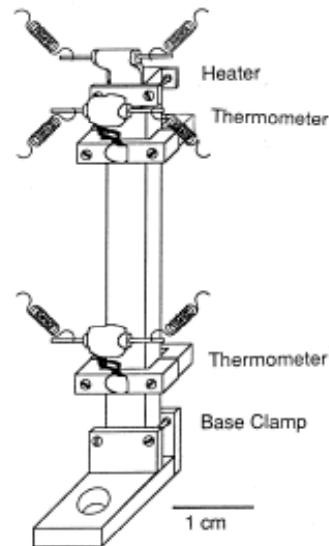
Define G , the thermal conductance, by

$$P = G\Delta T.$$

Simplest case: steady-state, one-dimensional (1-D) heat flow in a rod of length L :

$$G = \frac{a^2\Lambda}{L}$$

where Λ is the thermal conductivity and a^2 the cross sectional area.



For thermoelectrics, $\Lambda \sim 2 \text{ W m}^{-1} \text{ K}^{-1}$; let's assume $L = 4a$:

$$G \simeq 0.125L \text{ W m}^{-1} \text{ K}^{-1}.$$

Compare G to the radiative conductance for the same sample (temperature $T + \Delta T$ at one end and T at the other) radiating into an ambient at temperature T

$$G_{rad} = 2\epsilon\sigma(4aL + a^2)T^3$$

where ϵ is the emissivity and σ the Stephan-Boltzmann constant. At room temperature:

$$G_{rad} = 3.2L^2\epsilon \text{ W m}^{-2} \text{ K}^{-1}.$$

If we require $G_{rad}/G < .03$ for accurate measurements, then we need $L < 8/\epsilon$ mm.

- In practice, radiation from the heaters and thermometers greatly increase the errors from radiation

- The important results are: $G \sim L/16$ and $G_{rad} \sim L^2T^3$ and therefore

$$G_{rad}/G \sim (16L)T^3$$

- We must minimize the “effective” L to obtain accurate measurements.

Off to the complex plane...

For a complex number $z = a + ib$, a and b are real numbers referred to as the “real” and “imaginary” parts of z ; $i = \sqrt{-1}$.

The phase of z : $\theta = \arctan(b/a)$

The amplitude of z : $|z| = \sqrt{a^2 + b^2}$

$$\exp(z) = \exp(a) \exp(ib) ;$$

$$\exp(ib) = \cos(b) + i \sin(b)$$

$$\sqrt{i} = \frac{\sqrt{2}}{2} (1 + i)$$

Thermal Diffusivity Methods

Λ = thermal conductivity ($\text{W cm}^{-1} \text{K}^{-1}$)

C = heat capacity (J cm^{-3}) D = thermal diffusivity = Λ/C ($\text{cm}^2 \text{sec}^{-1}$)

(this is a consistent set of units, however, I will also use $\text{W m}^{-1} \text{K}^{-1}$ for thermal conductivity: meter units = 100 times cm units)

- One-dimensional (1-D) flow in an infinitely long solid
- 1-D flow in a finite-size sample
- Heat capacity

One-dimensional heat flow:

$$D \frac{\partial^2 T}{\partial x^2} - \frac{\partial T}{\partial t} = 0$$

$$D = \frac{\Lambda}{C}$$

where Λ is the thermal conductivity and C is the heat capacity per unit volume.

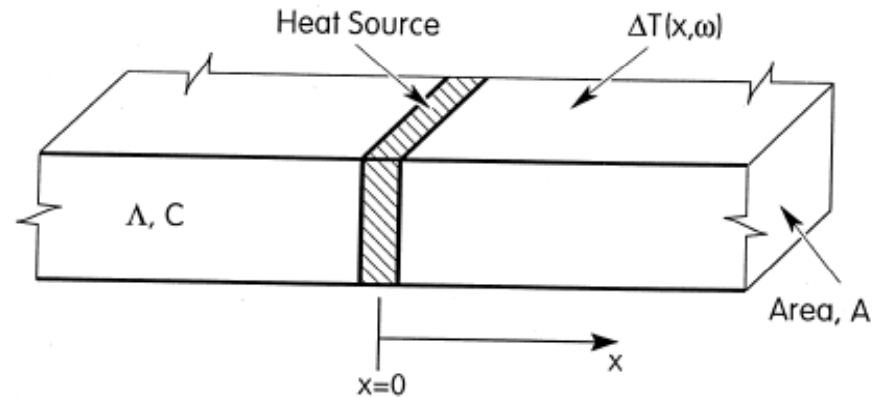
Take the Laplace transform (Carslaw, 1959).

$$\frac{\partial^2 T}{\partial x^2} - q^2 T = 0; \quad q^2 = \frac{i\omega}{D}$$

The general solution is

$$\Delta T = \alpha \cosh(qx) + \beta \sinh(qx)$$

1-D heat flow in an ∞ sample



Apply boundary conditions to find α and β .
For this case:

$$P = P_0 \cos \omega t$$

$$\Lambda \left. \frac{\partial T}{\partial x} \right|_{x=0} = -\frac{P}{A}; \quad \Lambda \left. \frac{\partial T}{\partial x} \right|_{x=\infty} = 0,$$

and the solution is

$$\Delta T(x, \omega) = \frac{P}{2A\sqrt{i\omega\Lambda C}} \exp(-q|x|); \quad q^2 = \frac{i\omega}{D}$$

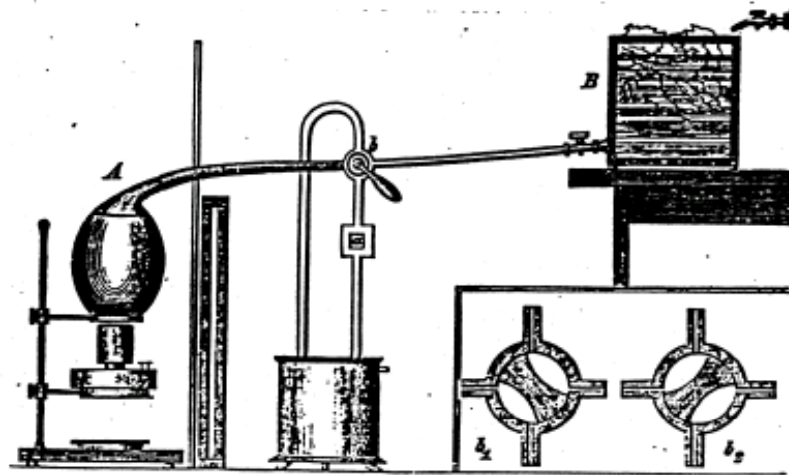
$$\sqrt{\Lambda C} = \text{effusivity}$$

Ångström (1861) used fixed temperature boundary conditions:

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

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

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



Thermal contact conductance of adhered microcantilevers

Scott T. Huxtable^{a)} and David G. Cahill

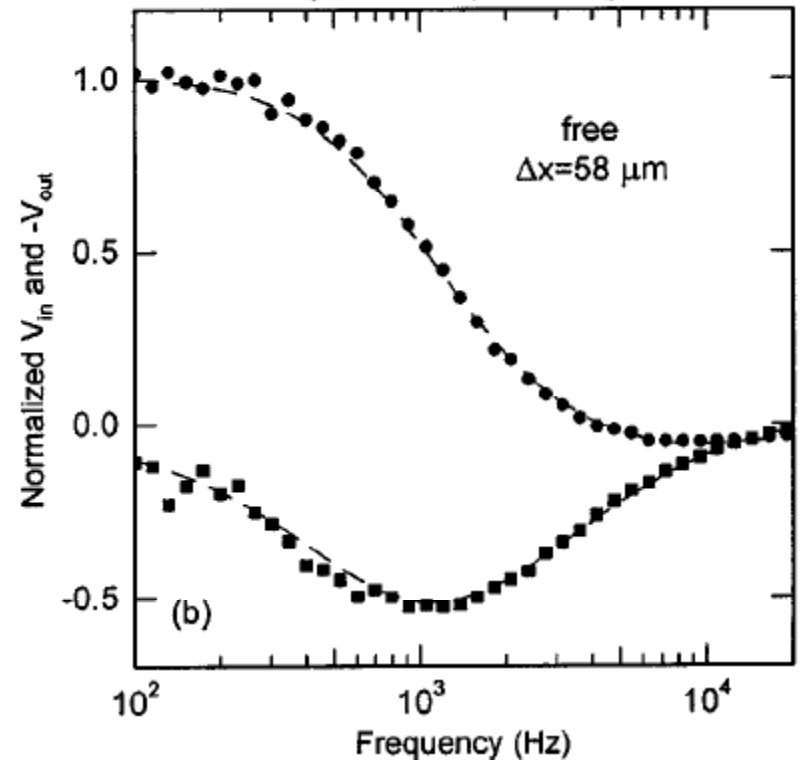
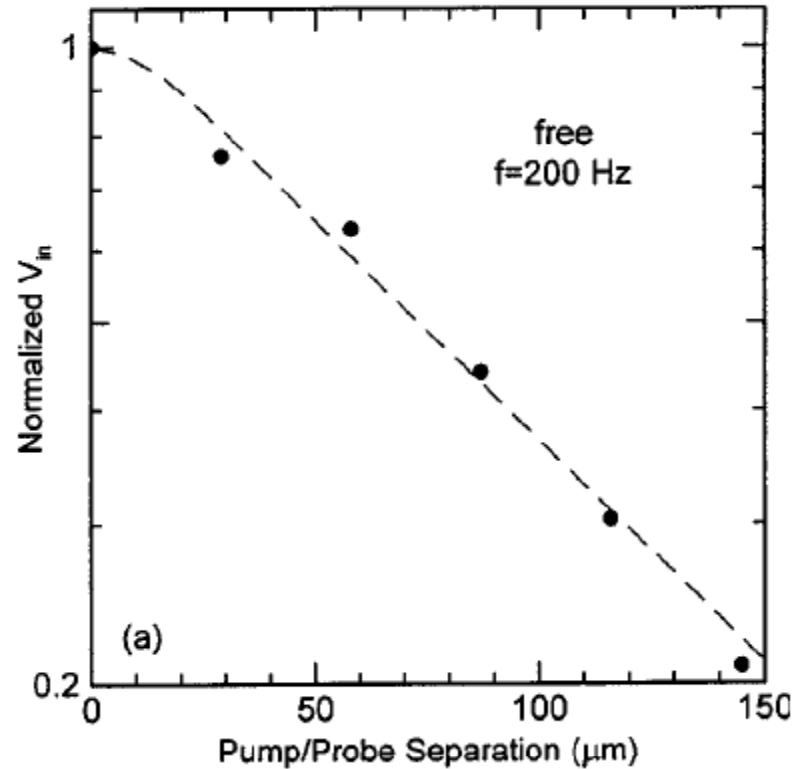
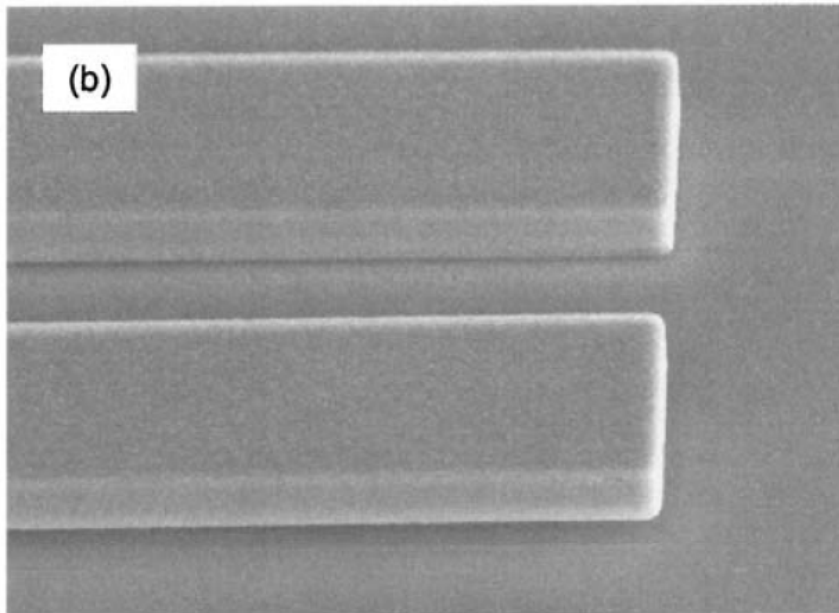
*Department of Materials Science and Engineering and the Frederick Seitz Materials Research Laboratory
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

Leslie M. Phinney^{b)}

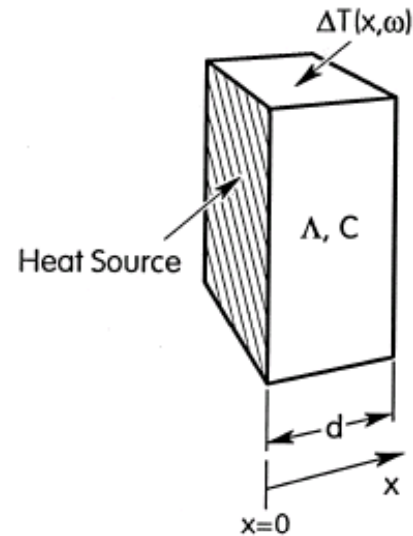
Department of Mechanical and Industrial Engineering, University of Illinois, Urbana, Illinois 61801

Modified Angstrom method takes into account thermal conductance from sidewalls to ambient

Modern application to suspended polycrystalline Si microcantilevers (10 micron width)



1-D heat flow in a finite-size sample



Now the boundary conditions are

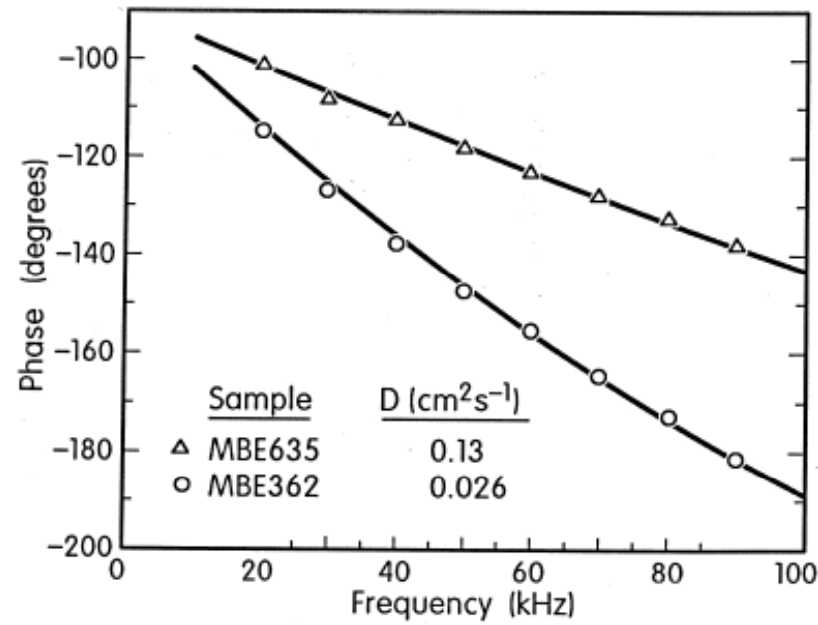
$$\Lambda \frac{\partial T}{\partial x} \Big|_{x=0} = -\frac{P}{A}$$

$$\Lambda \frac{\partial T}{\partial x} \Big|_{x=d} = 0$$

and the solution is

$$\Delta T(x, \omega) = \frac{P}{A\sqrt{i\omega\Lambda C}} \left[\frac{\cosh(qx)}{\tanh(qd)} - \sinh(qx) \right].$$

- at $x = d$, the term in brackets reduces to $\sinh^{-1}(qd)$.
- same as the “flash diffusivity” geometry; for time domain solution, see Taylor (1995).
- heat source is usually optical illumination. Chen used a thin film metal resistor to measure temperature at $x = d$ for a $\simeq 10$ μm thick III-V superlattice.



Data (Chen, 1994) for the phase of the temperature oscillations at $x = d$ used to measure the through-thickness thermal diffusivity of MBE grown semiconductor layers.

Analyze the radiation error: d thickness, area A .

The effective L is now d

$$G \simeq A\Lambda/d;$$

Neglecting radiation from the edges of the sample

$$G_{rad} \simeq 2\sigma\epsilon T^3(2A);$$

$$G_{rad}/G \simeq \frac{4\sigma\epsilon d T^3}{\Lambda}.$$

and putting this result in the same form as before

$$G_{rad}/G \sim (2L)T^3$$

This geometry is intrinsically ~ 10 better than previous two examples, steady state 1-D heat flow and Ångström methods.

Heat Capacity

To get Λ we need C , the heat capacity per unit volume. $\Lambda = CD$.

In many cases C is well known from careful measurements on bulk materials.

- when scaled for porosity, C is \sim independent of microstructure; i.e. the atomic density is the only thing that is important.
- materials with similar bonding and atomic weights will have similar heat capacities.

- Classical equipartition is a good approximation for most thermoelectrics near their operating temperatures: $C = 3Nk_B$, N is the number density of atoms per unit volume, and k_B is Boltzmann's constant.
- At low temperatures, deviations from equipartition are the result of quantum mechanics; at high temperatures, anharmonicity, see A. Miller (1988).
- Electronic heat capacity is too small to matter for this application.

- At high temperatures, anharmonicity also increases the heat capacity
 - thermal expansion causes the vibrational modes to soften, increasing the vibrational entropy per atom

α = volume coefficient of thermal expansion

γ = Grüneisen constant

κ = compressibility

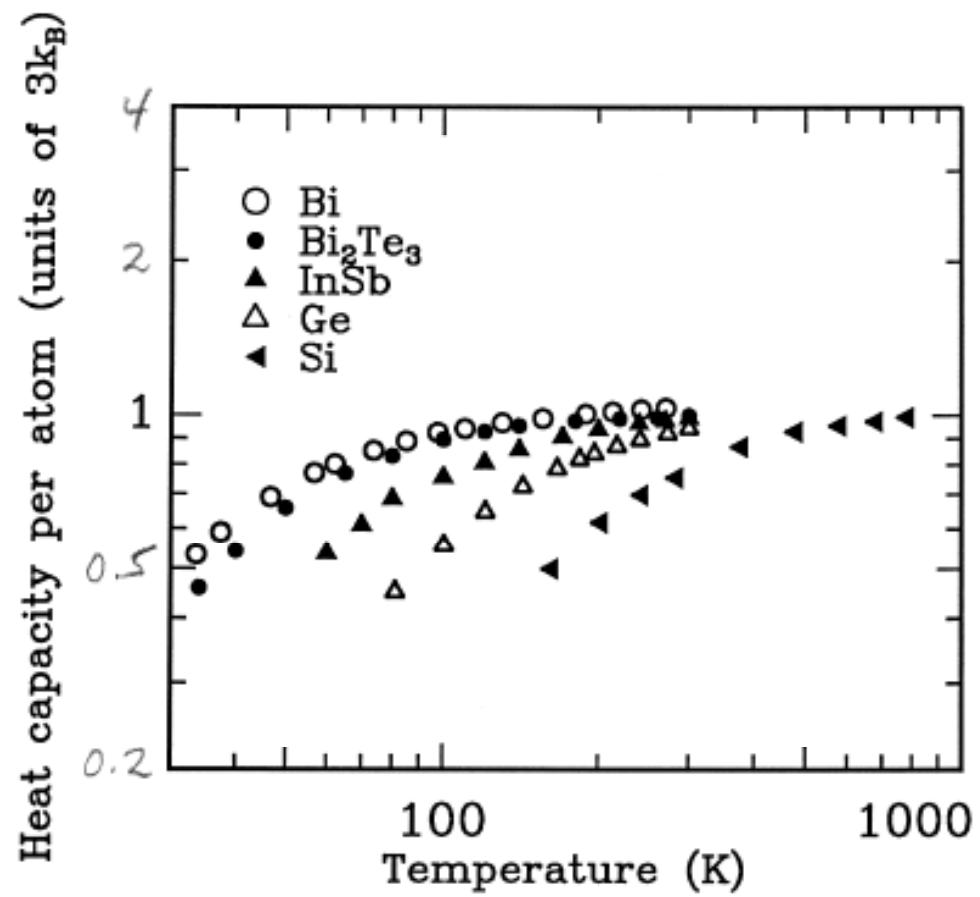
$$\alpha = \frac{1}{V} \frac{dV}{dT} \quad \gamma = \frac{V}{\Theta_D} \frac{d\Theta_D}{dV}$$

$$C_P - C_V = VT \frac{\alpha^2}{\kappa}$$

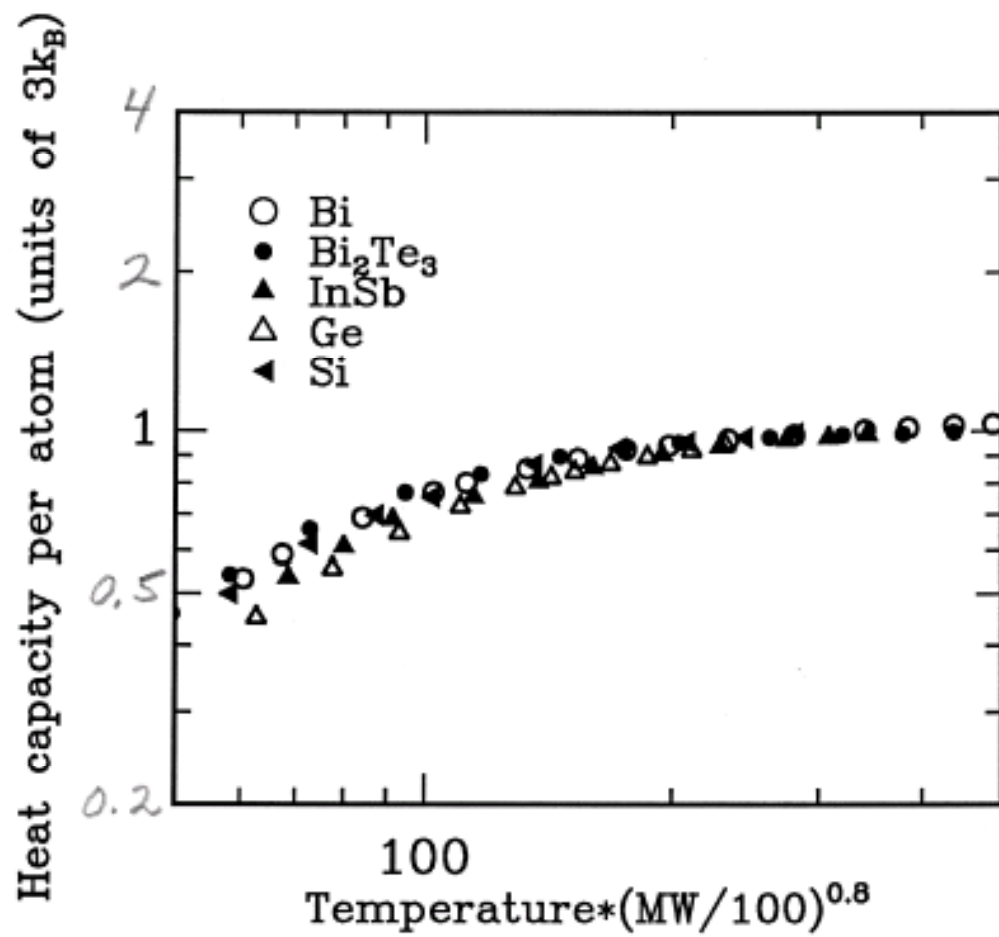
$$\alpha = \kappa \gamma \frac{C_V}{V}$$

$$C_V = 3Nk_B$$

$$\frac{C_P}{3Nk_B} - 1 = T \alpha \gamma$$



D-2.1



D-2.2

Direct measurement of Λ ?

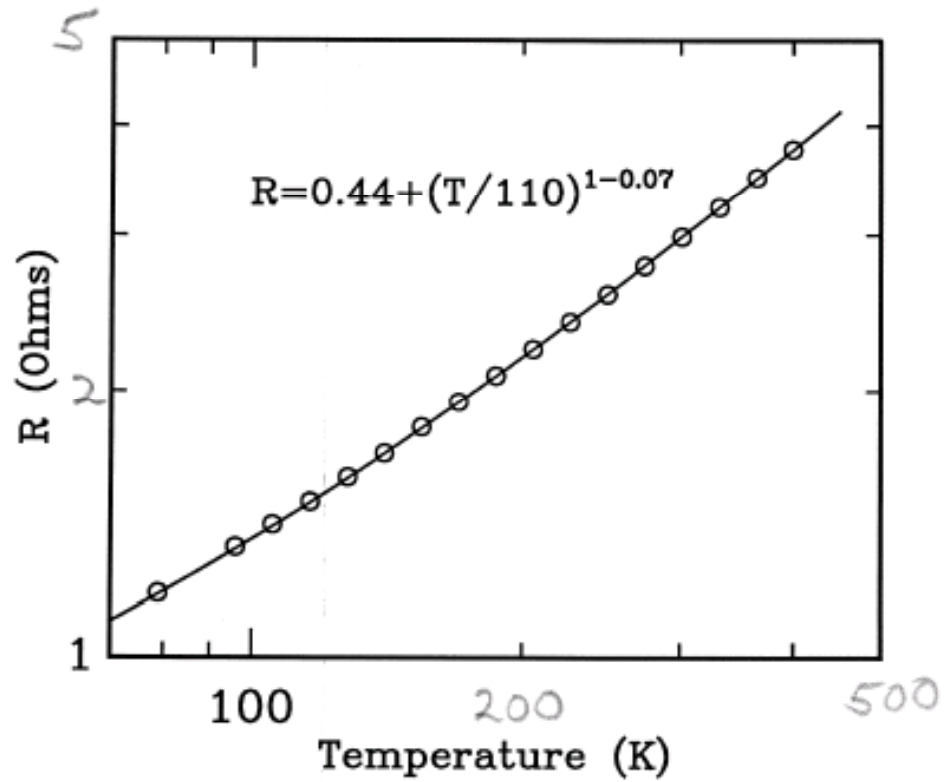
- possible, only if the absolute magnitude of P , the power, and ΔT , the temperature oscillations are known.
- Λ does not appear in the diffusion equation itself, only D . Λ appears in the *boundary conditions* in combination with P .
- For optical illumination as the source of P , the absorption is difficult to calibrate – therefore, D is all we get.

Can get around this with a multilayer where at least one layer is known

Metal film heaters and thermometers

- Advantages of using metal films in thermal measurements
 - Joule heating $P = I^2R$, gives an accurate method for knowing P .
 - temperature coefficient of resistance gives a measure of ΔT – for a pure metal, at $T > 40\text{ K}$, the resistivity $\rho = \rho_0 + \alpha T^{1+\epsilon}$ (ϵ provides an additional small parameter for fits)
 - unlike pyrometry and bulk thermocouples, no problems with response time.
 - wide temperature range, $30 < T < 800\text{ K}$.

Typical calibration of Au film resistance vs. T



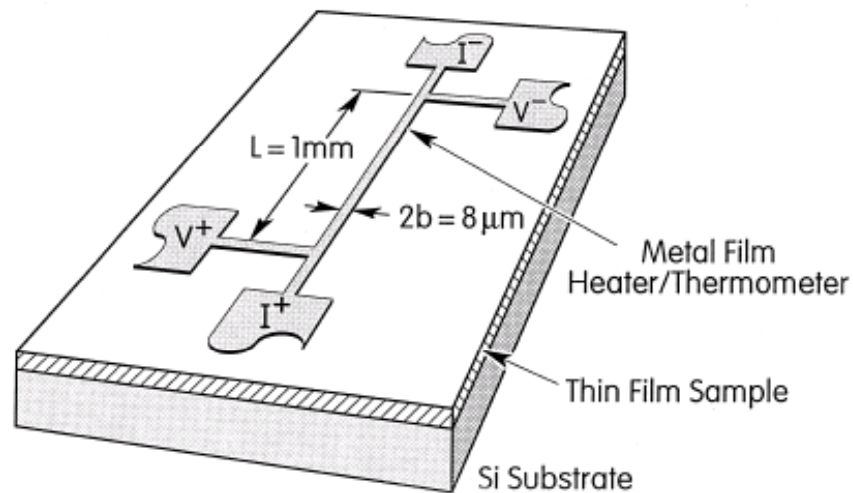
D-4.5

- Disadvantages

- need for deposition, lithography steps.
- at high T , problems with chemical and physical stability.
- for conducting samples, need an insulating layer.

3 ω Method

Uses single metal film for heater/thermometer
(Birge, 1987); (Cahill, 1990).



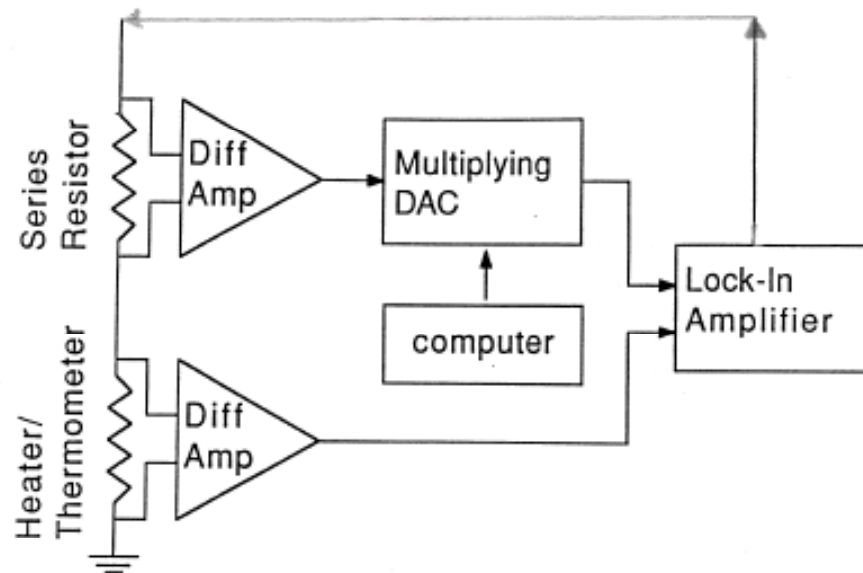
$$I \sim \exp(i\omega t)$$

$$P \sim \exp(i2\omega t) ; \quad \Delta T \sim \exp(i2\omega t)$$

$$\Delta R \sim \exp(i2\omega t)$$

$$\Delta V = I\Delta R \sim \exp(i3\omega t)$$

Measure ΔV with a bridge circuit and digital lockin amplifier.



Heat flow in a radial coordinate r .

$$\nabla^2 T - q^2 T = 0$$

$$\nabla^2 = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right).$$

Solution for an infinite half-space

$$\Delta T(r) = \frac{P}{l\pi\Lambda} K_0(qr)$$

K_0 is the zeroth order modified Bessel function
Think of this as the circular thermal wave

Take the Fourier transform of this frequency domain solution

$$\Delta T(k) = \int_0^\infty \Delta T(x) \cos(kx) dx,$$

$$\Delta T(k) = (P/2l\Lambda) [1/(k^2 + q^2)^{1/2}].$$

For a low thermal conductivity thin film
on a high thermal conductivity substrate

$$\Delta T(\omega) = \Delta T_s + \Delta T_f$$

$$\Delta T_s = \frac{P}{l\pi\Lambda_s} \int_0^\infty \frac{\sin^2(kb)}{(kb)^2(k^2 + q^2)^{1/2}} dk$$

$$\Delta T_f = \frac{Pd}{2Lb\Lambda_f}$$

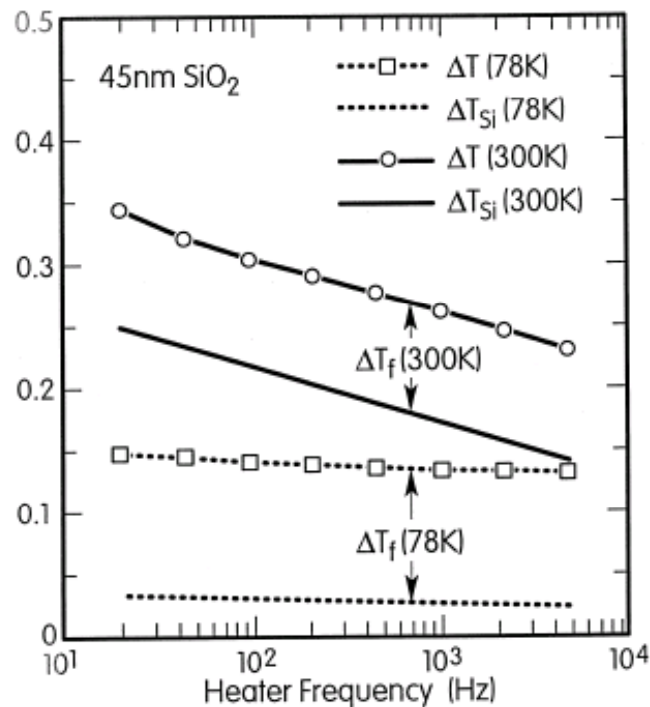
$$q^2 = \frac{2i\omega}{D_s}$$

(Factor of 2 because current is at frequency ω)

When $|q|b < 0.3$

$$\Delta T_s(\omega) = \frac{P}{l\pi\Lambda_s} \left[\frac{1}{2} \ln \left(\frac{D_s}{b^2} \right) + \eta - \frac{1}{2} \ln(2\omega) - \frac{i\pi}{4} \right]$$

numerically $|q|b \ll 1$, gives $\eta = 0.92$. Empirically, $\eta \simeq 1.05$.



In-phase ΔT for a 45 nm SiO₂ film deposited on a Si wafer (Lee, 1996). Curves ΔT_{Si} are the calculated response of the substrate.

Analyze the radiation error (crude estimate):

The effective L is $|1/q|$; the effective area is $|1/q|l$

$$G \simeq l\Lambda$$

$$G_{rad} \simeq 2\sigma\epsilon T^3(2l|1/q|) ;$$

$$G_{rad}/G \simeq \frac{4\sigma\epsilon|1/q|T^3}{\Lambda}.$$

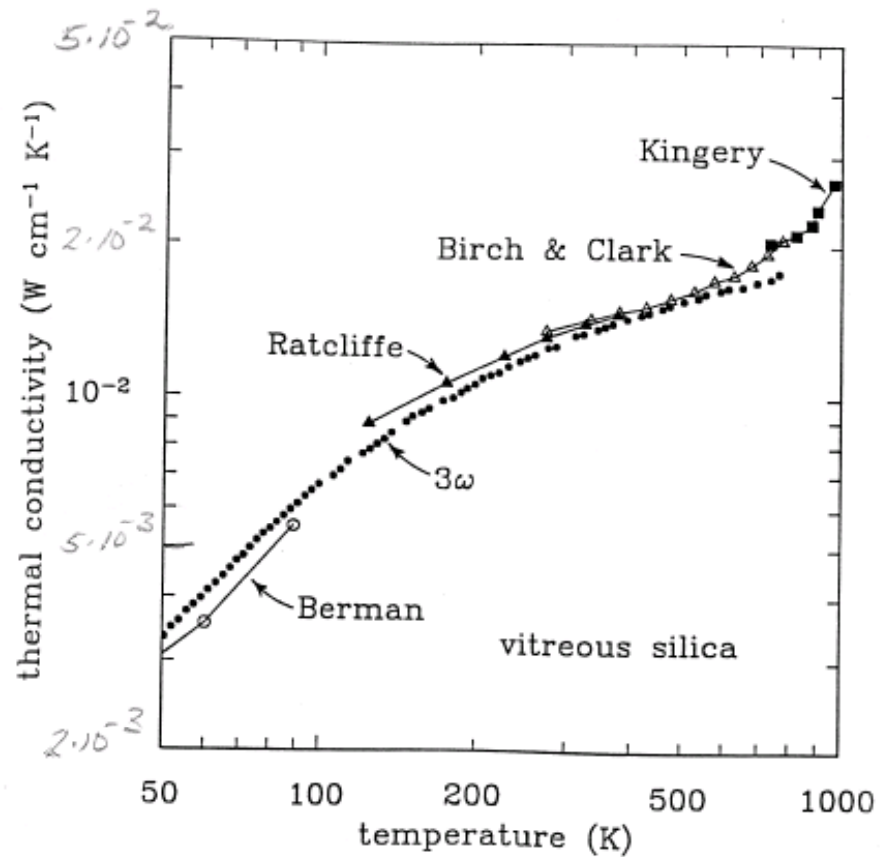
and putting this result in the same form as before

$$G_{rad}/G \sim (2L)T^3$$

Detailed analysis gives $G_{rad}/G \sim (0.5L)T^3$.

In practice $|1/q| < 100 \mu\text{m}$ and radiation errors are negligible.

Not important for thermoelectrics, but a similar analysis applies to radiation transport *through* the material.



3ω method (for thermoelectrics) needs an insulating layer:

- Dielectric film must be continuous. Pinholes are death.
- Must be “thermally thin”; i.e. $q_f d \ll 1$. Not a problem for thermoelectric samples. $d =$ a few μm is OK.
- Do not need to know Λ_f , or d . The slope used to measure Λ_s stays the same.

Is there anything better?

Wish list for the “perfect technique”

1. non-contact
2. measures Λ directly, not D .
3. user-friendly
4. simple, inexpensive equipment.

Difficult to achieve 1) and 2) simultaneously.
I believe 3ω is about the best we can do for
“contact” methods.

Is there a better “non-contact” method?

- Non-contact heat sources
 - optical illumination from laser or lamp
 - x-rays
 - electron beam

- Non-contact temperature measurement
 - black-body radiation (pyrometry)
 - acoustic emissions (photoacoustic)
 - thermal expansion of the surface (photodisplacement)
 - change in reflectivity (thermoreflectance)

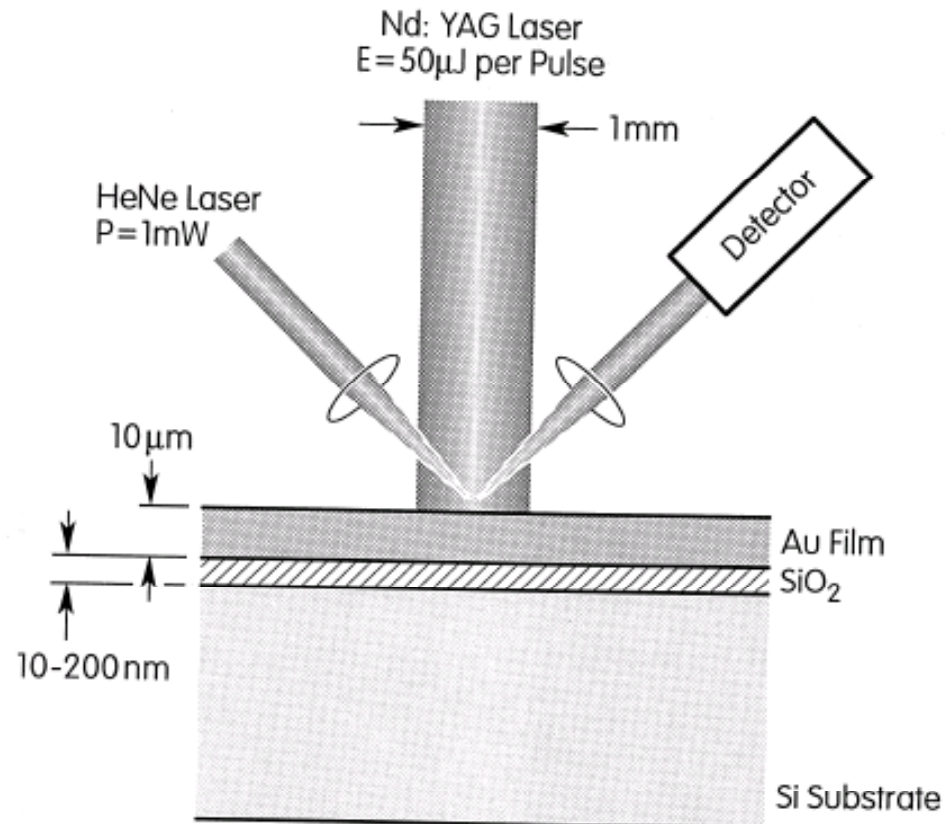
Flash diffusivity is the most widely used non-contact method but ...

- required sample geometry is not always available.
- measurements below room temperature are difficult
- deviations from 1-D heat flow require complex modeling

Thermoreflectance Methods

Useful for thin films. Modify for bulk samples?

Simple example: Käding (1994) measured Λ of thin SiO_2 films. See also (Morath, 1994) and (Stoner, 1993).



Short laser pulse increases T of Au to $T + \Delta T$; Au equilibrates quickly. Thin SiO_2 layer has $\Lambda_f \ll \Lambda_s$. Same eq. as capacitor discharging through a resistor.

$$\Delta T(t) = \exp(-t/\tau) ; \quad \tau = \frac{dhC}{\Lambda_f}$$

where d and h are the thicknesses of the SiO_2 and Au films, and C is the heat capacity of Au.

- ΔT is measured by the change in reflectance of Au as a function of T , $\sim 10^{-6} \text{ K}^{-1}$.
- different analysis needed if SiO_2/Si is replaced by thermoelectric sample; measures effusivity, ΛC .

How can we know Λ without knowing P ? Because of the additional layer (Au film) with known thermal properties (hC).

ÅNGSTRÖM, A. J., 1861, *Ann. Phys. Chem.* **114**, 513.

BIRGE, N. O. and NAGEL, S. R., 1987, *Rev. Sci. Instrum.* **58**, 1464.

CAHILL, D. G., 1990, *Rev. Sci. Instrum.* **61**, 802.

CARSLAW, H. S., and JAEGER, J. C., 1959, *Conduction of Heat in Solids* (Oxford: Clarendon), see Chapter 12.

CHEN, G., TIEN, C. L., WU, X. and SMITH, J. S., 1994, *J. of Heat Transfer* **116**, 325.

GOODSON, K. E., and FLIK, M. I., 1994, *Appl. Mech. Rev.* **47**, 101.

GRAEBNER, J. E., 1993, *Diamond Films Technol.* **3**, 77.

HATTA, I., 1985, *Rev. Sci. Instrum.* **56**, 1643.

KÄDING, O. W., SHURK, H., and GOODSON, K. E., 1994, *Appl. Phys. Lett.* **65**, 1629.

LEE, S.-M., and CAHILL, D. G., 1996, unpublished.

MILLER, A. D., 1988, *Specific Heat of Solids, CINDAS Data Series on Material Properties* Vol. 1-2, edited by C. Y. Ho (New York: Hemisphere), p 1.

MORATH, J. C., MARIS, H. J., CUOMO, J. J., PAPPAS, D. L., GRILL, A., PATEL, V. V., DOYLE, J. P., and SAENGER, K. L., 1994, *J. Appl. Phys.* **76**, 2636.

SCHMIDT, R., FRANKE, T., and P. HÄUSSLER, unpublished.

SWARTZ, E. T. and POHL, R. O., 1989, *Rev. Mod. Phys.* **61**, 605.

TAYLOR, R., 1995, *CRC Handbook of Thermoelectrics* (New York: CRC Press), p. 165.

WOOD, J. W., 1994, Ph. D. Thesis, South Dakota School of Mines.

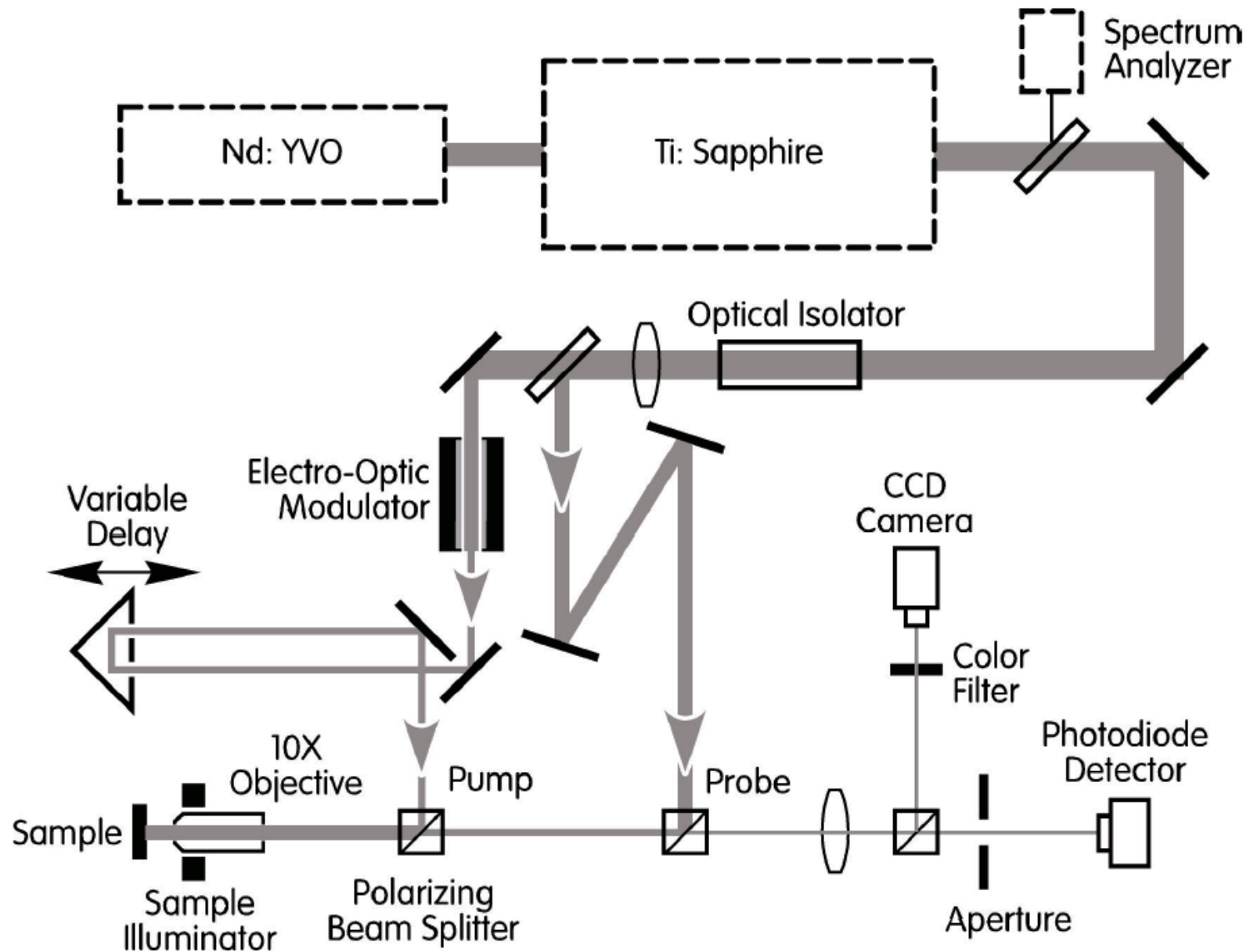
YAO, T., 1987, *Appl. Phys. Lett.* **51**, 1798.

Measurement of Thermal Conductivity Part B: Time-domain thermoreflectance

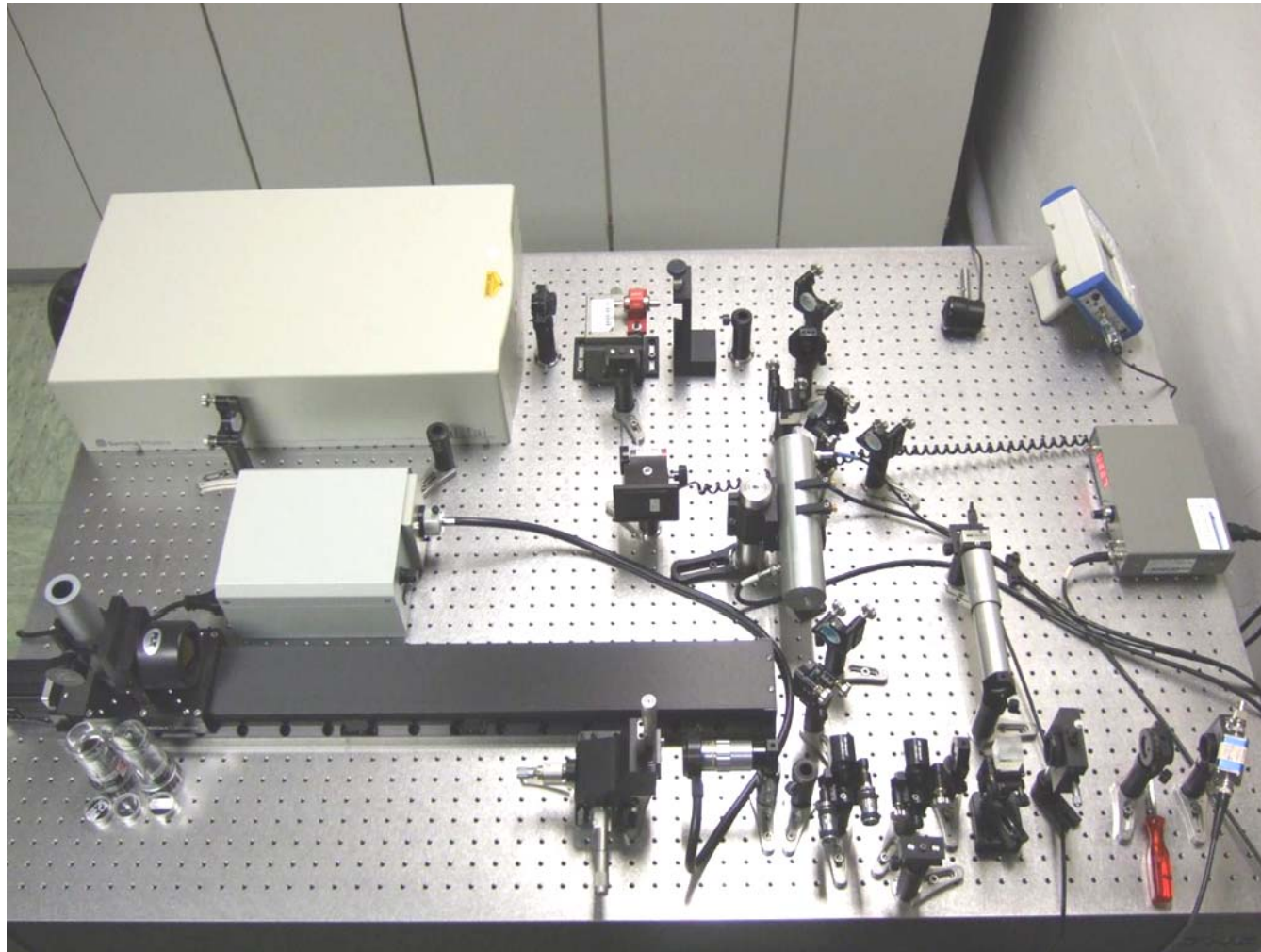
David G. Cahill,

*Materials Research Lab and Department of
Materials Science, U. of Illinois*

Time-domain thermoreflectance



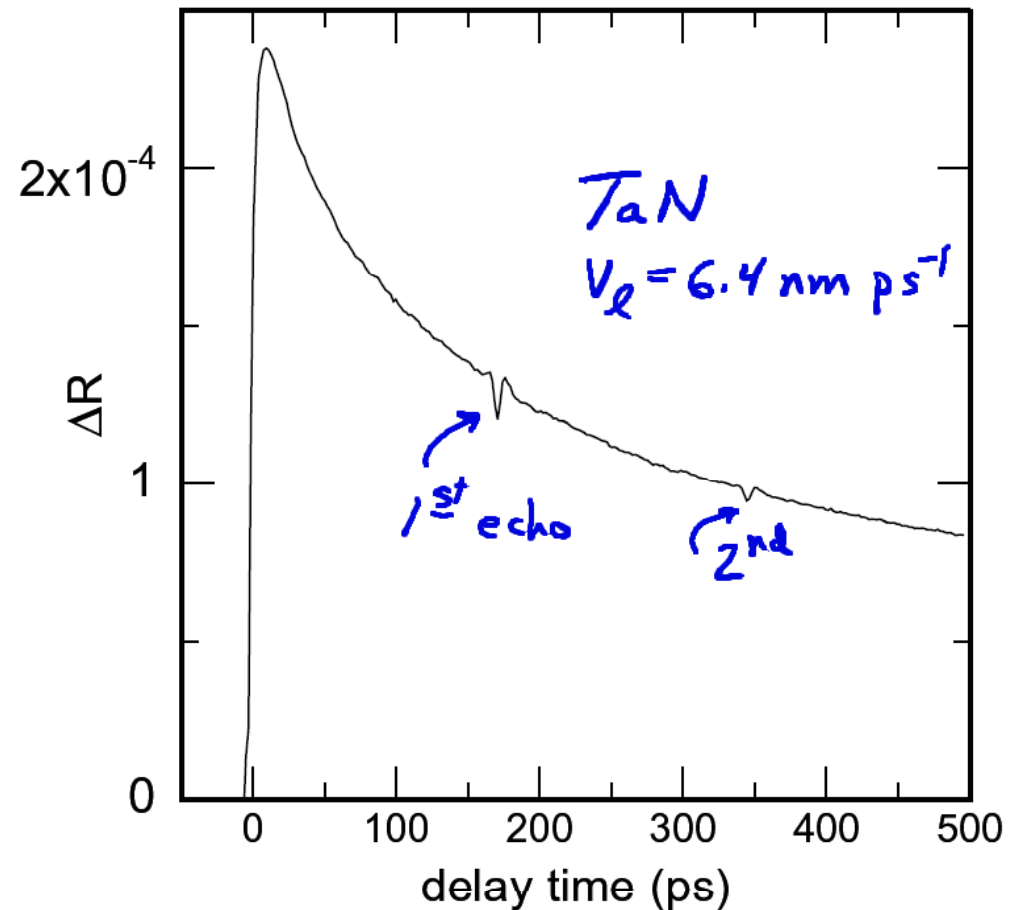
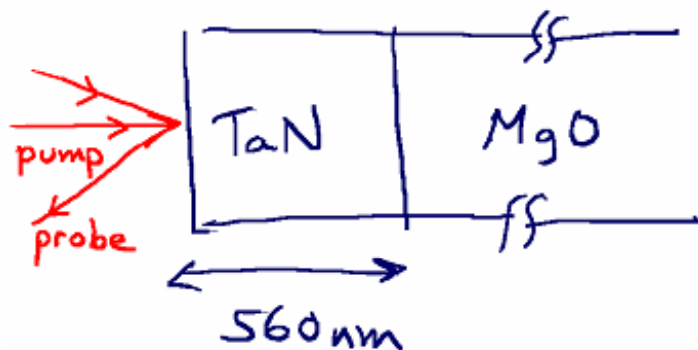
Time-domain thermoreflectance



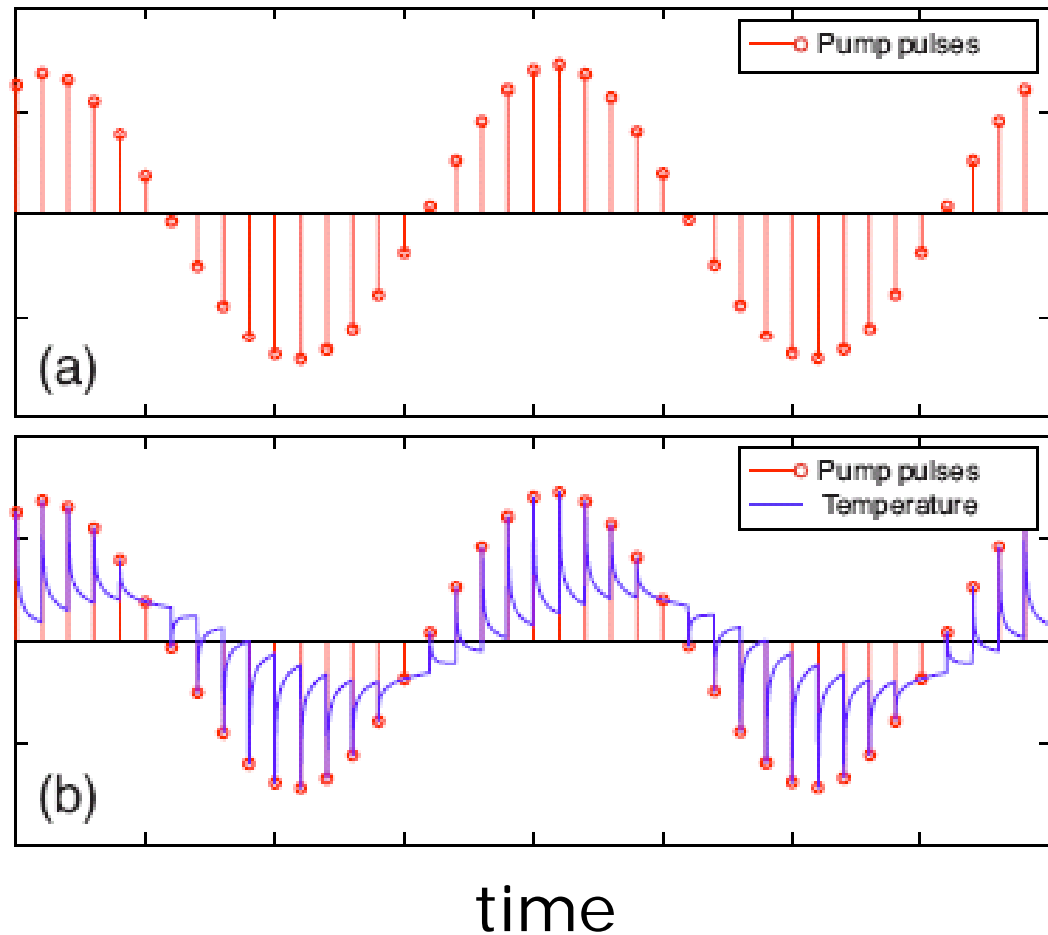
Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008

psec acoustics and time-domain thermorefectance

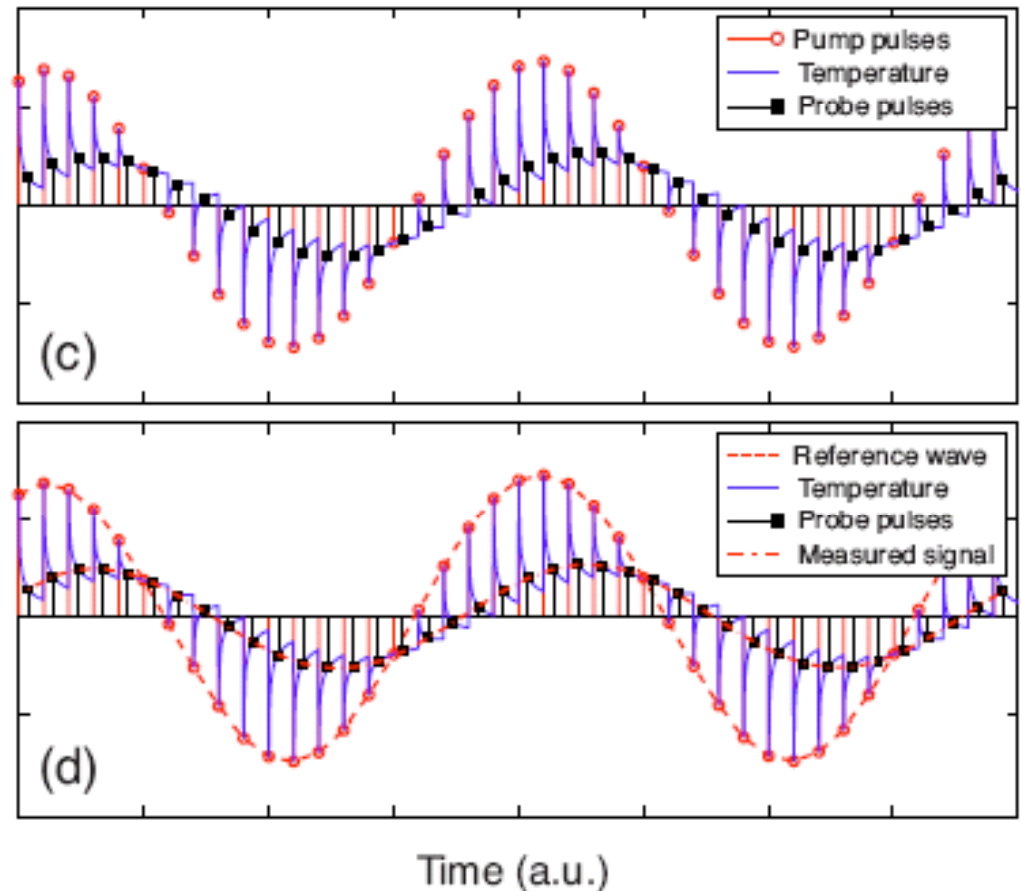
- Optical constants and reflectivity depend on strain and temperature
- Strain echoes give acoustic properties or film thickness
- Thermorefectance gives thermal properties



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



- Instantaneous temperatures measured by time-delayed probe
- Probe signal as measured by rf lock-in amplifier



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

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

Iterative solution for layered geometries

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

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

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

Signal analysis for the rf lock-in

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

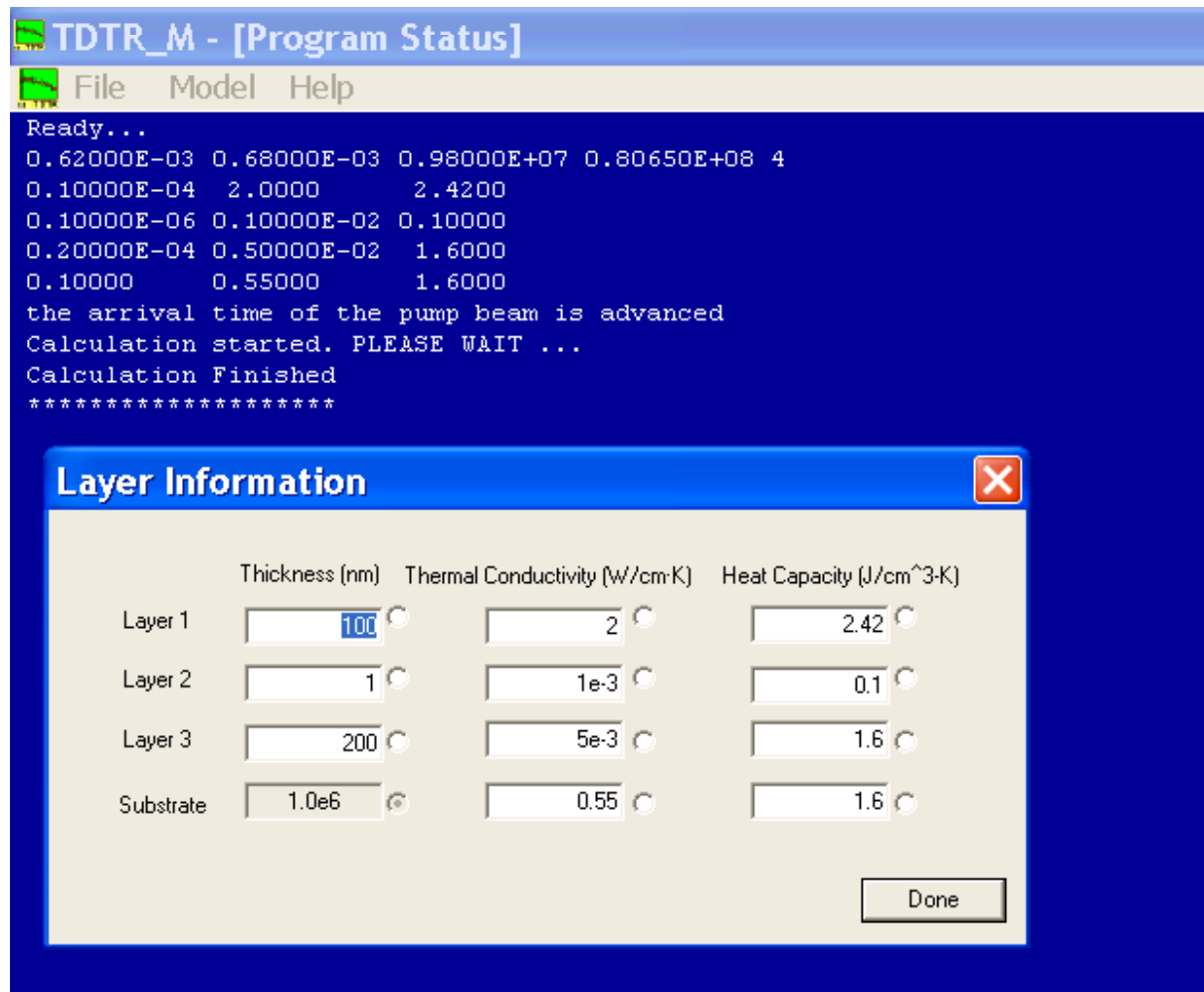
$$\text{Re} [\Delta R_M(t)] = \frac{dR}{dT} \sum_{m=-M}^M (\Delta T(m/\tau + f) + \Delta T(m/\tau - f)) \exp(i2\pi mt/\tau)$$

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

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

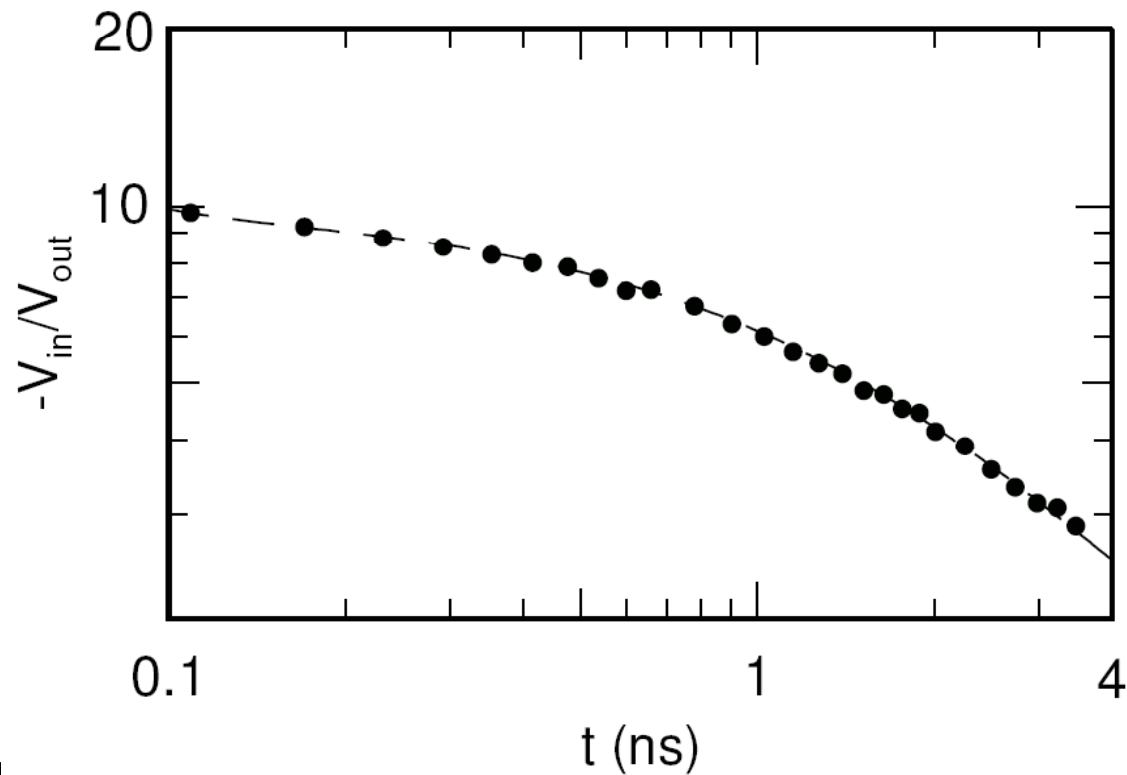
Windows software

author: Catalin Chiritescu,
users.mrl.uiuc.edu/cahill/tcdata/tdtr_m.zip

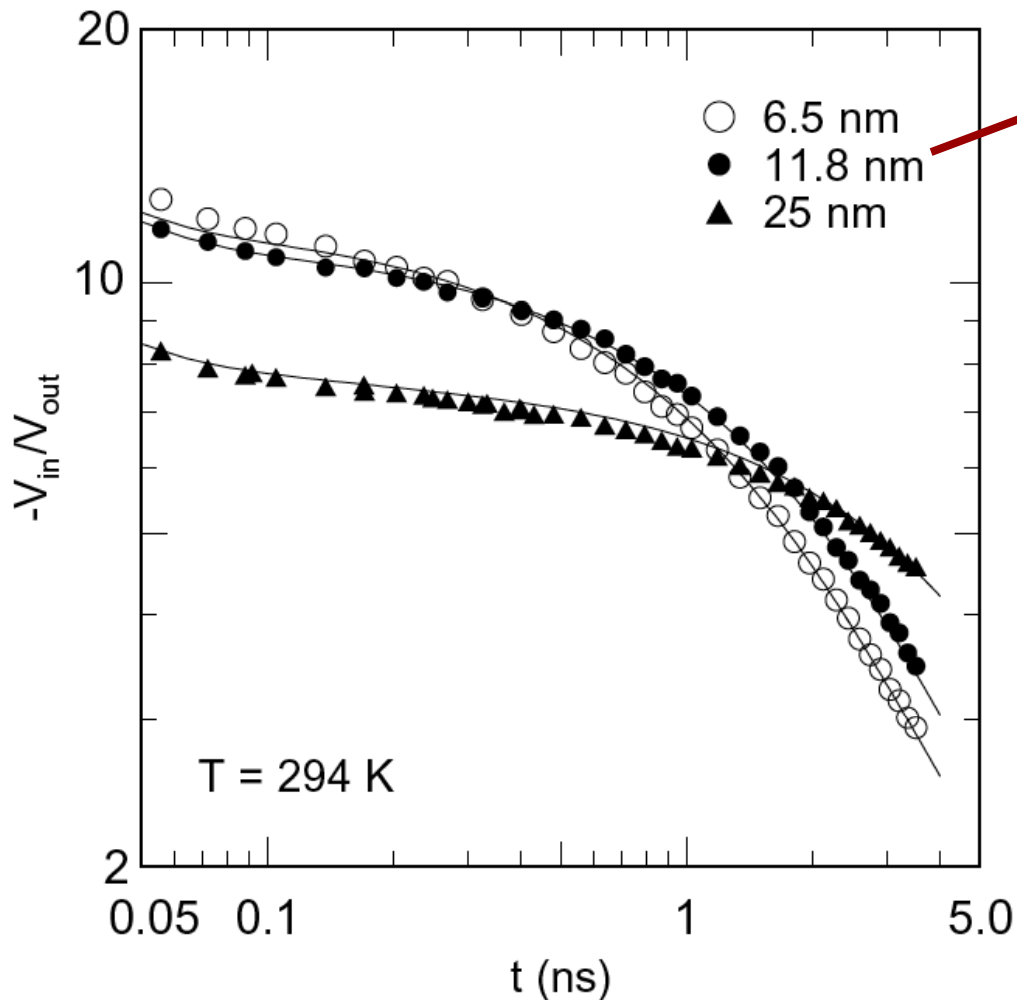


Thermoreflectance data for isotopically pure Si

- Two free fitting parameters
 - thermal conductivity, 165 W/m-K
 - Al/Si interface conductance, 185 MW/m²-K

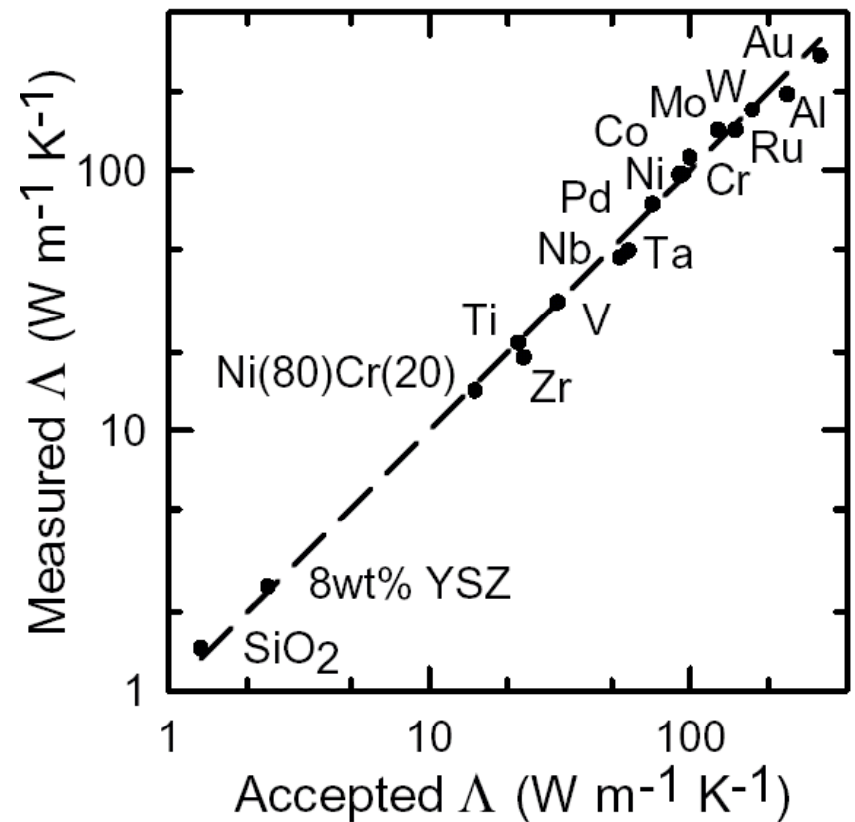
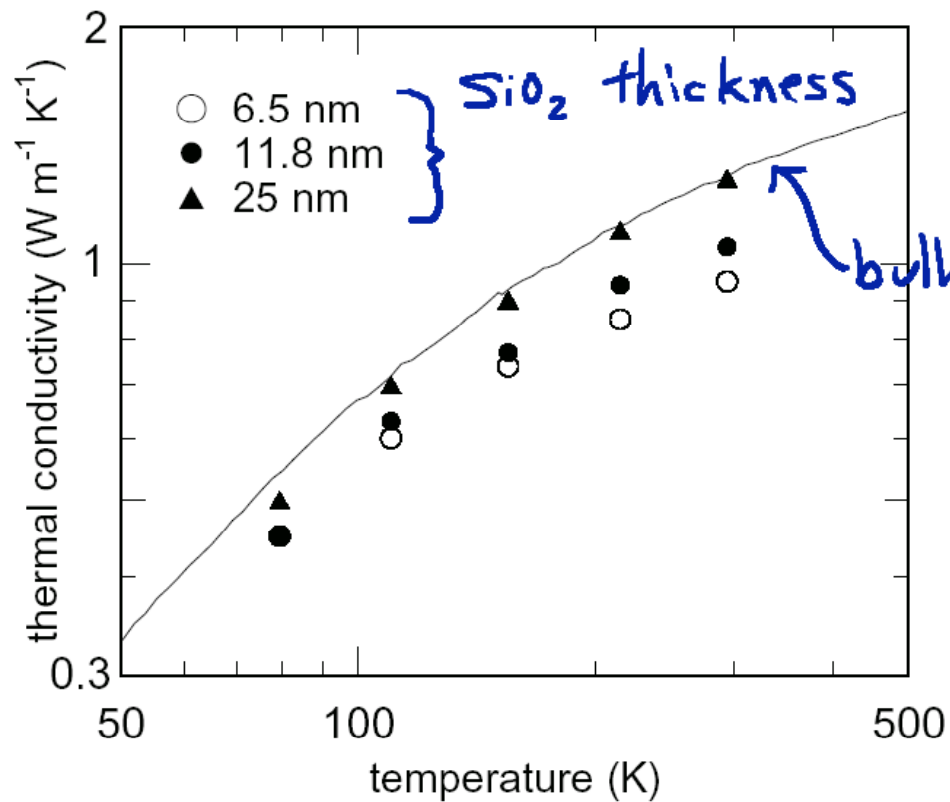


Time-domain Thermoreflectance (TDTR) data for TiN/SiO₂/Si



- reflectivity of a metal depends on temperature
- one free parameter: the “effective” thermal conductivity of the thermally grown SiO₂ layer (interfaces not modeled separately)

TDTR: early validation experiments

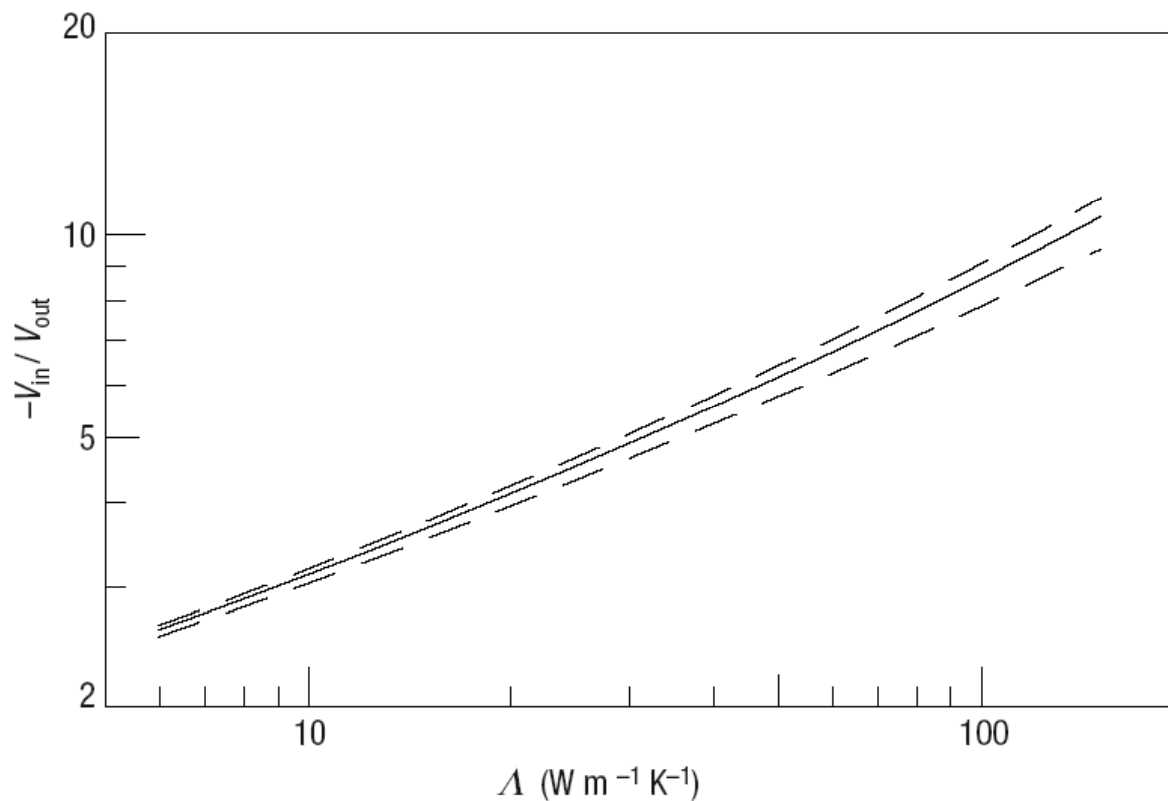


Nothing really new...just faster and smaller



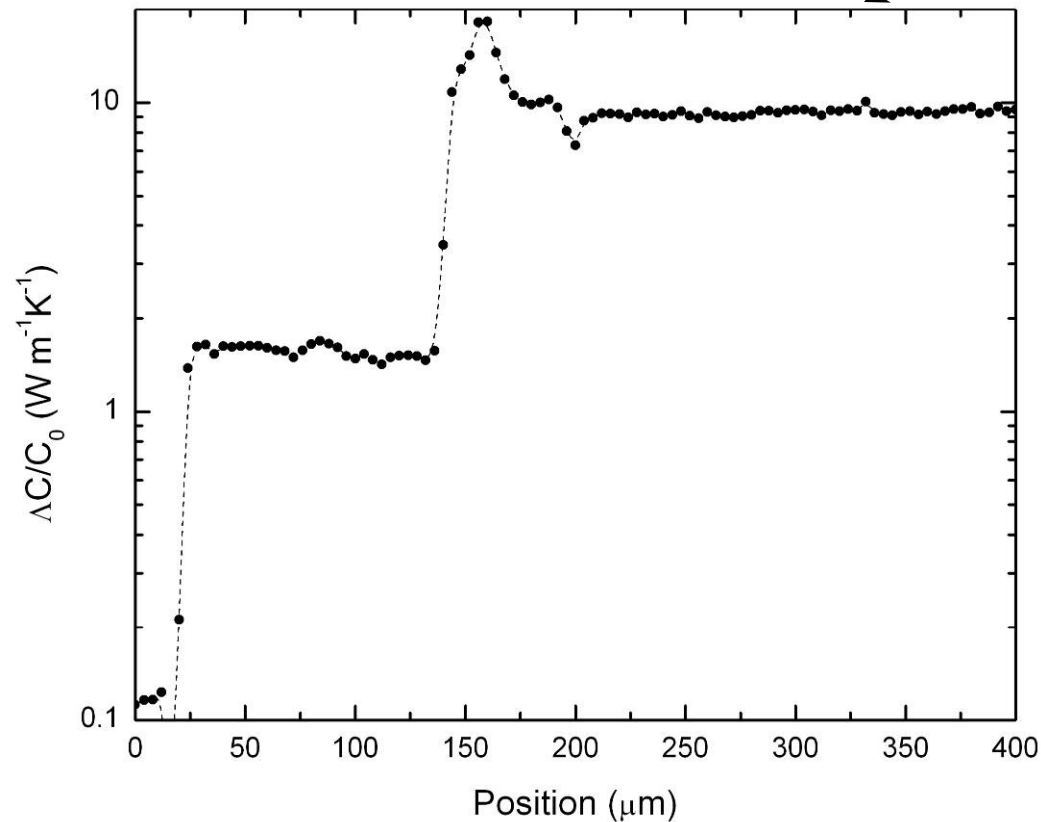
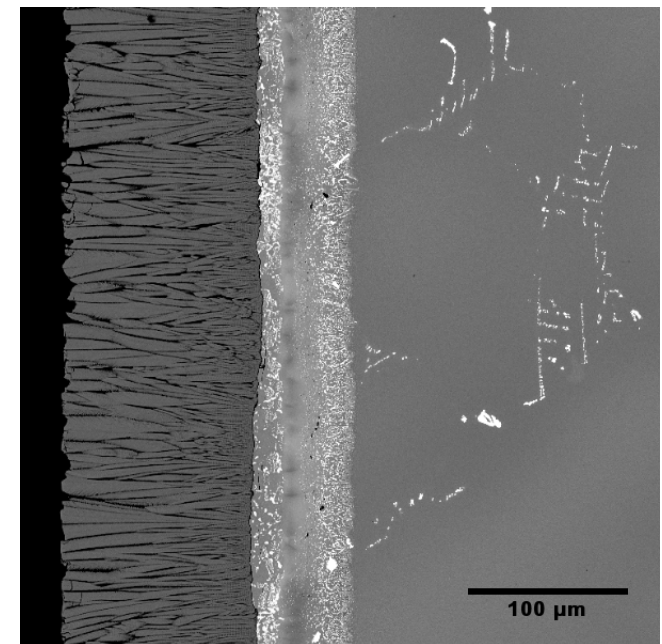
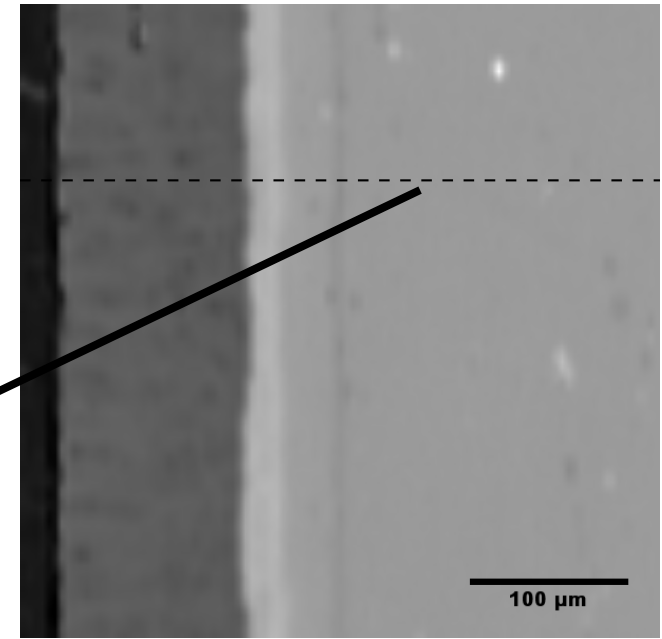
Thermal conductivity mapping

- At $t=100$ 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



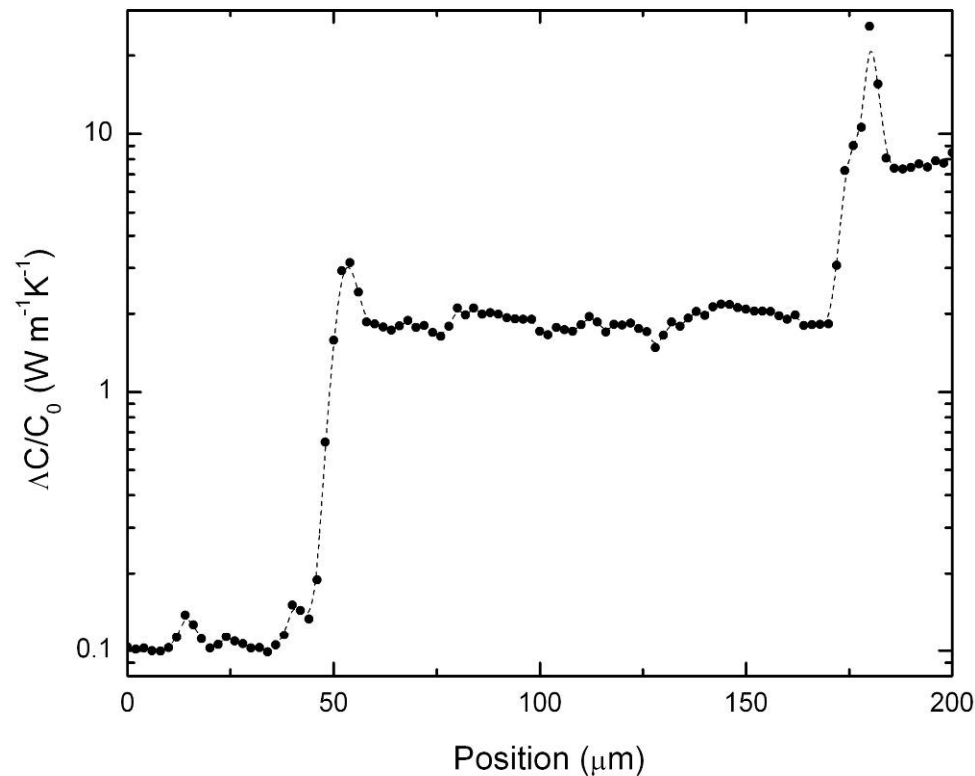
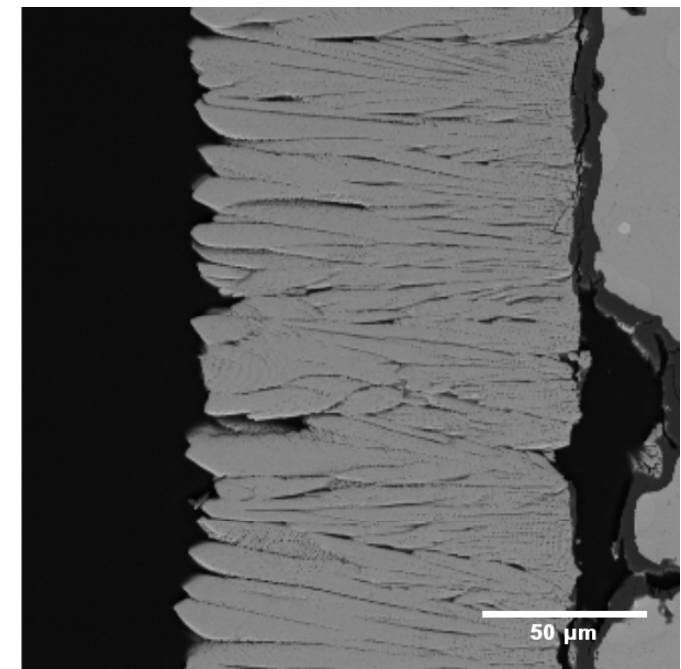
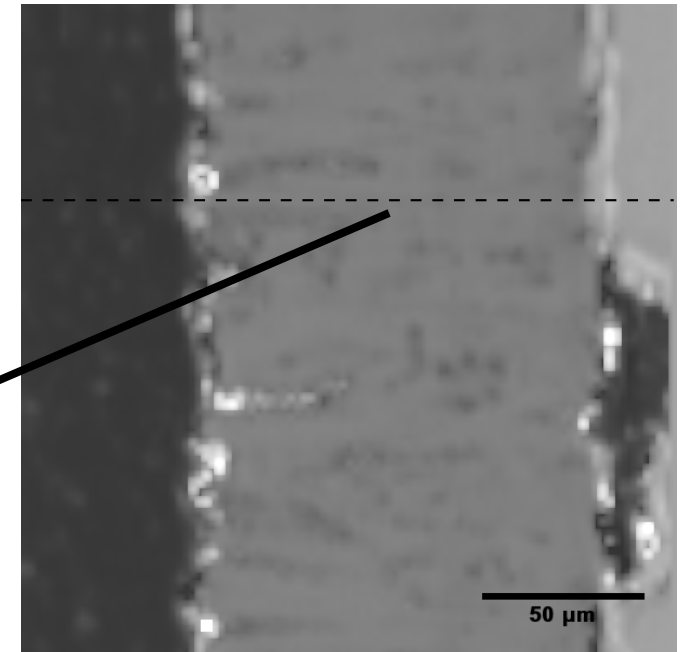
Thermal barrier coatings

- cross section of e-beam $\text{ZrO}_2\text{:Y}$ coating on (Ni,Pt)Al bond-coat on Ni-based super-alloy (Rene N5)



ZrO₂:Y thermal barrier

- 500 thermal cycles between room temperature and engine operating temperature



ZrO₂:Y thermal barrier, depth profile

- penetration depth of thermal waves is 100 nm
- angle polish and measure along a line to create a depth profile
- dull but important result: thermal conductivity is isotropic and homogeneous

