Measurement of thermal conductivity and thermal expansion on micron-length scales by thermo-optic phase spectroscopy (TOPS)

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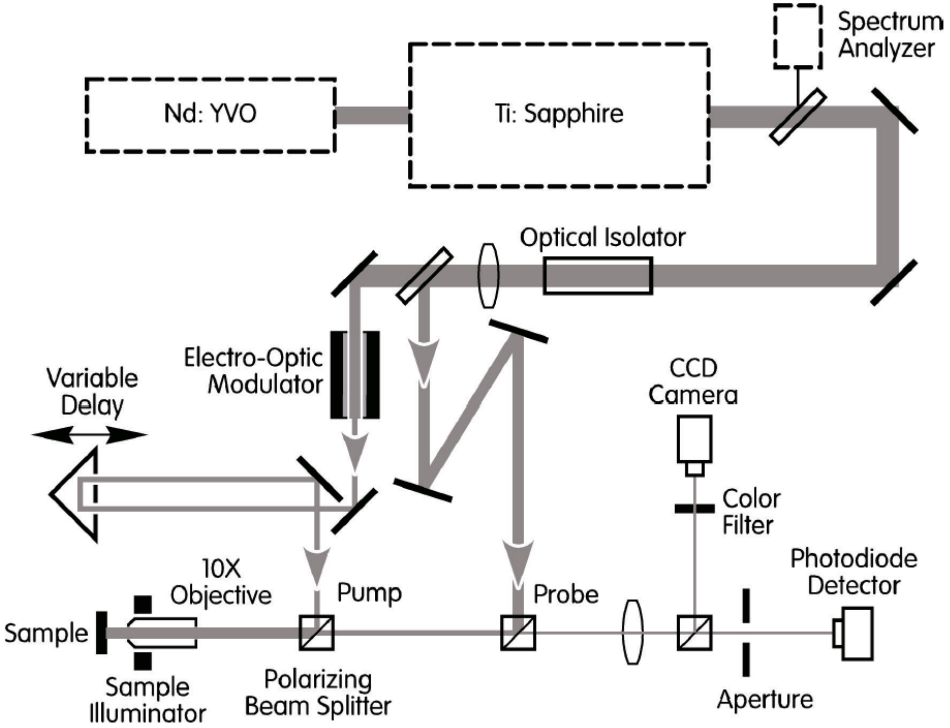
Our goal is to fill gaps in our ability to rapidly measure the thermal conductivity of small samples with less-than-ideal surfaces and geometries

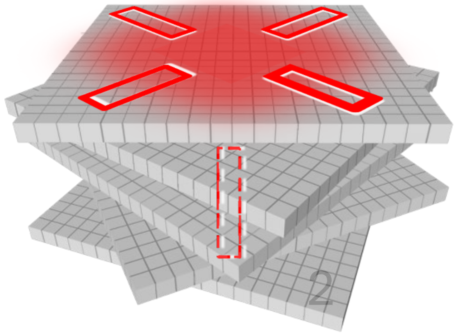
Time-domain thermoreflectance (TDTR) provides a near universal method for any sample with a smooth surface,

TDTR however has limitations for polymers. Too **sensitive to surface roughness** and can only measure the near surface (<100 nm) layer.

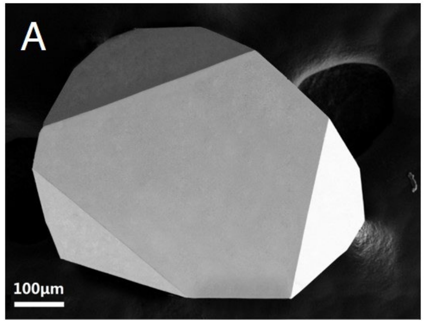
Beam-offset TDTR can provide data for **in-plane thermal conductivity** but only if the thermal conductivity is not too low.



Disordered WS_2 0.04 W/(m K)



c-BAs 1000 W/(m K)



Many of the technical advances in TDTR by Cahill group were developed to address these challenges (rough surfaces and in-plane conduction)

O’Hara	2001	optical layout
Cahill	2004	analytical model
Huxtable	2004	mapping
Kang	2008	two-tint
Feser	2012-14	beam offset
Wilson, Hohensee	2014	two-channel
Liu, Choi	2014	magneto-optic Kerr effect

Artifacts in thermoreflectance measurements created by a rough surface are made worse by a large coefficient of thermal expansion (CTE)

Scattered pump light does not affect the two-tint or two-color measurements.

Modulation of diffuse scattering of the probe by thermoelastic deformation changes the intensity of the probe.

- For diamond films, CTE is small, and we can tolerate 30% diffuse light scattering of the probe in a TDTR measurement
- For a polymer, CTE is large, and diffuse scattering of the probe must be <2%, and ideally <1%

Vast phase space of thermal conductivity measurement methods.

Heat source

- Joule
- Peltier
- Absorption of EM radiation

Thermometer

- Electrical resistance
- Seebeck
- Infrared radiation
- Thermoreflectance (intensity)
- Index gradient
- Expansion/displacement
- Magneto-optic

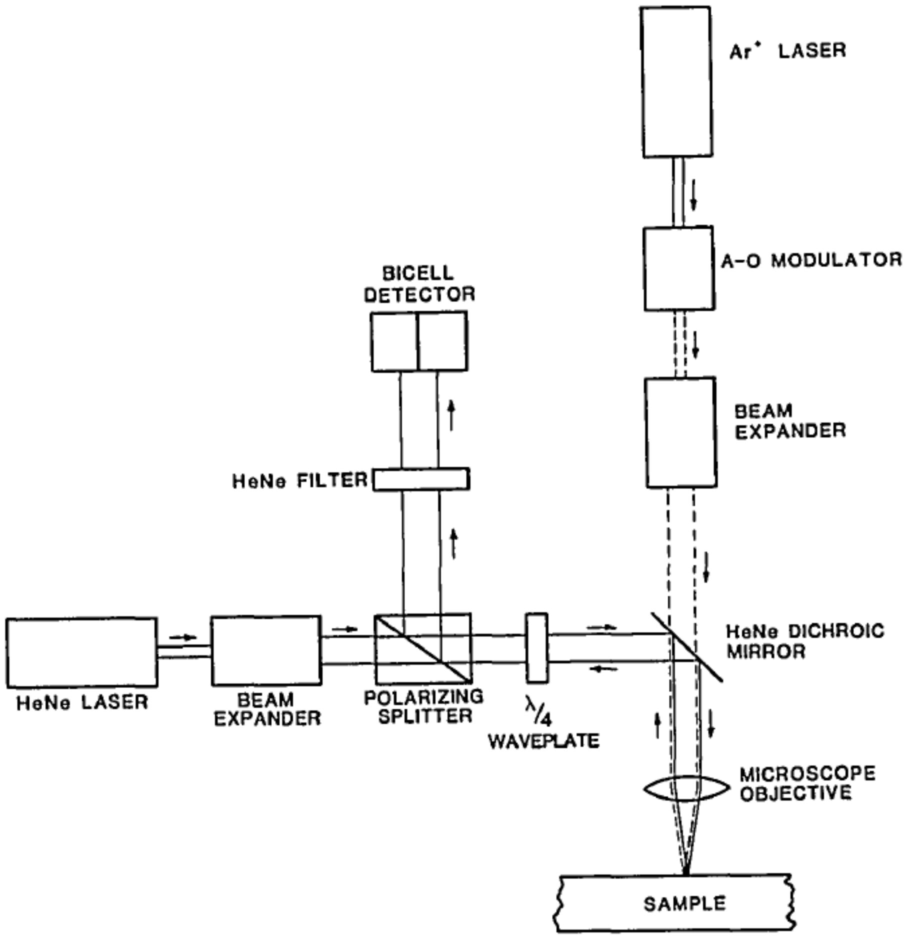
Temporal

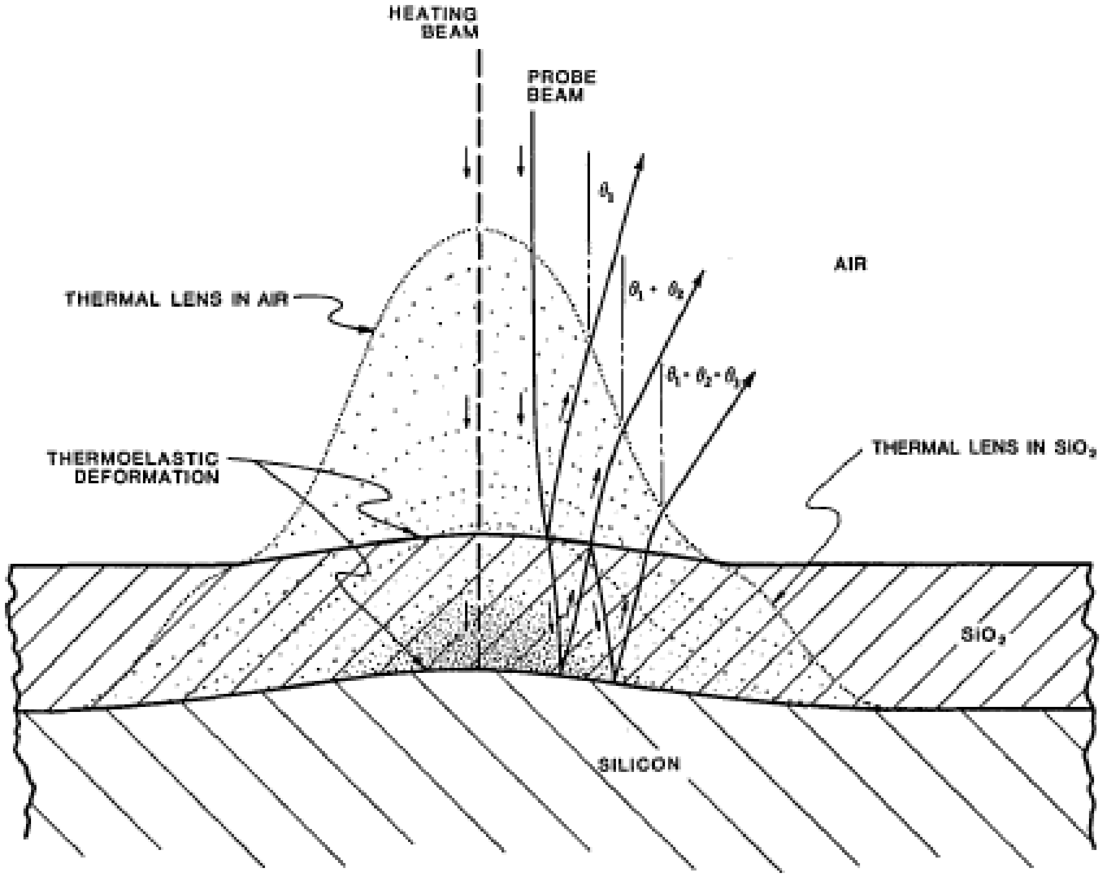
- Steady-state
- Pulsed
- Step
- Modulated (ac)

Dimensionality

- Planar (1D) high and low aspect
- Radial (2D)
- 3D

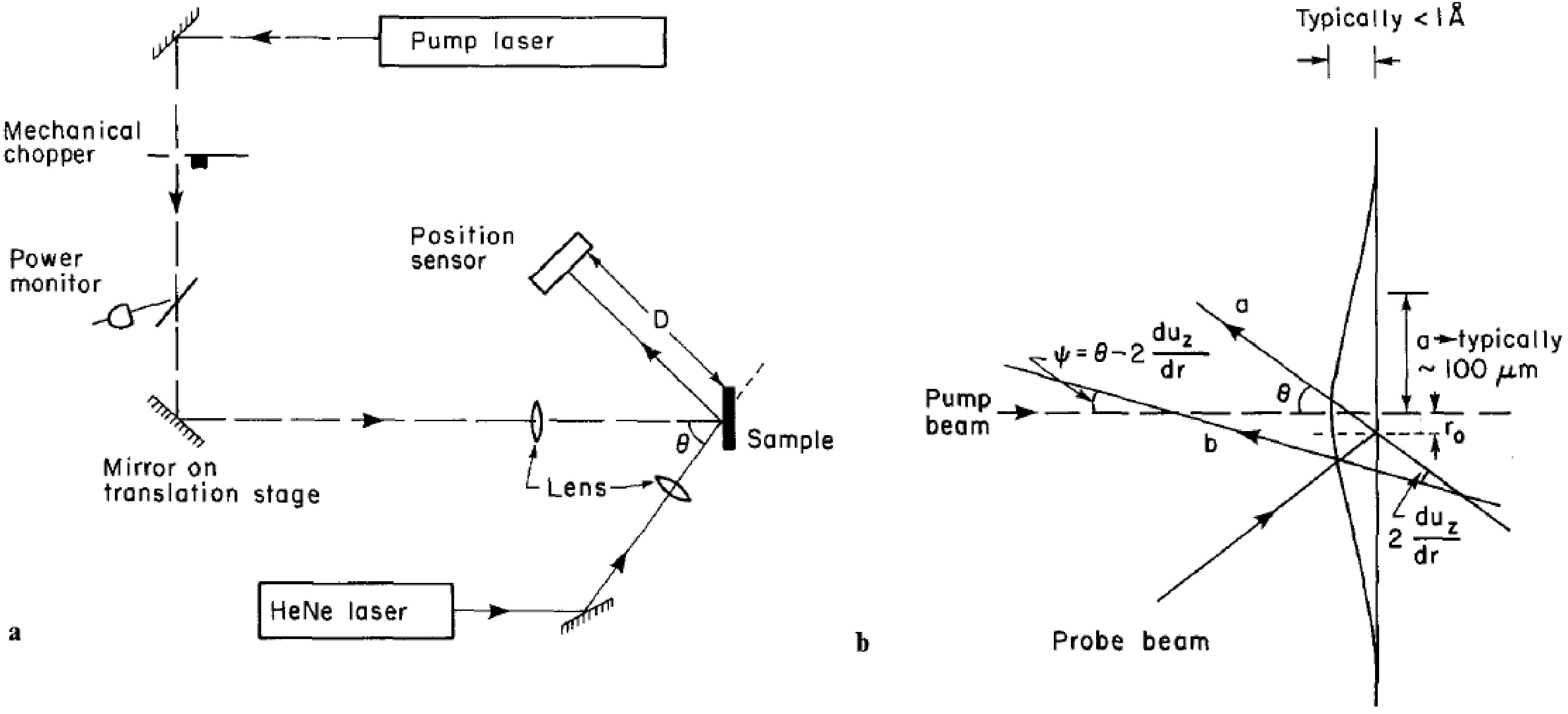
Opsal et al. (Thermawave, 1983) were mostly concerned with metrology for film thickness





See also our response to a comment, Sun et al., RSI (2024)

Olmstead, et al. (1983) were mostly concerned with absorption spectroscopy



Long history of beam deflection techniques in Cahill group

Putnam	2004	electrical heater (liquids, Soret effect)
Zheng	2008	time-domain probe-beam deflection (CTE)
Xie	2018	frequency domain (mass diffusion)
Shin	2018	back-side (mirage, thermal conductivity)
Lv	2021	dedicated system for back-side
Sun	2023	front-side (displacement)
Sun	2024	immersion (mirage)

Terminology became overly complicated (with too many syllables) and we now refer to our beam deflection methods as TOPS (thermo-optic phase spectroscopy)

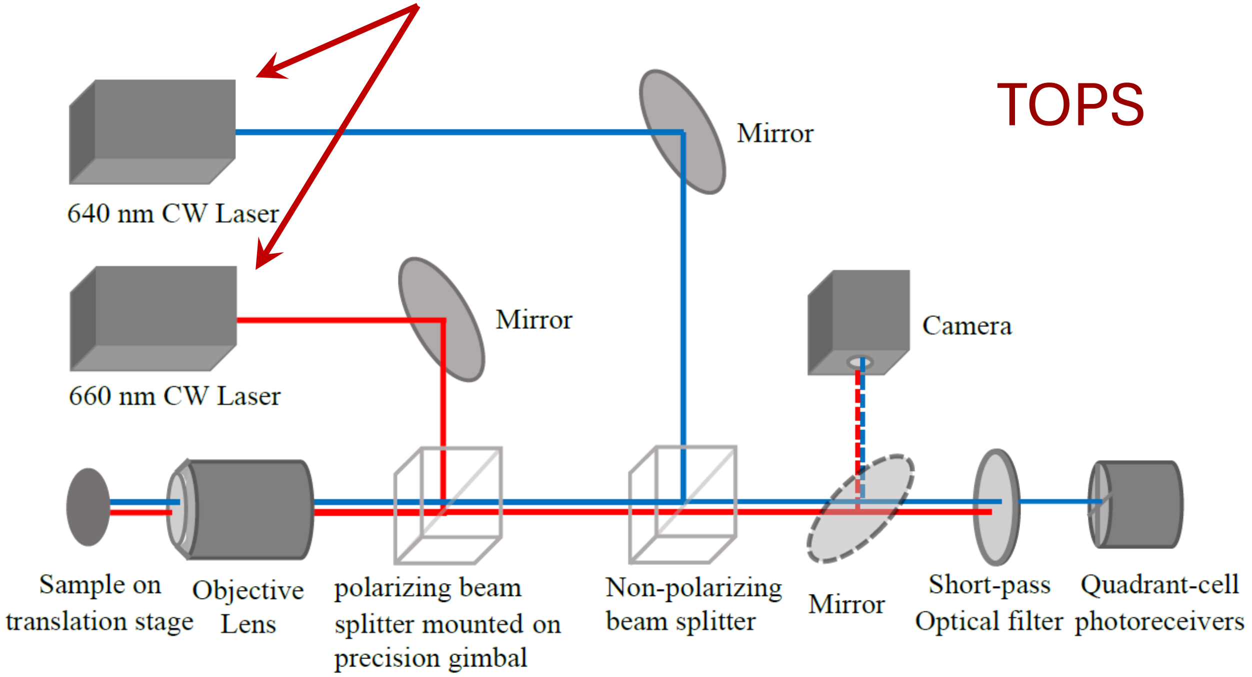
Thermo-optic phase spectroscopy (TOPS) uses essentially the same instrument as frequency-domain thermoreflectance (FDTR)

The photodiode used in FDTR is replaced by a quadrant photocell.

Advantages are higher signal-to-noise and less sensitivity to artifacts created by rough surface morphology.

Mostly sensitivity to in-plane thermal diffusivity. Need an independent measurement of heat capacity or effusivity.

Recently changed to fiber-coupled super-luminescent diodes to further reduce noise



Lv et al. *ACS Applied Polymer Materials*, 2021a

Two main categories of TOPS: immersion-TOPS (mirage effect) and displacement-TOPS (photothermal displacement)

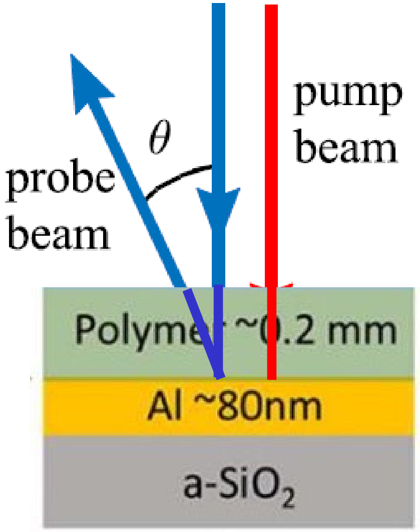
I-TOPS works well for transparent, i.e., fully amorphous polymers and liquids.

Not appropriate for anything that scatters light.

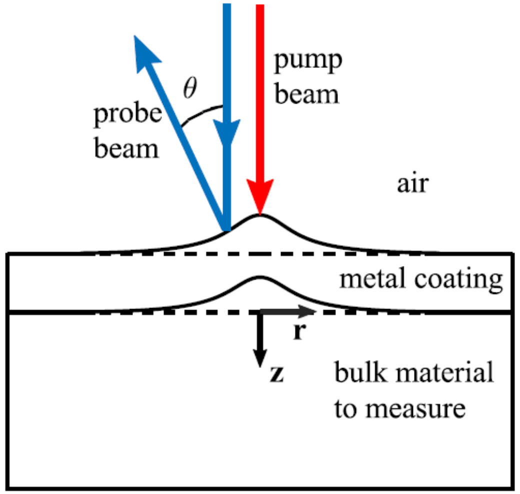
D-TOPS is now our go-to method for bulk polymer samples and small inorganic crystals.

We also use I-TOPS with a known transparent material (liquid or elastomer) to study an unknown sample.

I-TOPS



D-TOPS



Lv et al. *ACS Applied Polymer Materials*, 2021a
Sun et al. RSI, 2023

Beam-deflection signals are typically much larger than thermoreflectance signals

The normalized signal in a thermoreflectance measurement $\left(\frac{dR}{dT}\right)\Delta T$

The normalized signal in a beam deflection measurement $\left(\frac{w_0}{\lambda}\right)\Delta\theta$

For D-TOPS $\Delta\theta \approx \alpha_L \Delta T$

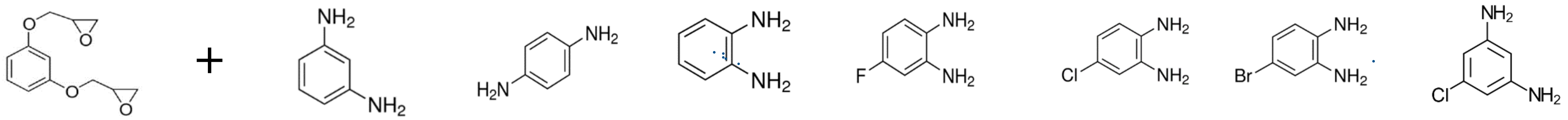
For I-TOPS $\Delta\theta \approx \left(\frac{dn}{dT}\right)\Delta T$

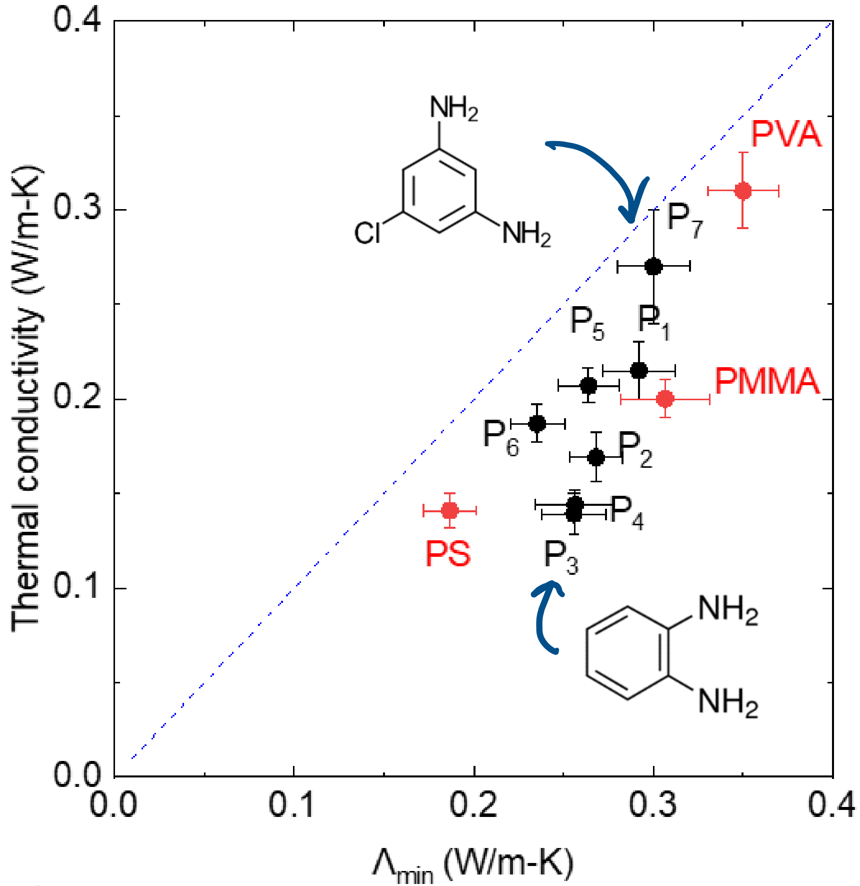
Maximum values for thermoreflectance *dR/dT*, linear thermal expansion α_L, and thermo-optic coefficients *dn/dT*, are all on the order of $10^{-4}\ \mathrm{K}^{-1}$

Beam deflection signals are enhanced by a factor of $\approx \left(\frac{w_0}{\lambda}\right)$

$w_0 = 1/e^2$ intensity radius; $\lambda =$ wavelength

We used I-TOPS to measure the thermal conductivity of amorphous epoxies as a function of the chemical structure of the diepoxide and diamine

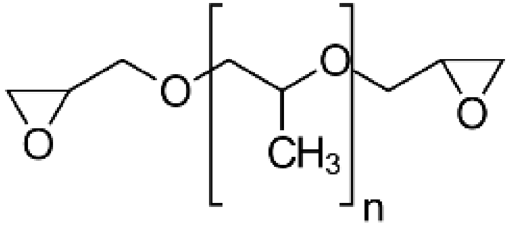




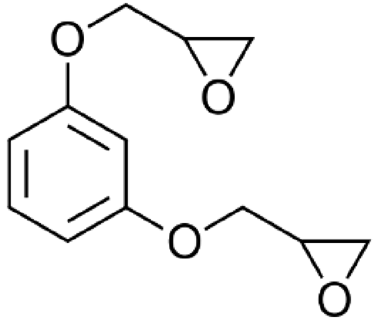
Lv et al. *ACS Applied Polymer Materials*, 2021a

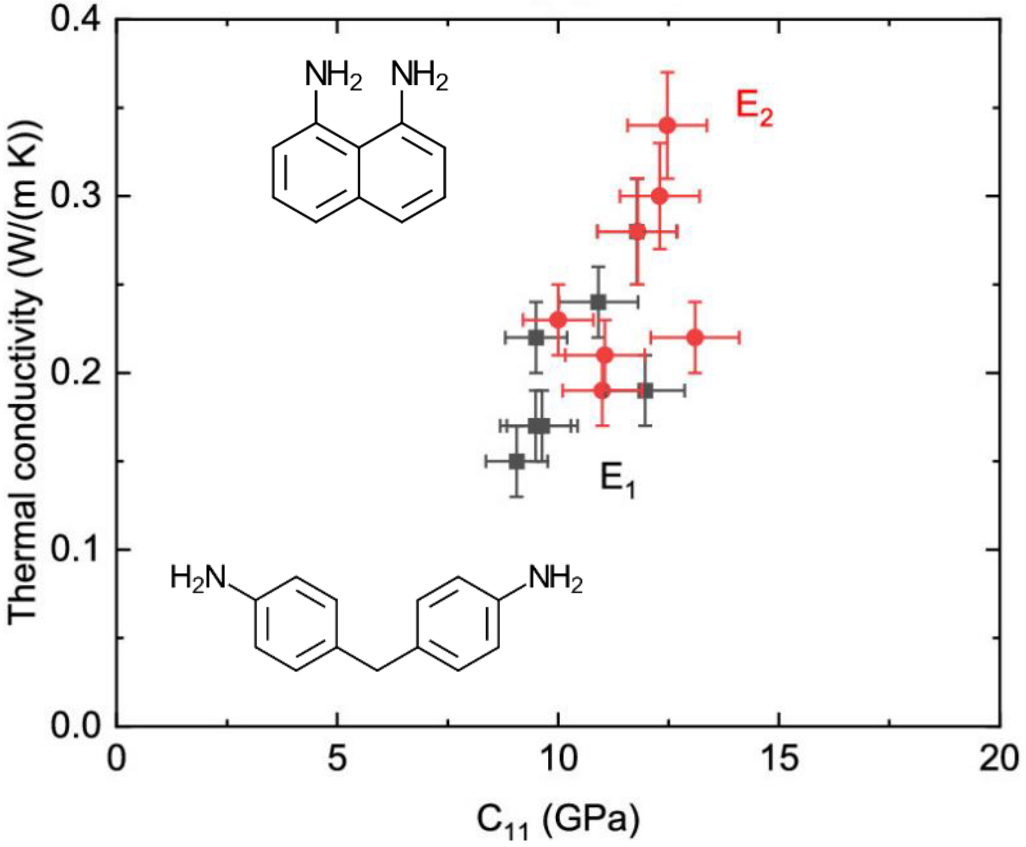
Comparison of aliphatic and aromatic monomers

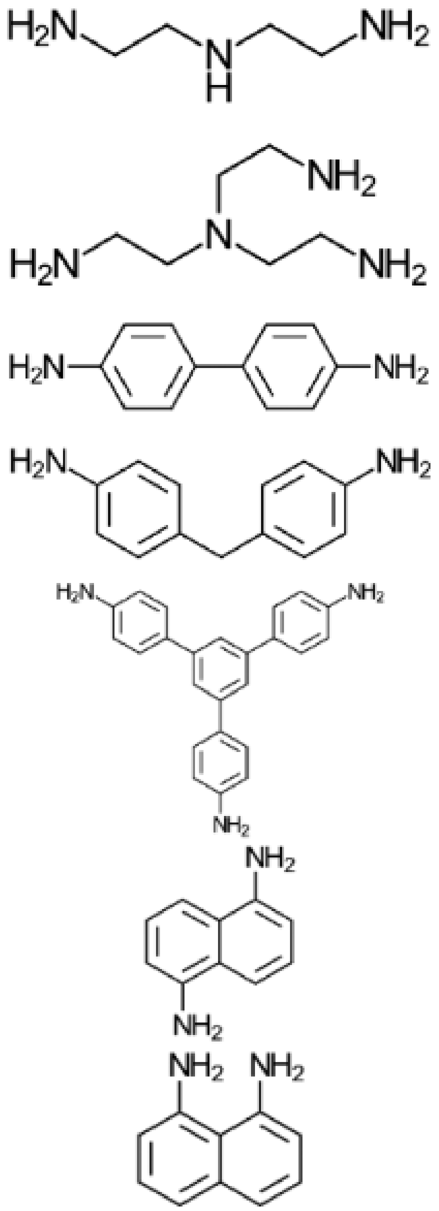
E_1



E_2



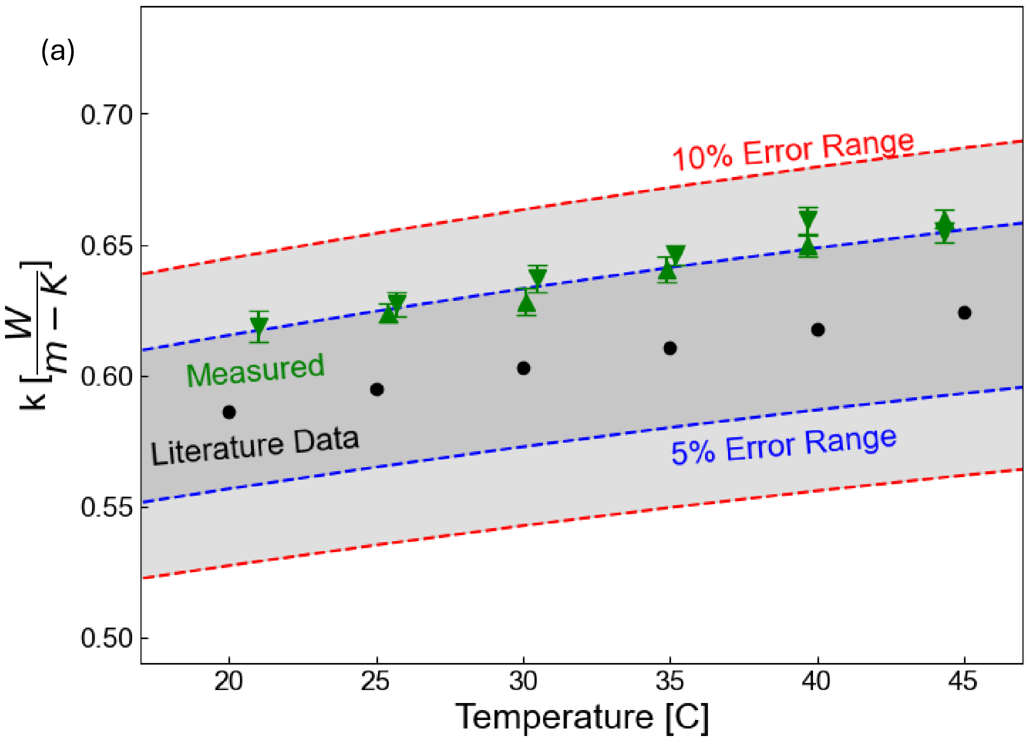




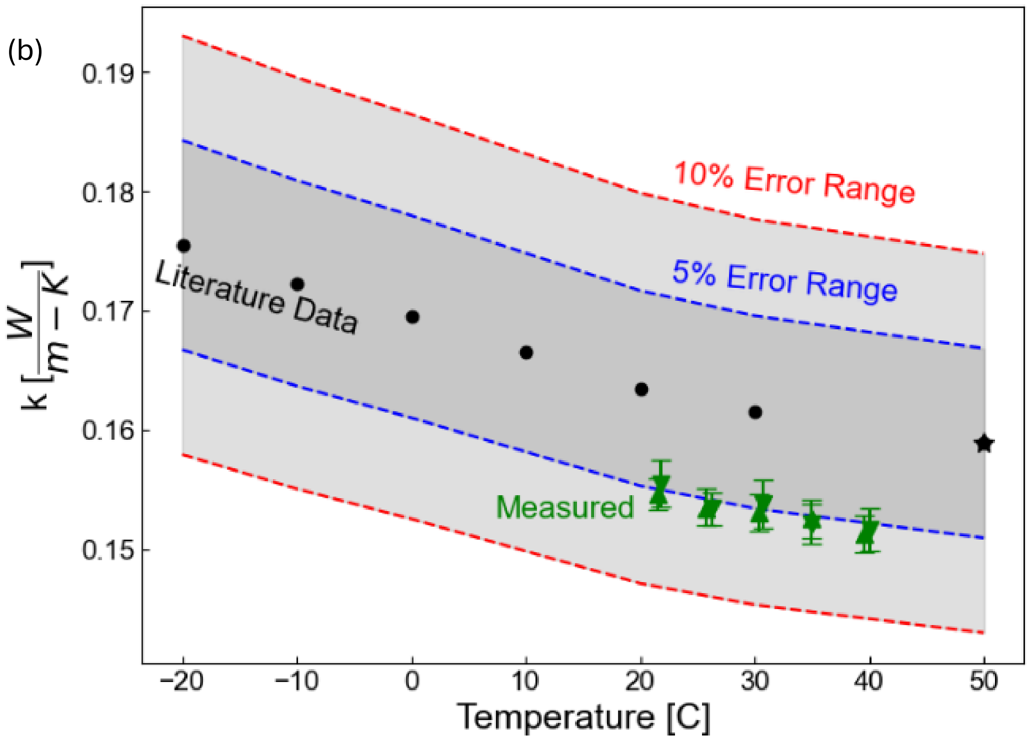
Lv et al. *ACS Applied Polymer Materials*, 2021b

This approach can also be used to measure the thermal conductivity of liquids

water



ethanol



Yeon, unpublished

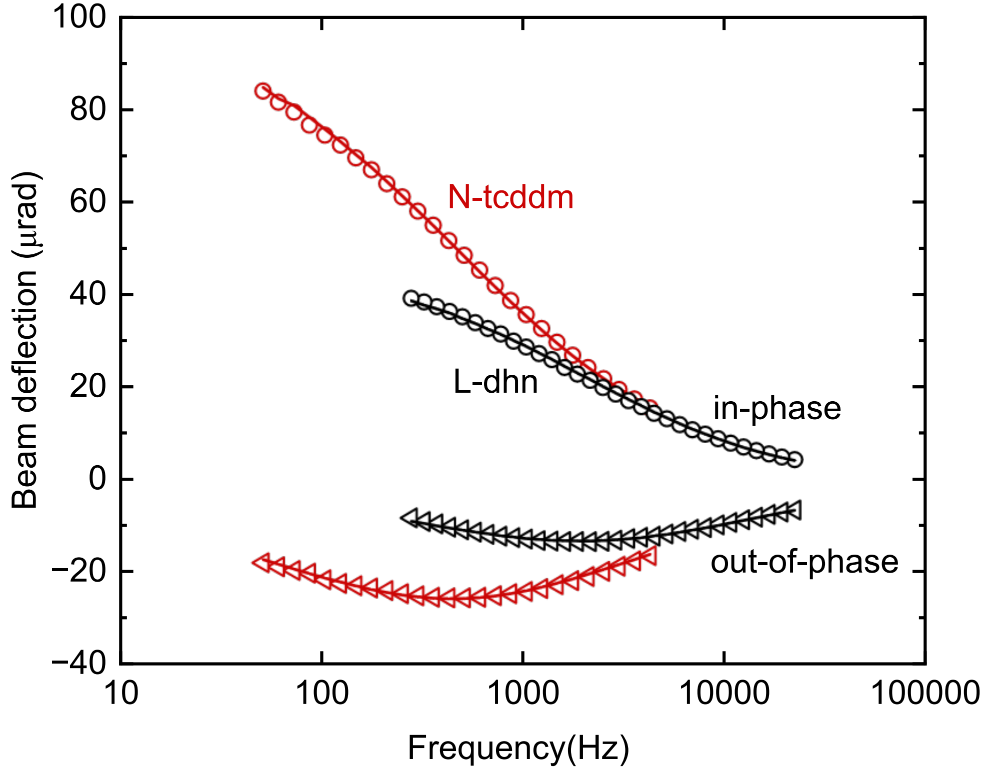
We now exclusively use D-TOPS in our studies of bulk polymers, combined with TDTR when possible

Measure deflection as a function of frequency and compare to quantitative model of the thermoelastic response of a multilayer sample.

That model is complex in general but in most cases can be simplified to an isotropic model

The frequency response gives the in-plane thermal diffusivity, and the amplitude of the response gives the coefficient of thermal expansion (CTE).

Example data and model fits for two polyesters with high and low thermal conductivity



Sun, Lv, Cahill, RSI (2003); Chowdhury et al., unpublished

Isotropic CTE and elastic constants + anisotropic thermal conductivity

$$\tilde{\tilde{\bar{Z}}}_{iso-free}(k,\omega) = \frac{\alpha_T(3\lambda + 2\ \mu)/(\lambda + 2\ \mu)}{1 - v_T^2/v_L^2}\frac{\tilde{\tilde{\bar{T}}}_{bs}}{k+\zeta} = 2(1+\nu)\alpha_T\frac{T_{bs}}{k+\zeta},$$

$$\zeta = \left(\frac{\Lambda_r}{\Lambda_z}k^2 + \frac{i\omega C}{\Lambda_z}\right)^{1/2}$$

$T_{bs}(k,\omega)$ is the surface temperature

$$\tilde{\theta}_{iso-free}(r_0,\omega) = \frac{C_{probe}}{\pi}\int_0^{+\infty}\tilde{\tilde{\bar{Z}}}_{iso-free}(k,\omega)e^{-w_0^2k^2/8}(-J_1(kr_0))k^2dk,$$

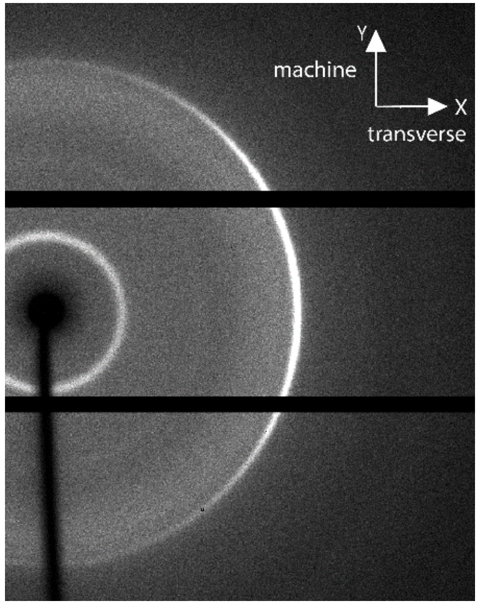
Sun, Lv, Cahill, RSI (2003)

Analysis of data for laminated Kapton films requires the more complex anisotropic model due to in-plane anisotropy

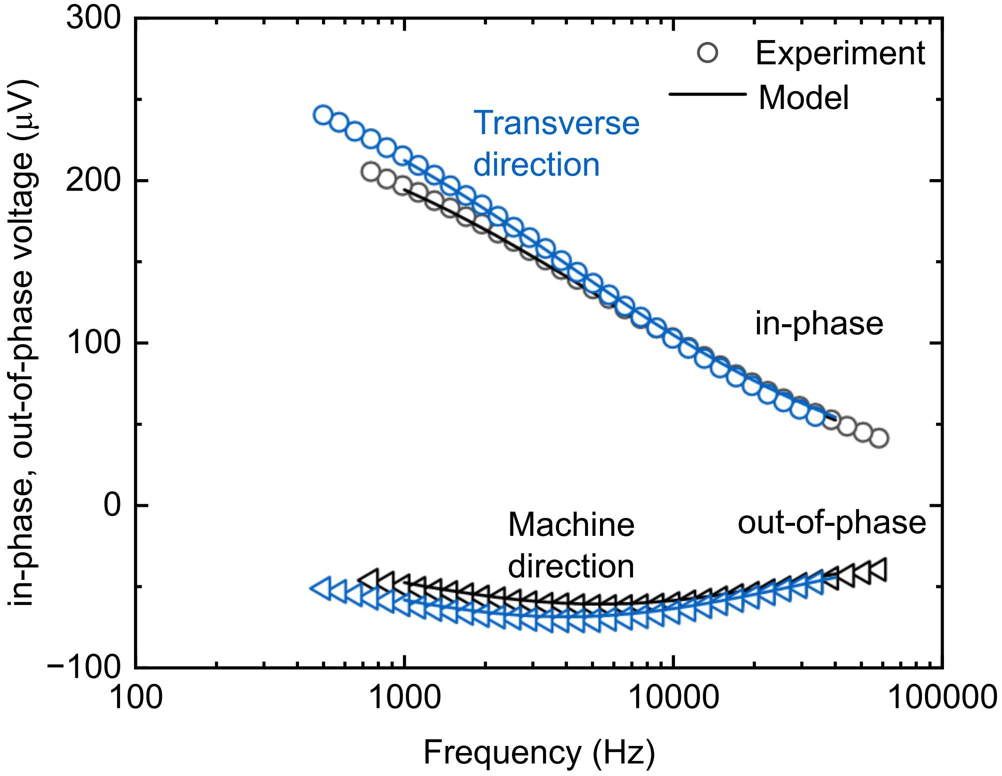
Kapton FN is a laminate (sandwich) of polyimide as the “meat” (25 μm) and fluorinated ethylene propylene as the “bread” (12.5 μm)

WAXS data

0.24 W/(m K)



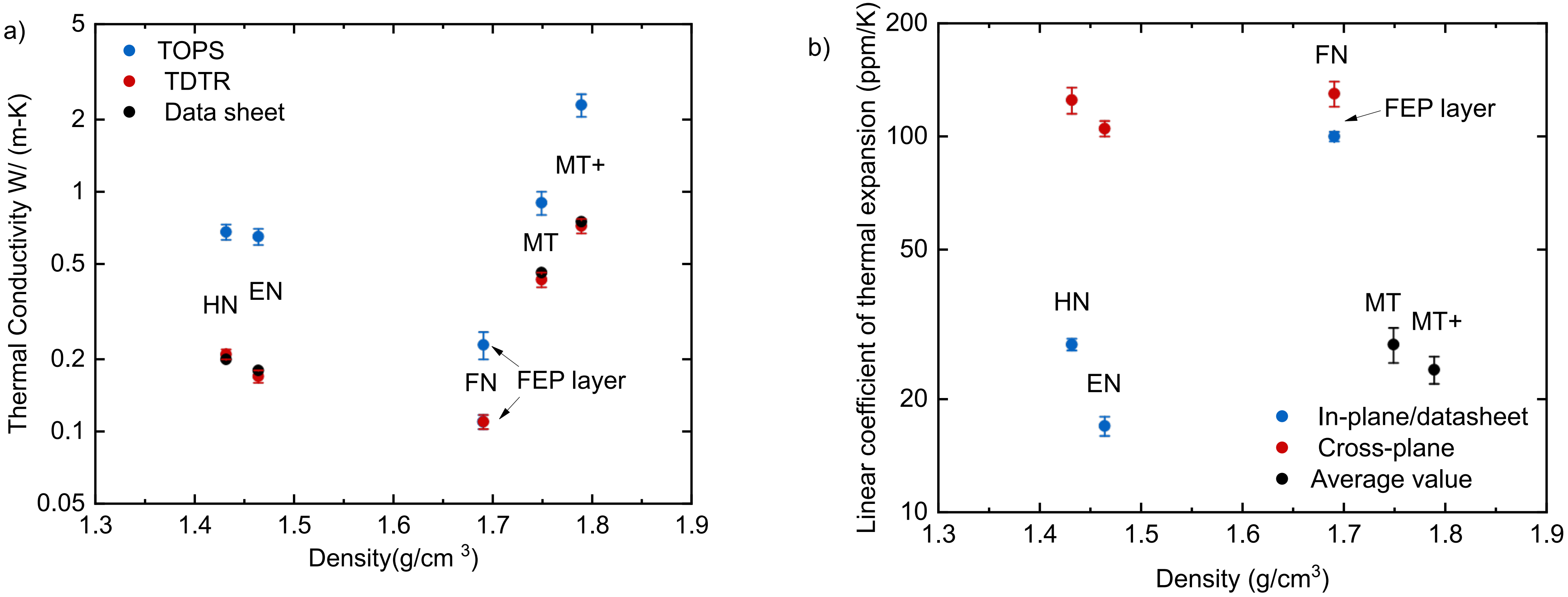
0.11 W/(m K)



Chowdhury et al., submitted

We use a standard reference (usually CaF_2) to calibrate the absorbed pump power and amplitude of beam deflection to determine CTE

Thermal conductivity and CTE of several varieties of Kapton films, laminates and composites



Chowdhury et al., submitted

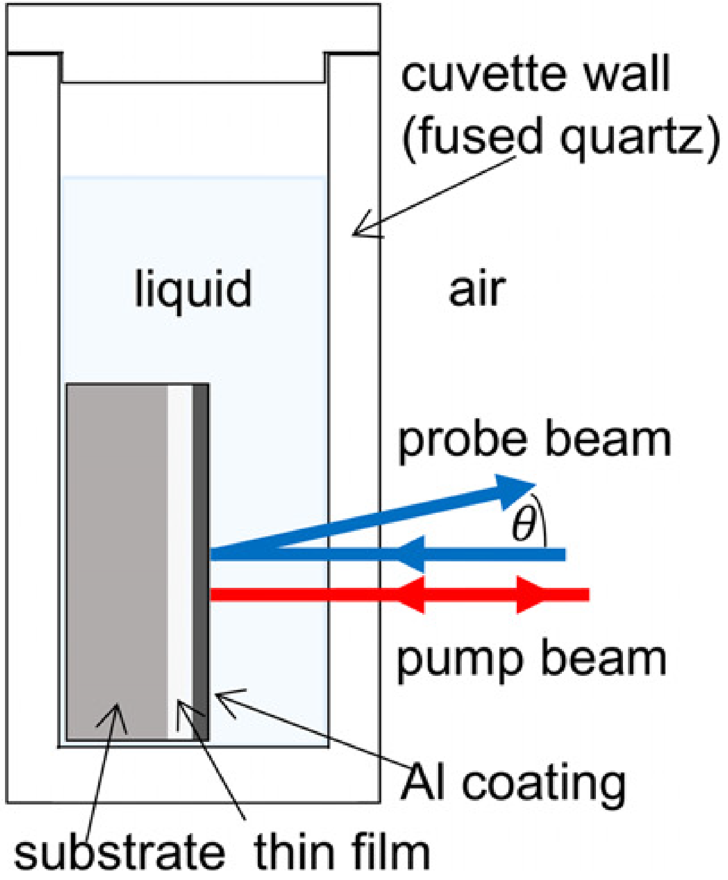
We also use I-TOPS in the more conventional geometry where the transparent medium is the temperature sensor

Useful for multilayer materials or assemblies where the thermoelastic displacement is too complicated to model quantitatively for D-TOPS.

Introduces sensitivity to conduction in the through-thickness direction.

Instead of gas typically used in the mirage effect, we use a liquid or elastomer with a large thermo-optic coefficient.

Philosophy of the approach is similar to steady-state thermoreflectance (SSTR) with the thermometry coming from beam deflection instead of intensity.



Sun et al., APL (2024)

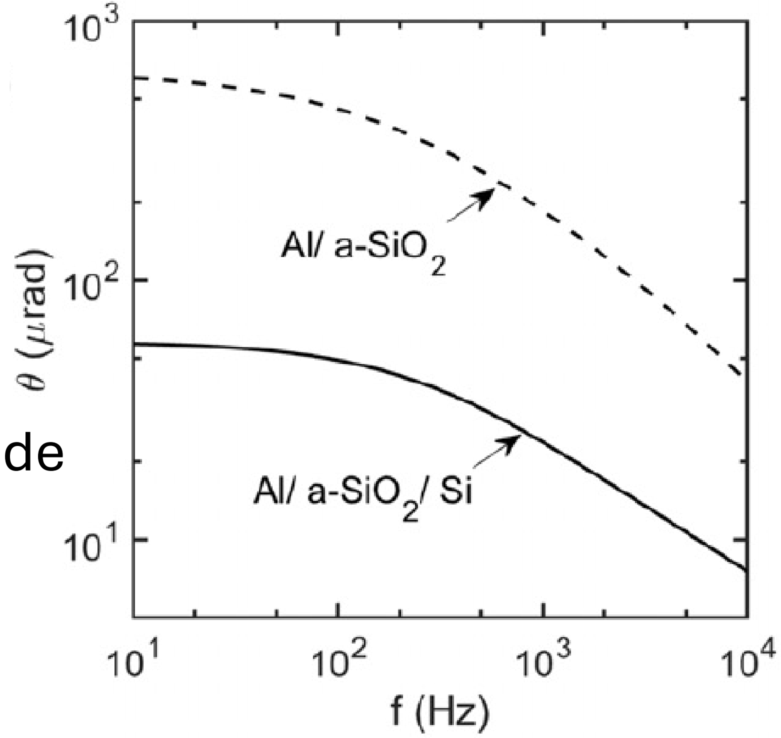
Calculated amplitude of temperature excursions and beam deflection signals test samples using 2 mW pump power, spot size and beam offset ≈10 μm

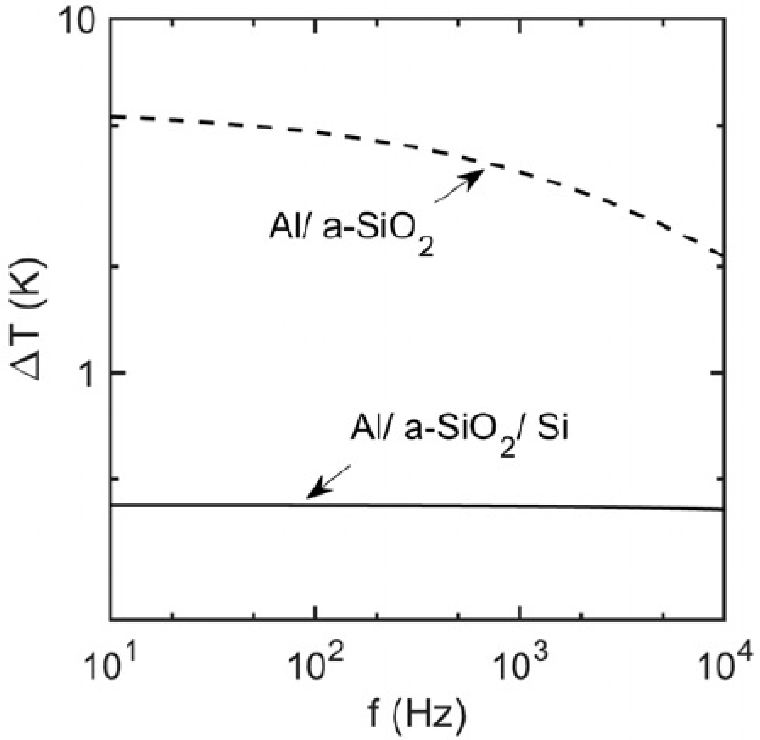
Liquid used for detection is a fluorinated “dielectric fluid” NOVEC

(No longer available due to concerns about “forever chemicals”, i.e., PFAS)

bulk a-SiO_2

300 nm thermal oxide





Sun et al., APL (2024)

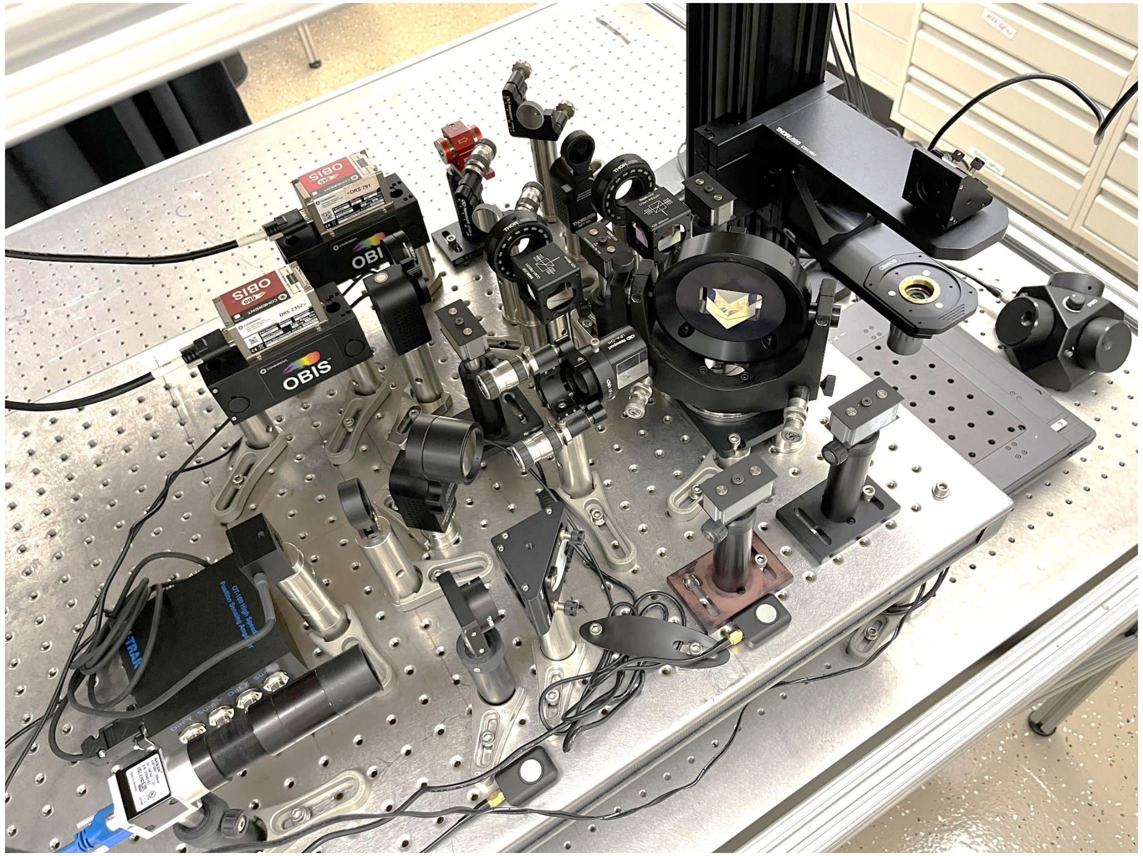
Initial mapping study of SiC (≈1 μm thick) bonded to diamond using lock-in time constant of 3 ms

Sun et al., APL (2024)

We recently completed a new system dedicated to mapping using I–TOPS with large spot size (large probing depth) and horizontal sample

The large beam-deflection signal could accelerate mapping of thermal conductance in comparison to thermoreflectance methods.

Will eventually need to enclose the system to reduce noise created by air turbulence at low frequencies.



Research questions for further development of D-TOPS and I-TOPS

What are the systematic errors created by diffuse reflectance and how can we minimize those errors?

How can we reduce the systematic errors in measurement of coefficient of thermal expansion (CTE)?

Use of low coherence light sources (superluminescent diodes) improved the precision. What other changes to the measurement approach can further improve precision?

Accuracy is often limited by uncertainty in the volumetric heat capacity. How can we do that measurement better than DSC?

What are the limits to the probing depth (spot size and modulation frequency) that we can achieve in I-TOPS?