Comparison of the $3\omega$ method and time-domain thermoreflectance

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• Introduction to time-domain thermoreflectance (TDTR)

• Pros and cons: $3\omega$ versus TDTR

• Digression: what limits $3\omega$ accuracy and precision?

• TDTR advantages for high thermal conductivity thin layers, spatial resolution, and semiconductors.

• Additional issues: Frequency dependent thermal conductivity of semiconductor alloys.
Time-domain thermoreflectance
Time-domain thermoreflectance

Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008
- Optical constants and reflectivity depend on strain and temperature
- Strain echoes give acoustic properties or film thickness
- Thermoreflectance gives thermal properties
- Heat supplied by modulated pump beam (fundamental Fourier component at frequency \( f \))

- Evolution of surface temperature

\[ \text{time} \]
• 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**
  \[ g(r) = \frac{\exp(-qr)}{2\pi r} \quad q^2 = (i\omega/D) \]

- **Hankel transform of surface temperature**
  \[ G(k) = \frac{1}{4\pi^2 k^2 + q^2} \]

- **Multiply by transform of Gaussian heat source and take inverse transform**
  \[ P(k) = A \exp(-\pi^2 k^2 w_0^2/2) \]
  \[ \theta(r) = 2\pi \int_0^\infty P(k)G(k)J_0(2\pi kr) k \, dk \]

- **Gaussian-weighted surface temperature**
  \[ \Delta T = 2\pi A \int_0^\infty G(k) \exp\left(-\pi^2 k^2 \left(w_0^2 + w_1^2\right)/2\right) k \, dk \]
Iterative solution for layered geometries

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

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

\[
G(k) = \left(\frac{B_1^+ + B_1^-}{B_1^- - B_1^+}\right) \frac{1}{\gamma_1}
\]
Frequency domain solution for $3\omega$ and TDTR are essentially the same

**$3\omega$**
- “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.
TDTR signal analysis for the lock-in signal as a function of delay time $t$

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

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

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

- 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
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: early validation experiments

Each have advantages and disadvantages

3\(\omega\)

- High accuracy, particularly for bulk materials and low thermal conductivity dielectric films
- Accuracy is reduced for semiconducting thin films and high thermal conductivity layers
  - Need electrical insulation: introduces an additional thermal resistance.
  - Cannot separate the metal/film interface thermal conductance from the thermal conductivity
- Wide temperature range (30 < \(T< 1000\) K)
  - But very high temperatures are not usually accessible for semiconductors
Each have advantages and disadvantages

**TDTR**

- Accuracy is typically limited to several percent due to uncertainties in the many experimental parameters
  - Metal film thickness
  - Heat capacity of the sample if film is thick
- But many experimental advantages
  - No need for electrical insulation
  - Can separate the metal/film interface thermal conductance from the thermal conductivity
  - High spatial resolution
  - Only need optical access: high pressures, high magnetic fields, high temperatures
Digression: what limits the accuracy of $3\omega$ data?

- 1990’s: approximations made for low thermal conductivity film on high thermal conductivity substrate and film thickness < heater-width
  - No need for those approximations now. Feldman and co-workers (1999), and others shortly after, pointed out that a transfer matrix approach for layered geometries is equally applicable for linear and radial heat flow.
  - DOS program: multi3w.exe available at users.mrl.uiuc.edu/cahill/tcdata.html
  - Anisotropy is easy to add
Digression: what limits the accuracy of $3\omega$ data?

- Contributions from the heater line.
  - Not explicitly included in the heat flux boundary conditions of the solutions.
  - Heat capacity matters at very high frequencies, see, for example, Tong et al. RSI (2006).
  - Lateral heat flow in heater line was considered recently by Gurrum et al., JAP (2008).
Digression: what limits the accuracy of $3\omega$ data?

- In my experience, the $dR/dT$ calibration is the biggest issue.
  - use physics to fix the calibration

$$R(T) = \frac{l}{A} \rho_{BG}(T) + R_o,$$

Bloch-Grüneisen resistivity of a metal

$$\rho_{BG}(T) = C_{BG} \left( \frac{T}{\theta_D} \right)^{5} \int_{0}^{\theta_D/T} \frac{z^5}{(\exp(z) - 1)(1 - \exp(-z))} dz,$$
Calibration of Au thermometer line

- Materials with large coefficient of thermal expansion create an interesting problem
  - during calibration of $R(T)$ substrate strain is homogeneous
  - but during $3\omega$ measurement, ac strain field is complex so the determination of $dR/dT$ is not really correct.
High thermal expansion coefficients

- Add terms to account for effect of strain on the Bloch-Grüneise resistivity and the residual resistivity.

\[
R(T) = \frac{l}{A} \rho_{BG}(T) \left[ 1 + c_3 \ 5.75 \ (\alpha(T) - \alpha(T_o)) \right] \\
+ R_o \left[ 1 + c_3 \ 2.45 \ (\alpha(T) - \alpha(T_o)) \right],
\]

- CTE of PMMA is \(\approx 50 \text{ ppm/K}\)
- CTE of PbTe is \(\approx 20 \text{ ppm/K}\)
Highest precision measurements at Illinois using $3\omega$: polymer nanocomposites

- PMMA mixed with 60 nm $\gamma$-Al$_2$O$_3$ nanoparticles

Putnam et al., JAP (2003)
Something not possible with $3\omega$: TDTR data for isotopically pure Si epitaxial layer on Si

- Two free fitting parameters
  - thermal conductivity, 165 W/m-K
  - Al/Si interface conductance, 185 MW/m$^2$-K

Cahill et al., PRB (2004)
Thermal conductivity map of a human tooth

Tooth Anatomy

- Enamel
- Dentin
- Pulp
- Canals (containing periodontal membrane)
- Nerves and blood vessels
- Root and opening
- Enamel
- Dentin

www.enchantedlearning.com/
High throughput data using diffusion couples

![Graph showing thermal conductivity vs. Al concentration](image)

- **Present experiment**
- **Terada et. al.**

**SEM** image showing Ni and Ni-54.5at%Al with a scale bar of 200 μm.
Thermoreflectance raw data at t=100 ps

- fix delay time and vary modulation frequency $f$.
- Change in $V_{in}$ doesn’t depend on $f$. $V_{out}$ mostly depends on $(f\Lambda C)^{-1/2}$
- semiconductor alloys show deviation from fit using a single value of the thermal conductivity

Koh and Cahill PRB (2007)
Same data but fit $\Lambda$ at each frequency $f$

Frequency dependent thermal conductivity of semiconductor alloys

Koh and Cahill PRB (2007)
How can thermal conductivity be frequency dependent at only a few MHz?

- $2\pi f\tau \ll 1$ for phonons that carry significant heat. For dominant phonons, $\tau \sim 50$ ps, and $2\pi f\tau \sim 10^{-3}$.

- But the thermal penetration depth $d$ is not small compared to the dominant mean-free-path $l_{\text{dom}}$.

- Ansatz: phonons with $l(\omega) > d$ do not contribute to the heat transport in this experiment.

- True only if the “single-relaxation-time approximate” fails strongly. For single relaxation time $\tau$, $l \ll d$ because $f\tau \ll 1$.
For non-equilibrium, add effusivity instead of conductivity

- Consider a "two-fluid" model with
  \[ \Lambda_1 \approx \Lambda_2 \]
  \[ C_1 \gg C_2 \]

- Equilibrium,
  \[
  (\Lambda C)^{1/2} = \left[ (\Lambda_1 + \Lambda_2)(C_1 + C_2) \right]^{1/2}
  \]

- Out-of-equilibrium,
  \[
  (\Lambda C)^{1/2} = (\Lambda_1 C_1)^{1/2} + (\Lambda_2 C_2)^{1/2}
  \approx (\Lambda_1 C_1)^{1/2}
  \]
$f < 1$ MHz frequency TDTR agrees with $3\omega$

2 $\mu$m thick $(\text{In}_{0.52}\text{Al}_{0.48})_x(\text{In}_{0.53}\text{Ga}_{0.47})_{1-x}\text{As}$

Koh et al., JAP (2009)
Summary and Conclusions

• Usually, $3\omega$ has higher accuracy because Joule heating and dR/dT calibration are electrical measurements and geometry is precisely known.

• For semiconducting thin films, because of extra thermal resistance of electrical isolation layers, accuracy of TDTR is comparable.

• TDTR has tremendous advantages in experimental convenience—once the high initial cost and set-up has been overcome.