SCHOOL of ENGINEERING & APPLIED SCIENCE
UNIVERSITY of VIRGINIA

Vacancy and interface effects on phonon thermal transport in oxide nanostructures

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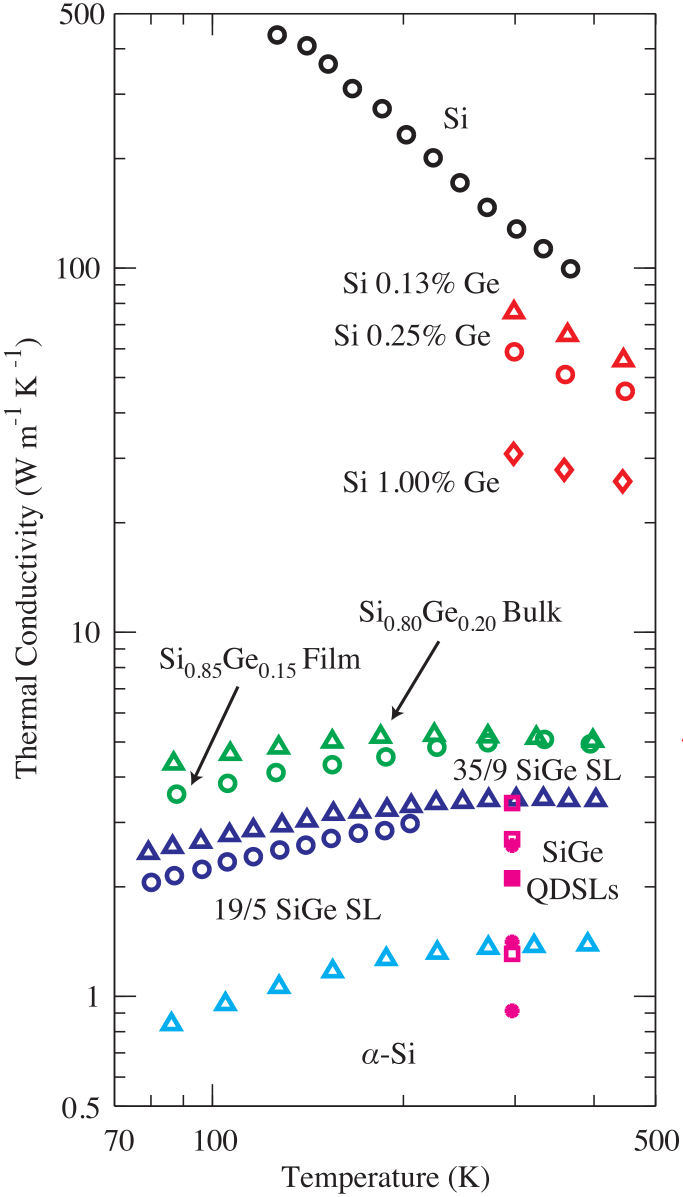
Defect and interface effects on thermal conductivity



PRL 109, 195901

$$\kappa = \frac{1}{3}Cv\lambda = \frac{1}{3}Cv_g^2\tau$$

$$\tau = f\left(\tau_{\text{intrinsic}}, \tau_{\text{impurity}}, \tau_{\text{boundary}}\right)$$

Dilute alloy

Alloy

Interface

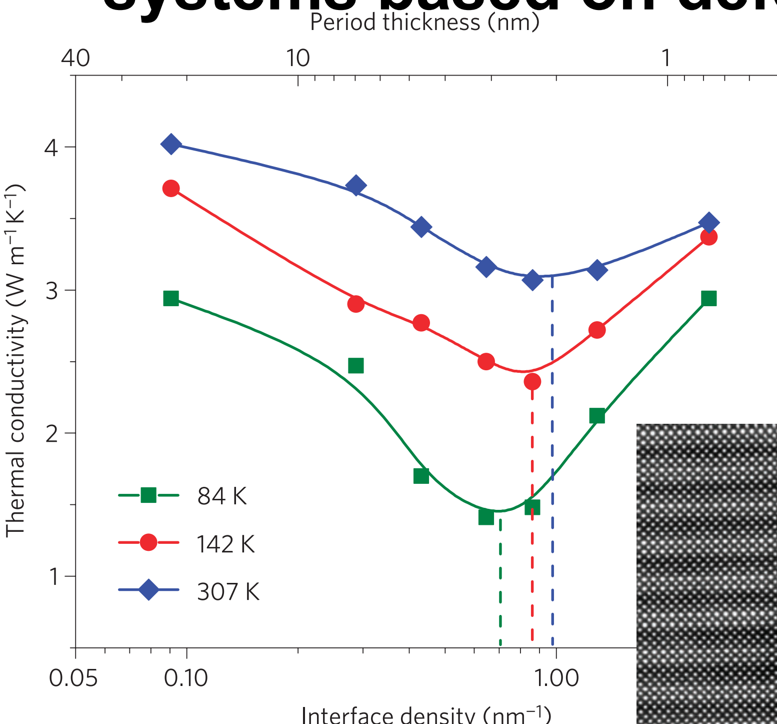
Disorder/ amorphous

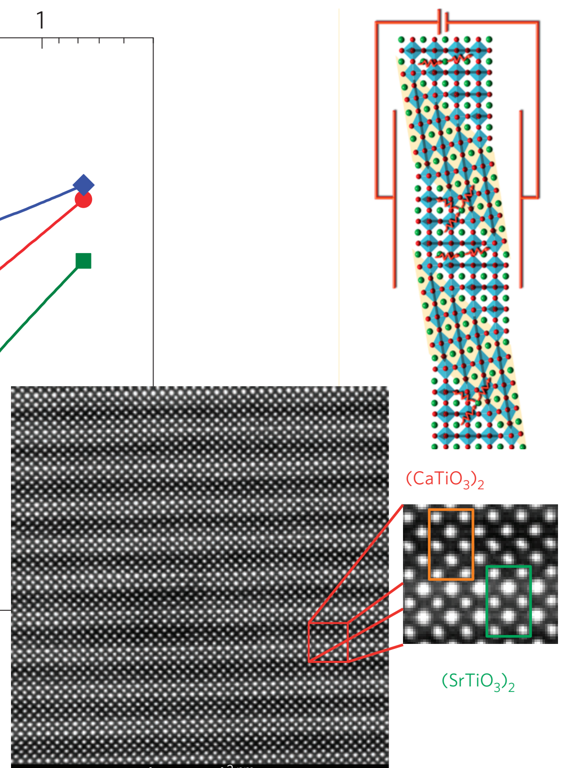
Increasing disorder decreases phonon thermal conductivity in Si

Typically lower limit in disordered/amorphous systems

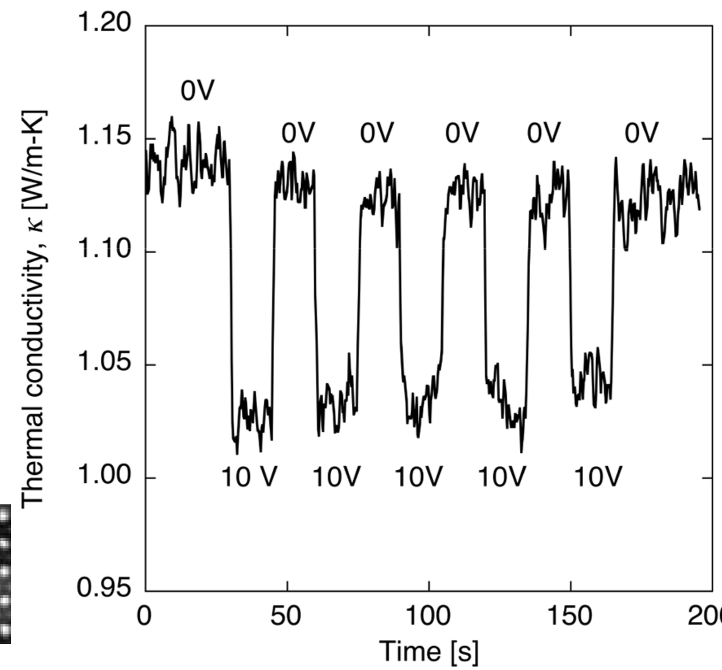
Question

- At room temperature, over 2 orders of magnitude in intricate tunability in κ in silicon based on disorder/interfaces/ nanostructuring
- **What is the range and precision in tuning κ in oxide systems based on defects and interfaces?**





Nat. Mat. **13** 168
Student: Ramez Cheaito
Collaboration: J. Ravichandran (USC), R. Ramesh (Berkeley), D. Schlom (Cornell)



Nano Lett. **15** 1791
Student: Brian Foley
Collaboration: J. Ihlefeld (SNL), S. Trolier-McKinstry (PSU)

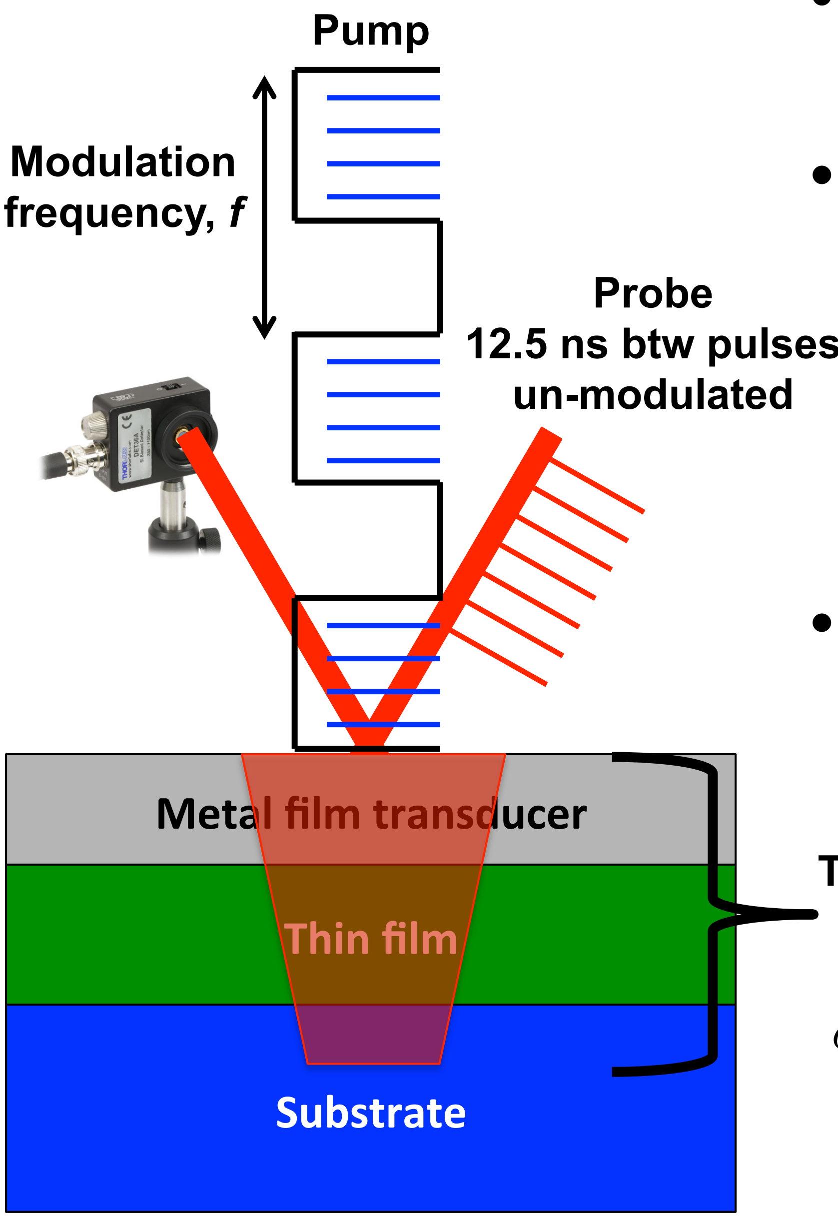
Outline – Can we achieve this level of control in oxides?

- Thermal property measurements in thin films and nanosystems: Time domain thermoreflectance (TDTR)

- Impurity effects on thermal conductivity of oxides
    - Vacancy scattering vs. electron transport in doped CdO
    - Beating the amorphous limit to κ in TiO_2 with molecular layers
    - What modes scatter and carry the heat at interfaces?

- Advances in thermoreflectance techniques via frequency modulation
    - Depth profiling and measuring buried interfaces
    - Alloy effects on thermal boundary conductance across $CaTiO_3/Ca_{0.5}Sr_{0.5}TiO_3/SrTiO_3$ interfaces

Time domain thermoreflectance (TDTR)



- Pump-probe technique
- Sub-picosecond transient resolution via pulse (rule of thumb: 100 ps for heat to diffuse across 100 nm Al film)
- Frequency-dependent heating event via the modulation of multiple pulses

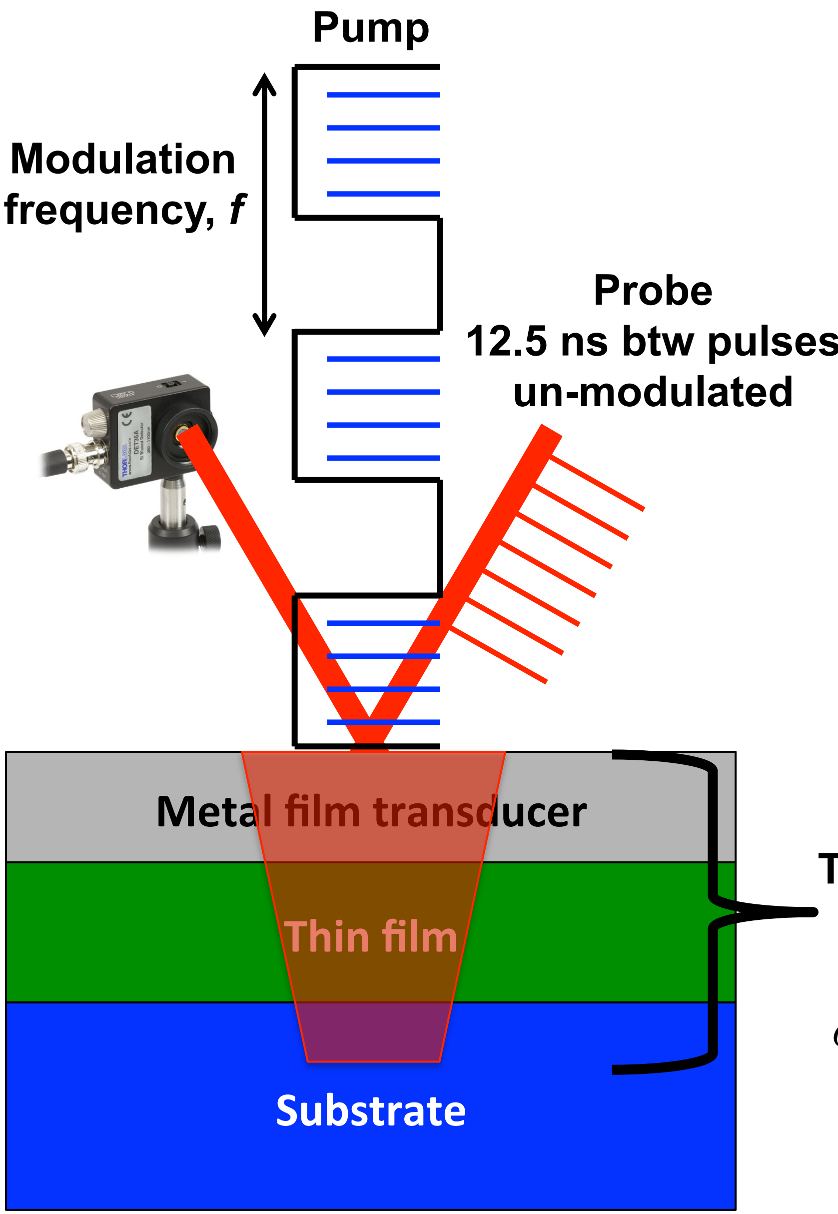
Thermal penetration depth
"Measurement volume"

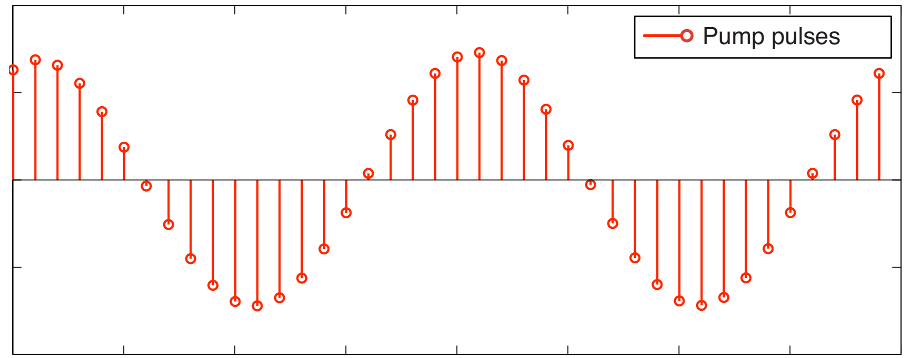
$$\delta_{\text{thermal}} = \sqrt{\frac{\kappa}{\pi C f}}$$

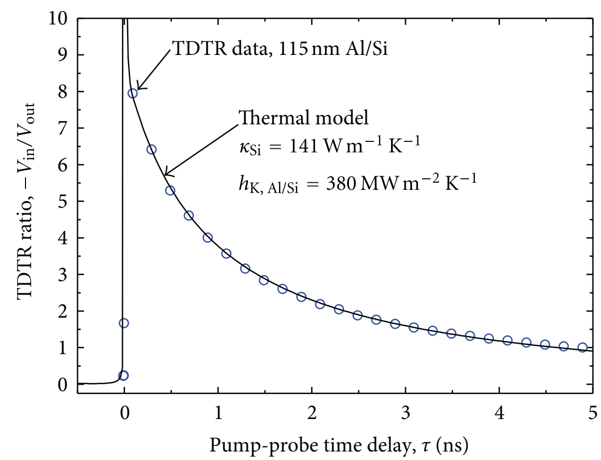
TDTR Reviews and Analyses

Rev. Sci. Instr. **75**, 5119
Rev. Sci. Instr. **79**, 114902
J. Heat Trans. **132**, 081302
Ann. Rev. Heat Trans. **16**, 159

Time domain thermoreflectance (TDTR)







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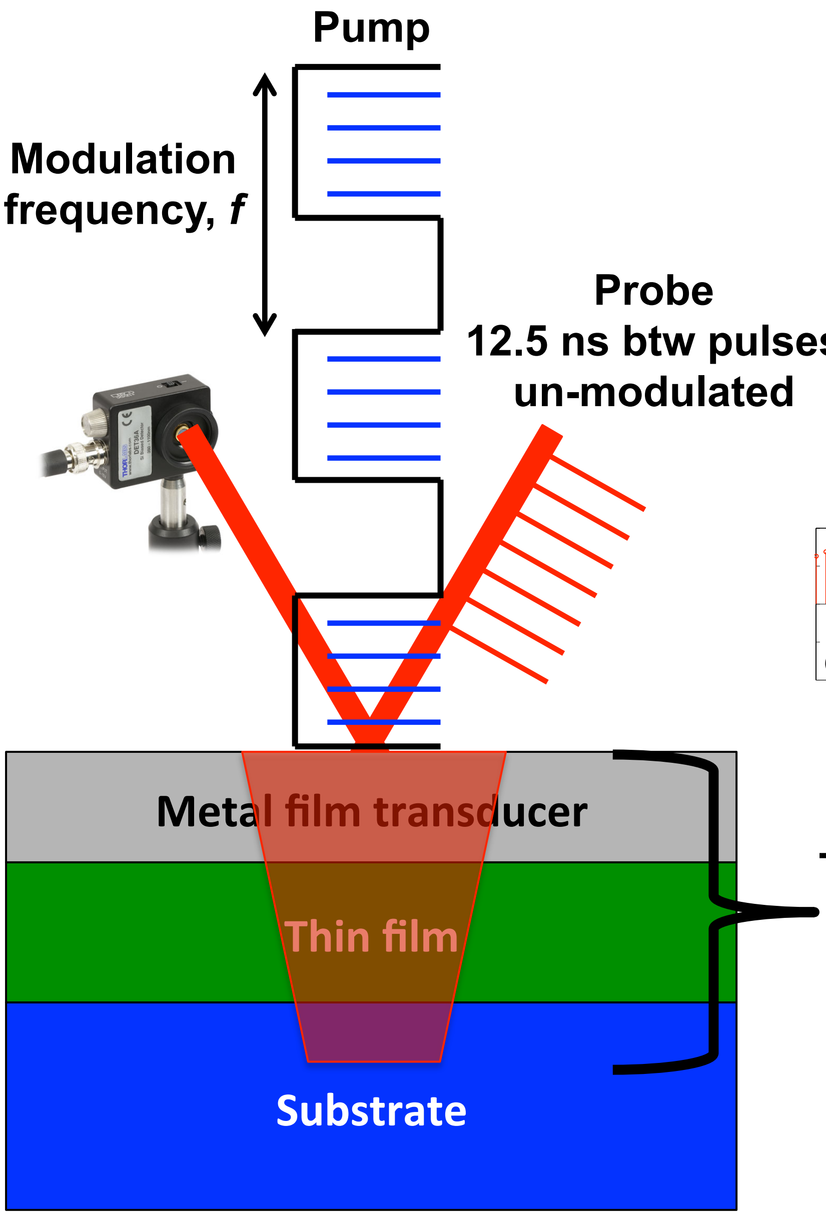

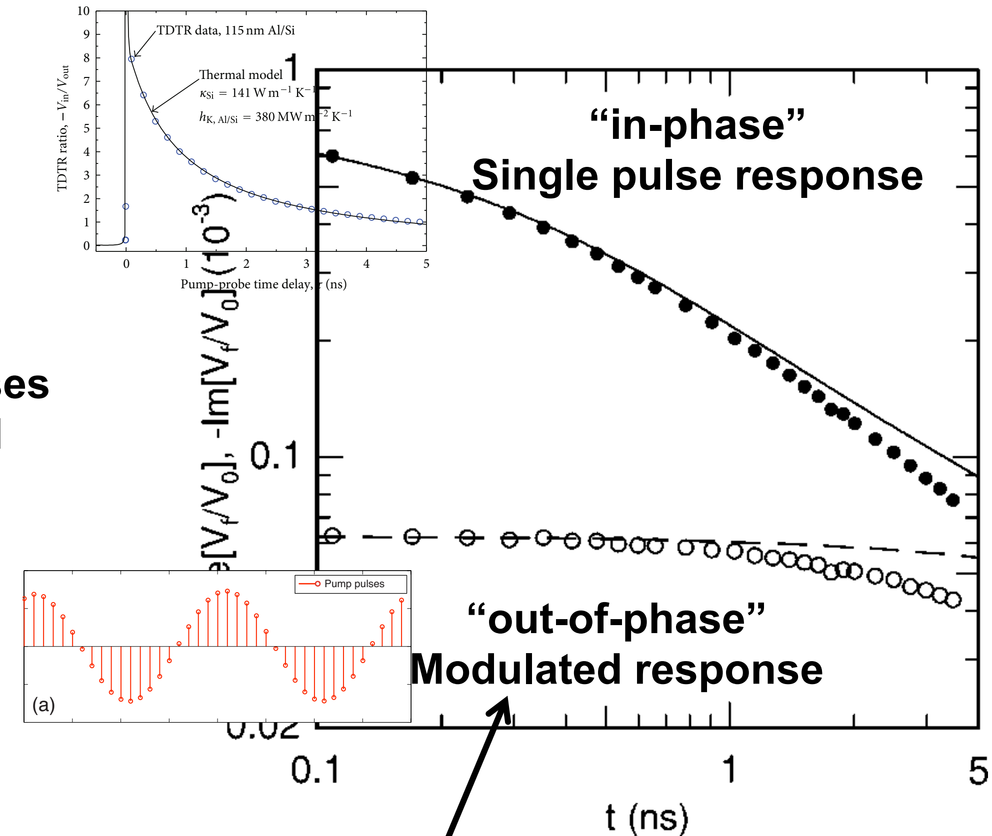

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Rev. Sci. Instr. **79**, 114902

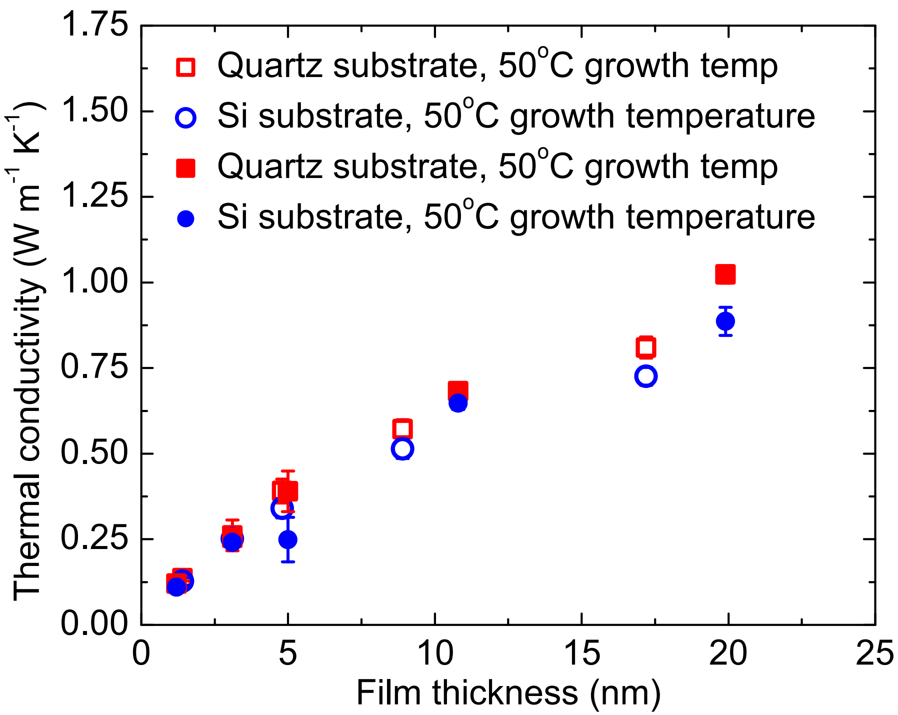
J. Heat Trans. **132**, 081302

Ann. Rev. Heat Trans. **16**, 159

Time domain thermoreflectance (TDTR)

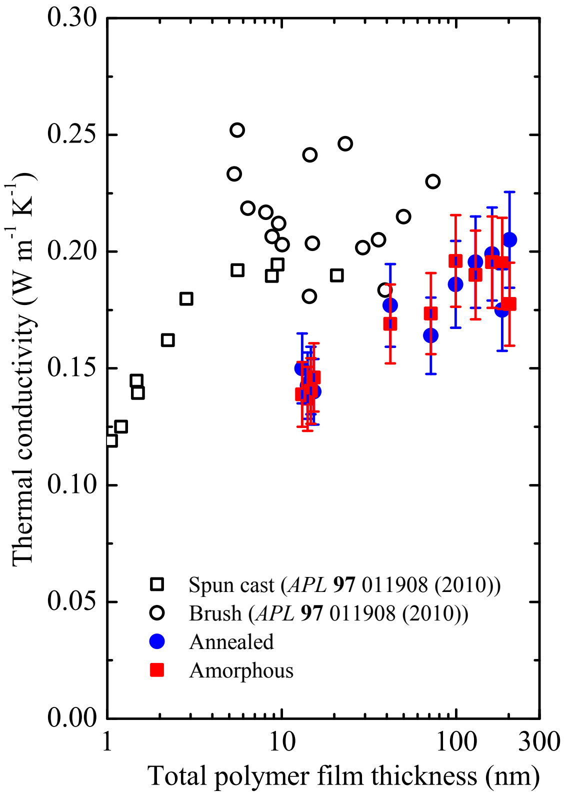
Can measure thermal resistance of thin films

Thermal conductivity of amorphous Al_2O_3 films down to <5nm



APL **104** 253107
Student: Kelsey Meyer
Collaboration: M. Losego (Ga. Tech)

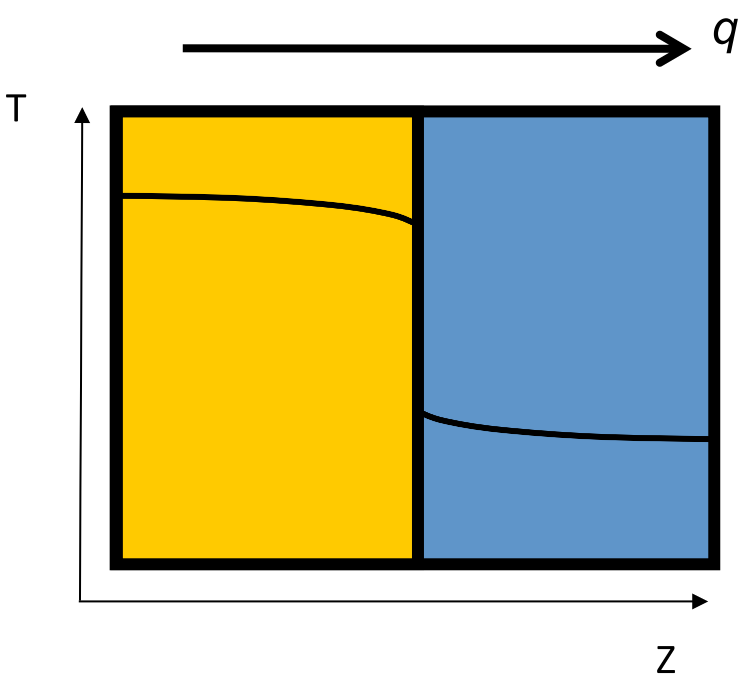
Single to multi-layers of block-co-copolymer thin films



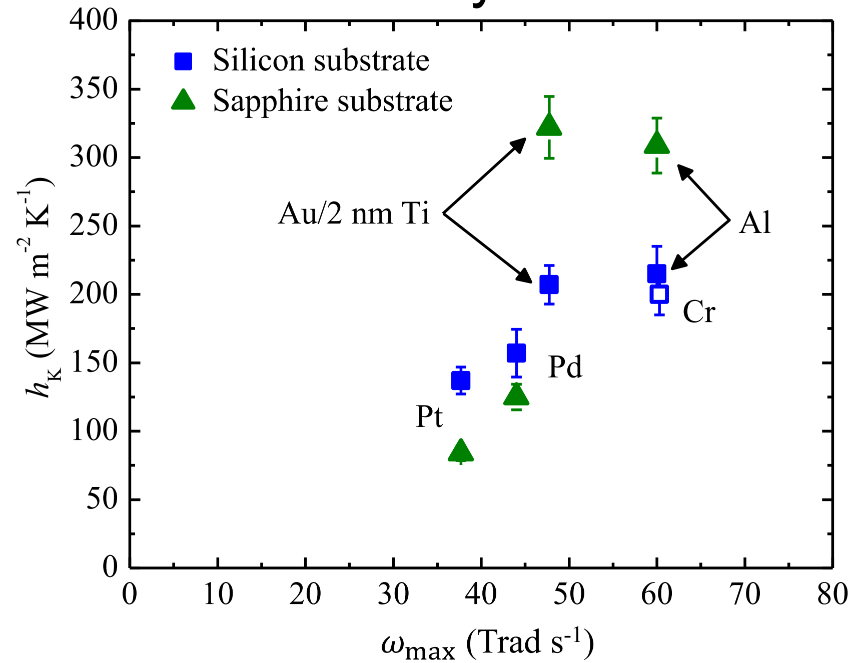
J. Heat Trans. **138** 024505
Collaboration: G. Brennecka (Mines)

Time domain thermoreflectance (TDTR)

Can measure thermal resistance of thin films and thermal boundary conductance across interfaces



Spectral phonon transmission across interfaces and role on thermal boundary conductance



PRB **91** 035432

Student: Ramez Cheaito

Collaboration: J. Ihlefeld

Outline

•Thermal property measurements in thin films and nanosystems: Time domain thermoreflectance (TDTR)

•Impurity effects on thermal conductivity of oxides

- •Vacancy scattering vs. electron transport in doped CdO
- •Beating the amorphous limit to κ in TiO_2 with molecular layers
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•Advances in thermoreflectance techniques via frequency modulation

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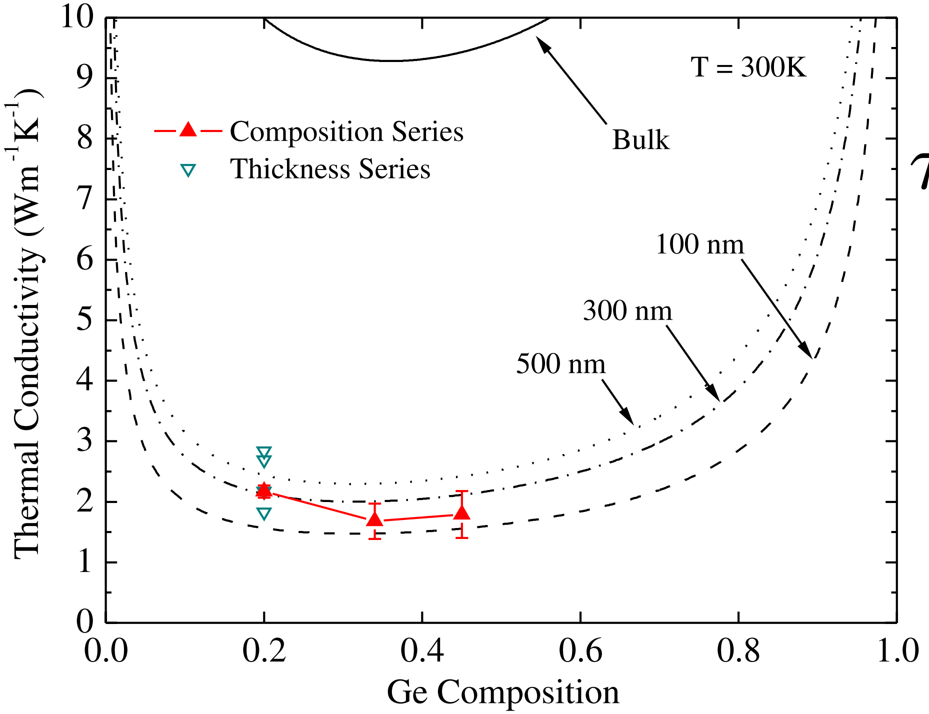
Mass-impurity scattering….what about vacancies??

•Phonon scattering with mass impurities (such as dopants) causes a reduction in phonon thermal conductivity

Example: Thermal conductivity of $Si_{1-x}Ge_x$ films



PRL **109** 195901
Student: Ramez Cheaito
Collaboration: J. Ihlefeld (SNL)

$$\kappa = \frac{1}{3}Cv\lambda = \frac{1}{3}Cv_g^2\tau$$

$$\tau^{-1} \propto \tau^{-1}_{\text{mass impurity}} \propto \Delta M$$

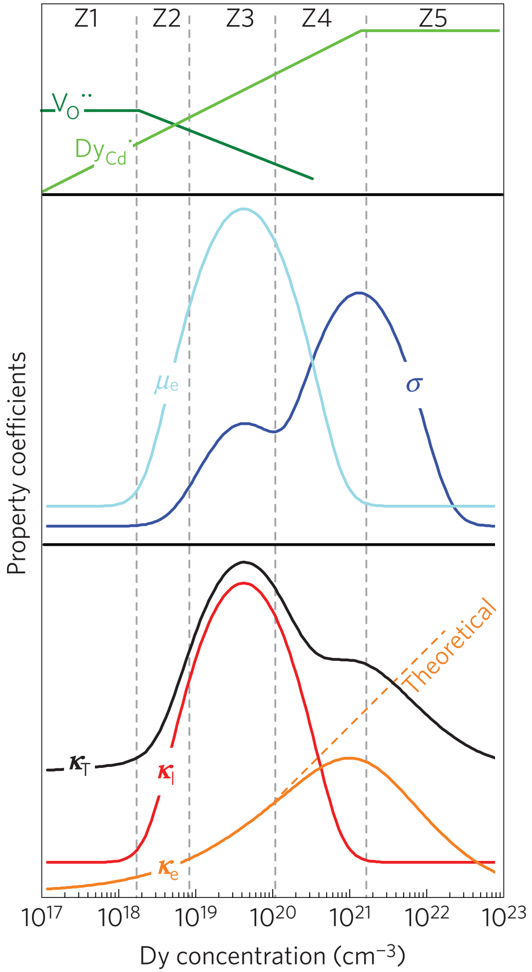
Very rigorously vetted over time

What about phonon-vacancy scattering? Not nearly as vetted

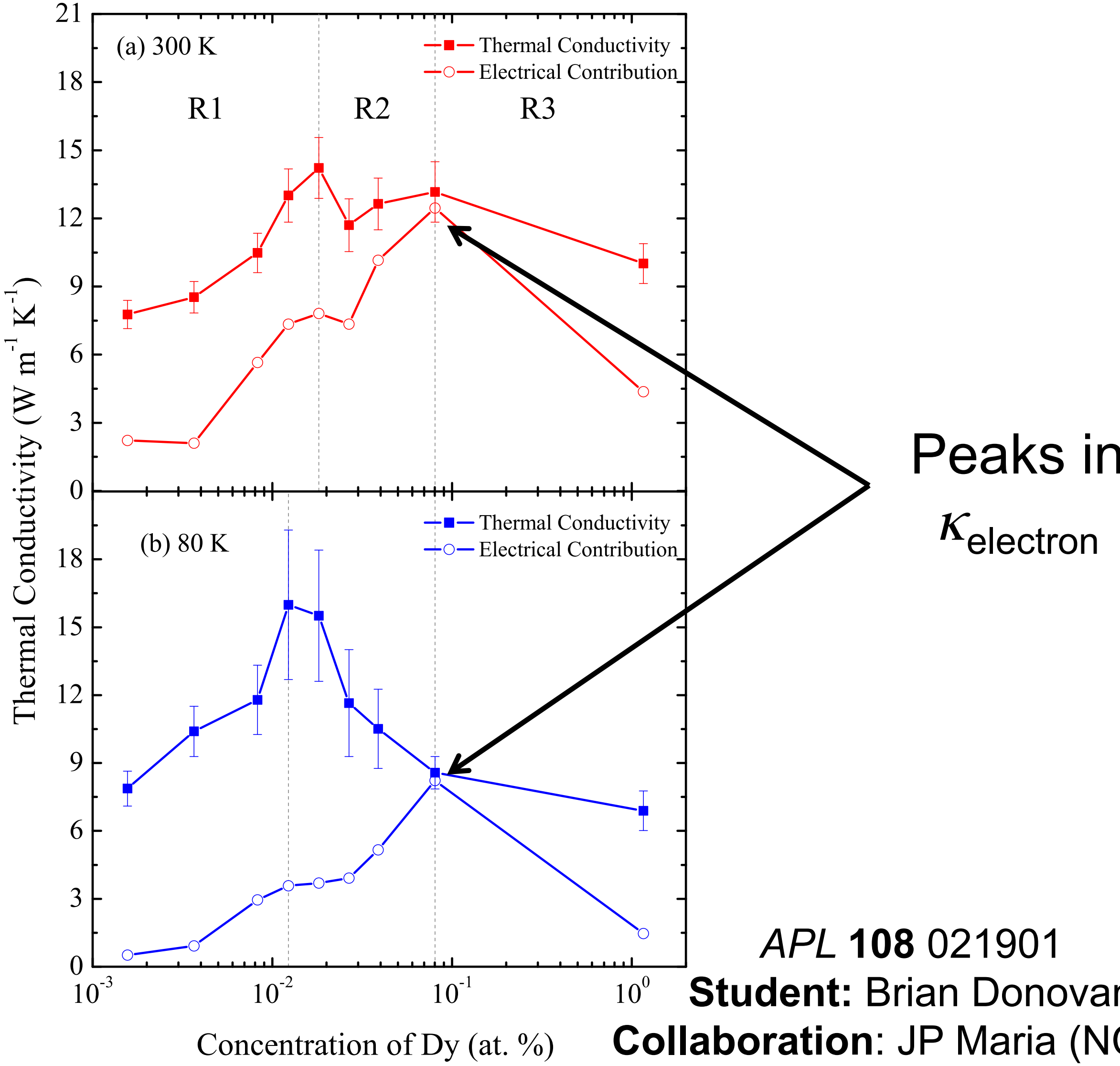
$$\tau^{-1}_{\text{vacancy}} \propto -\frac{M_{absent\,atom}}{M} - 2$$

Vacancy effects on the thermal conductivity of CdO

•Lower temperature changes relative contribution of electron thermal conductivity and phonon-impurity scattering

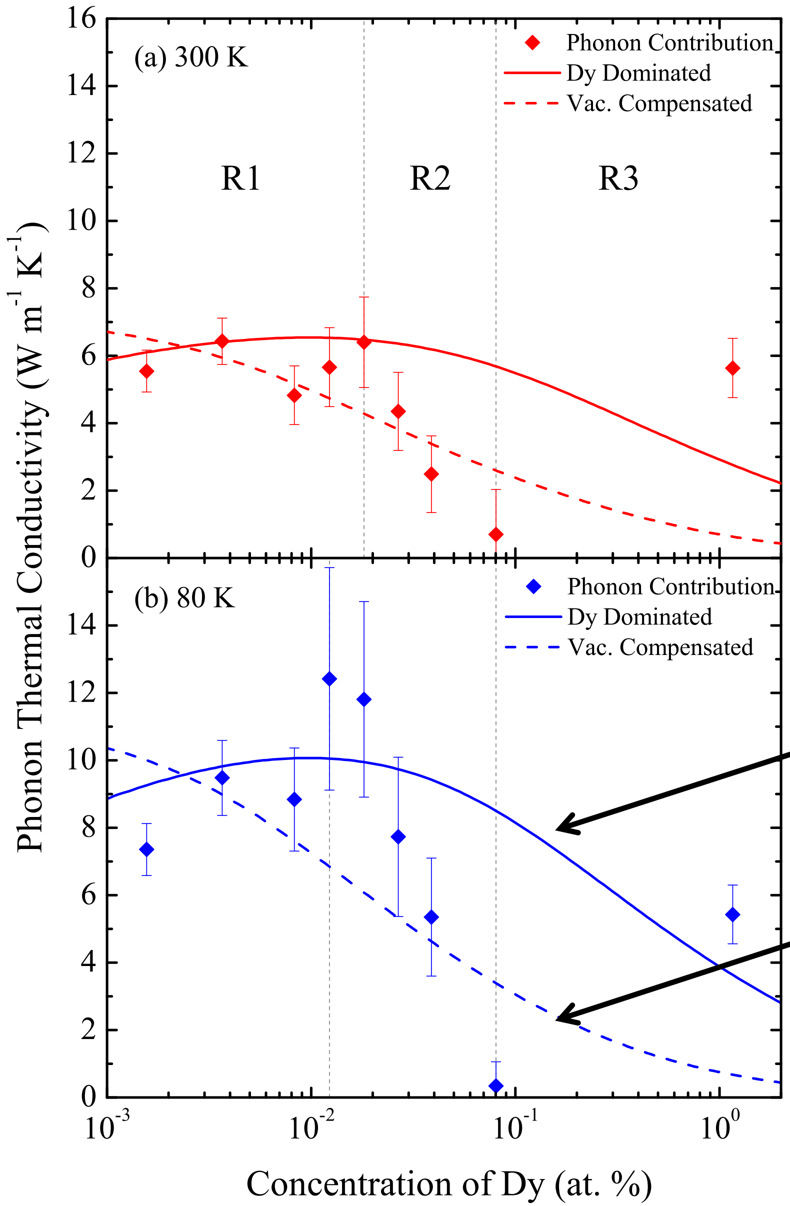


Nat. Mat. **14** 414
Student: Brian Donovan
Collaboration: JP Maria (NCSU)



APL **108** 021901
Student: Brian Donovan
Collaboration: JP Maria (NCSU)

Vacancy effects on the thermal conductivity of CdO



- Cation vacancies responsible for majority of phonon scattering and reduction in thermal conductivity in "Region 2"

$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

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APL **108** 021901
Student: Brian Donovan
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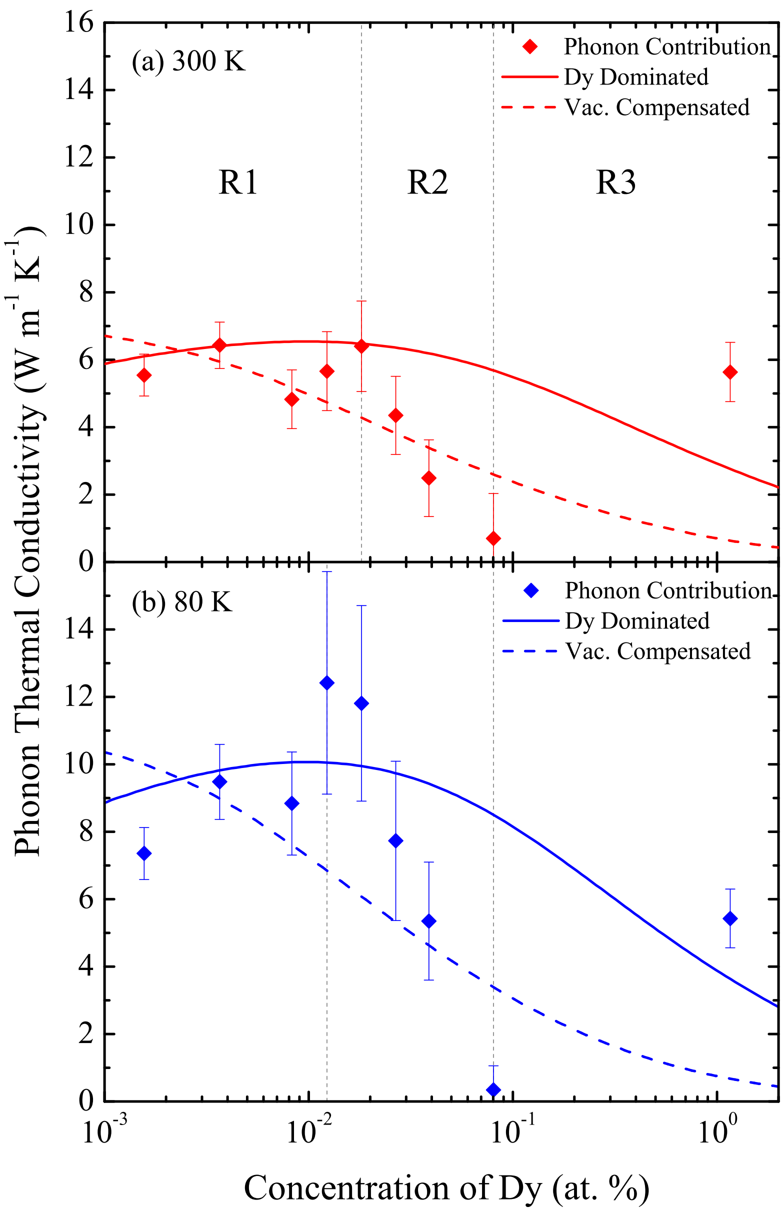
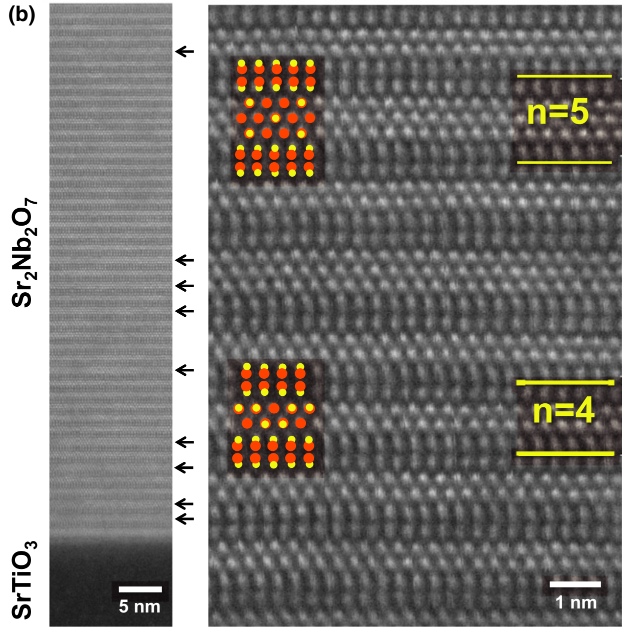


- Cation vacancies responsible for majority of phonon scattering and reduction in thermal conductivity in “Region 2”
- Can achieve very low phonon thermal conductivity with disorder
- How much more can we push it?.......turn to interfaces!

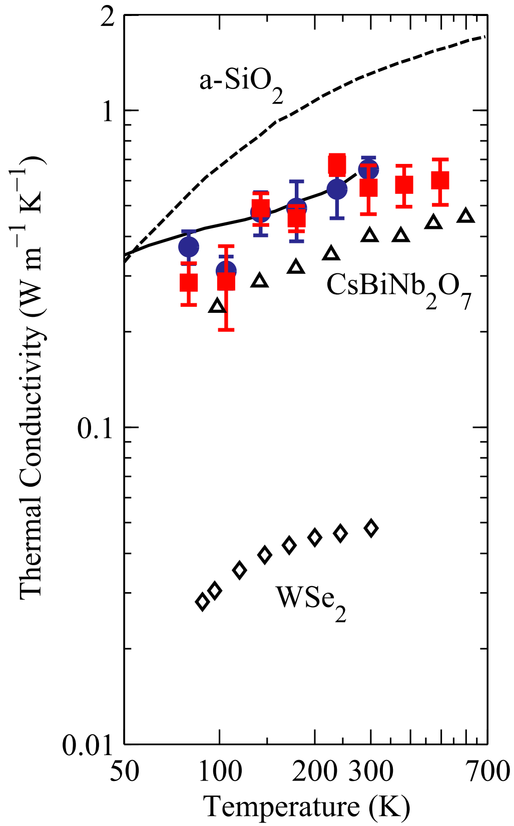
APL **108** 021901
Student: Brian Donovan
Collaboration: JP Maria (NCSU)

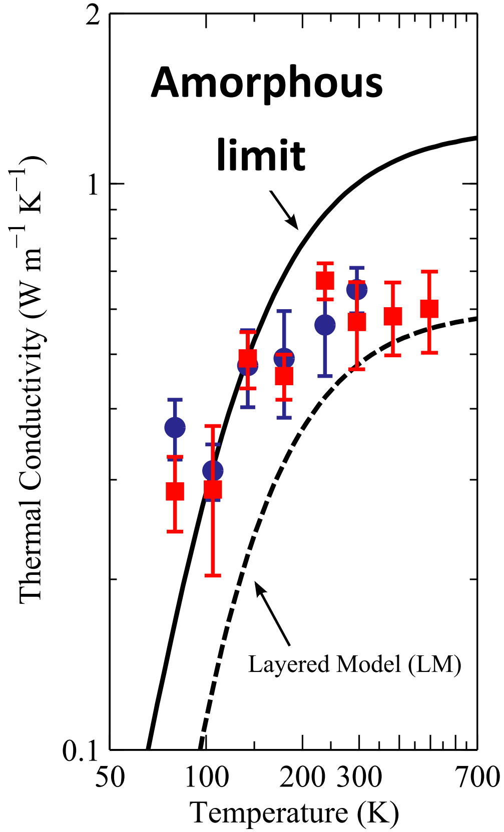
Low phonon thermal conductivities with interfaces

- Don't necessarily need crystalline disorder/dopants/impurities to reduce the thermal conductivity
- Interfaces will reduce phonon transport via phonon-boundary scattering and thermal boundary resistances
- Previously reported in superlattices and layered crystals

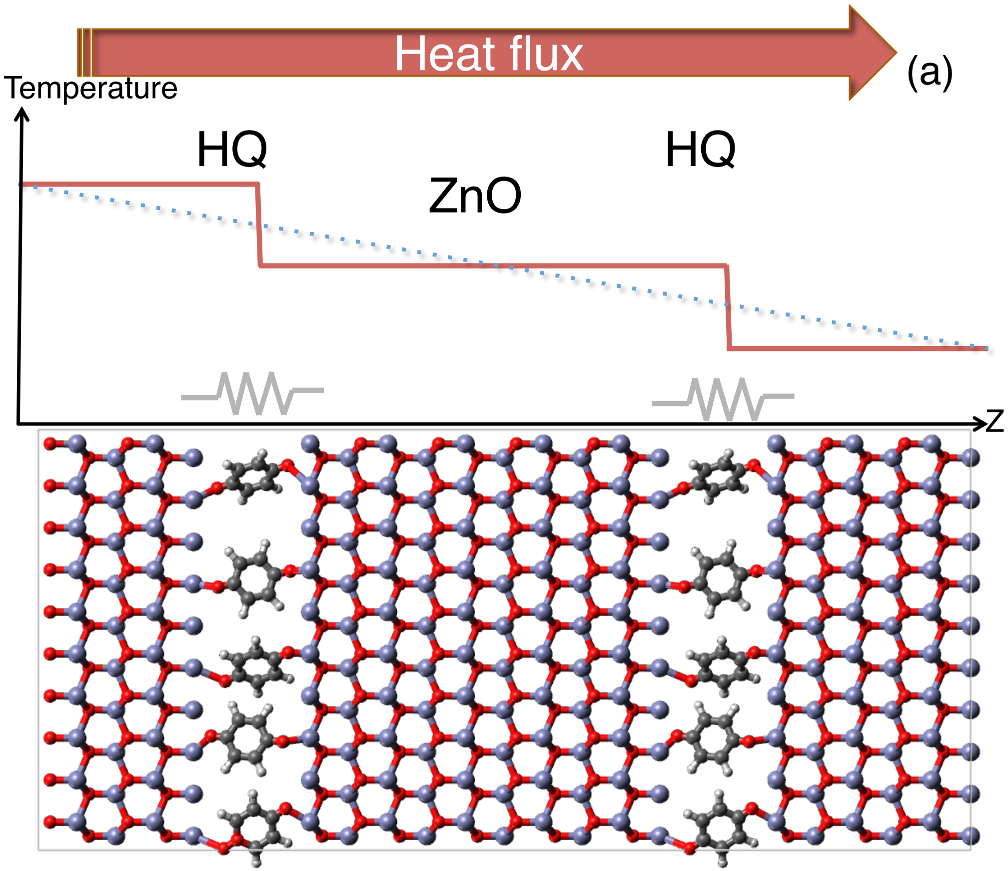


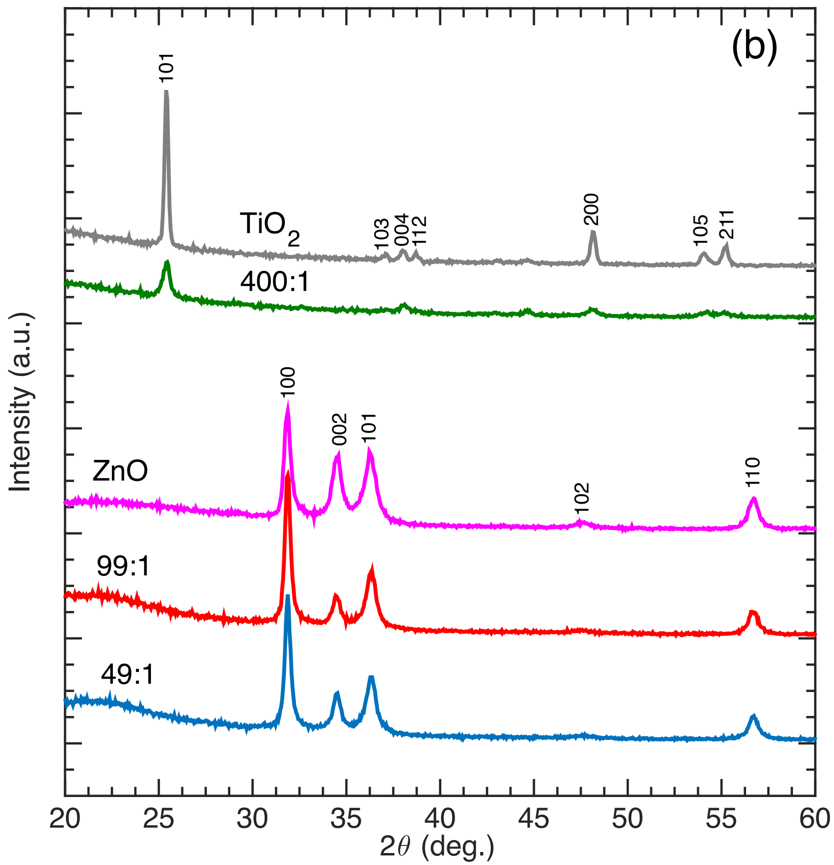
JACerS **98** 624
Student: Brian Foley
Collaboration: J. Ihlefeld (SNL)





Combined ALD/MLD to reduce κ in oxides

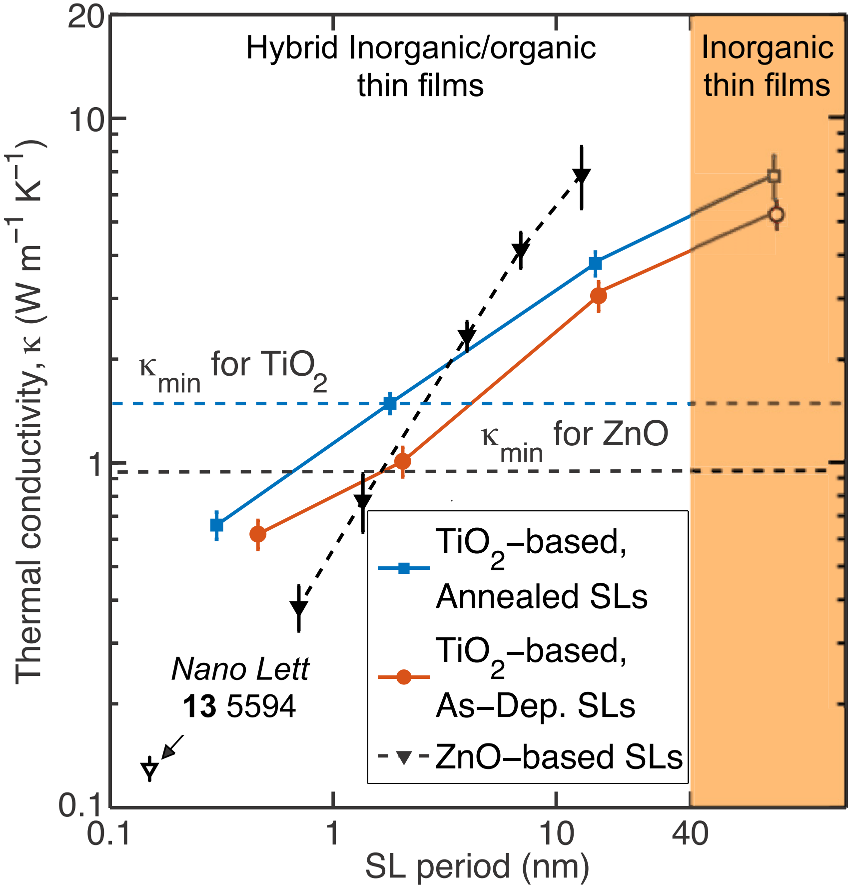


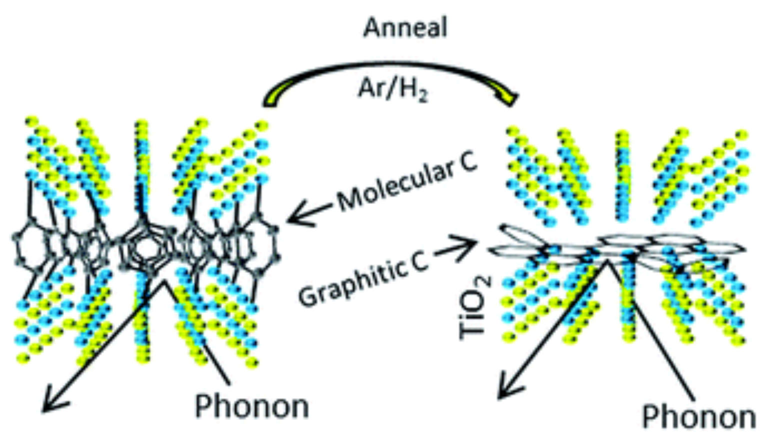


PRB **93** 024201
J. Mat. Chem. A **3**, 11527
J. Mat. Chem. A **2**, 12150
Student: Ashutosh Giri
Collaboration: M. Karppinen (Aalto)

Combined ALD/MLD to reduce κ in oxides

- Phonon scattering at organic/inorganic interface can lead crystalline composites achieving κ less than amorphous phase





- Reductions due to the thermal boundary resistance across organic/inorganic interfaces

PRB **93** 024201
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J. Mat. Chem. A **2**, 12150
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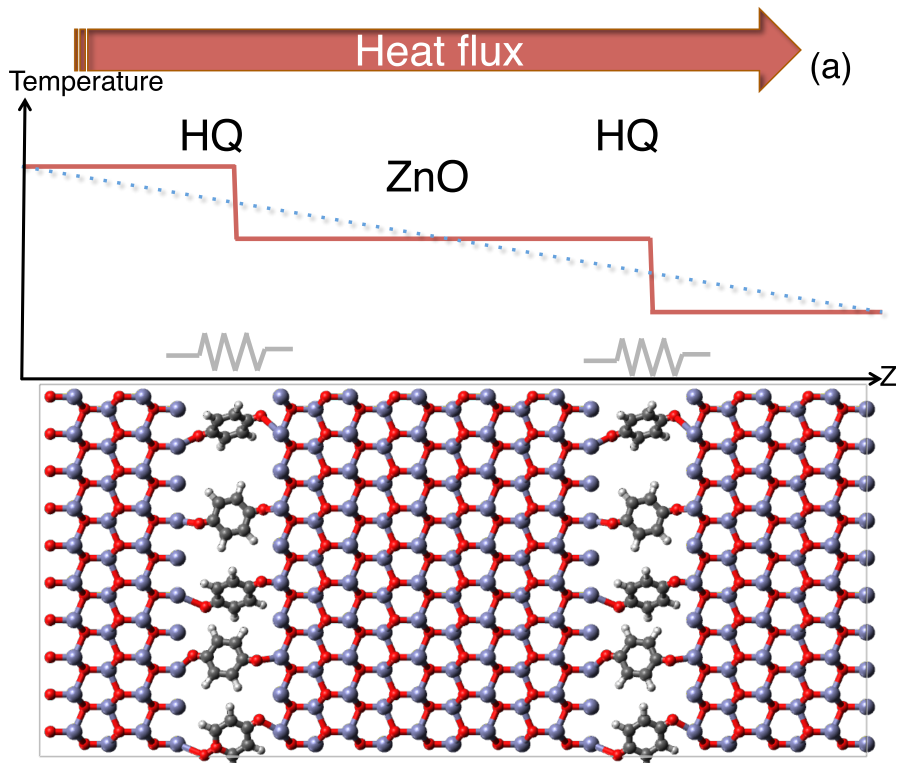

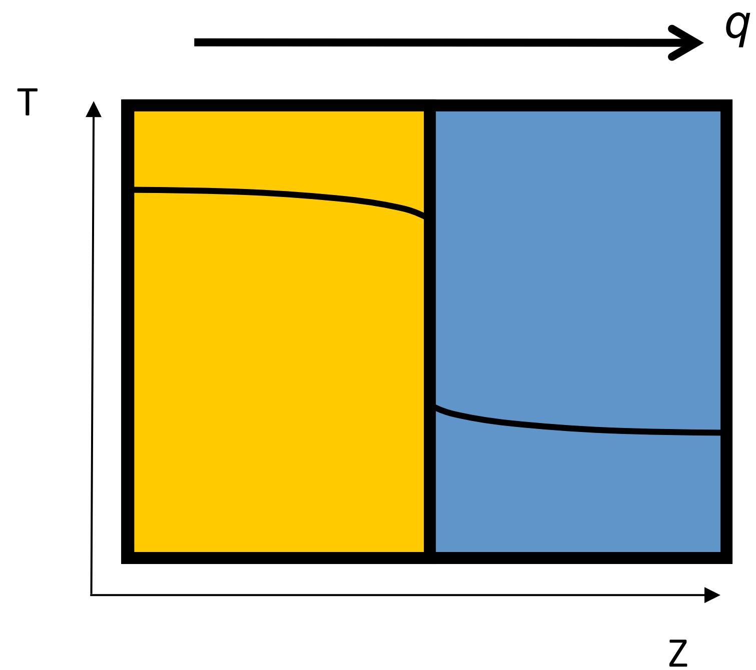

$$q = h_K \Delta T = \frac{1}{R_K} \Delta T$$

PRB **93** 024201
J. Mat. Chem. A **3**, 11527
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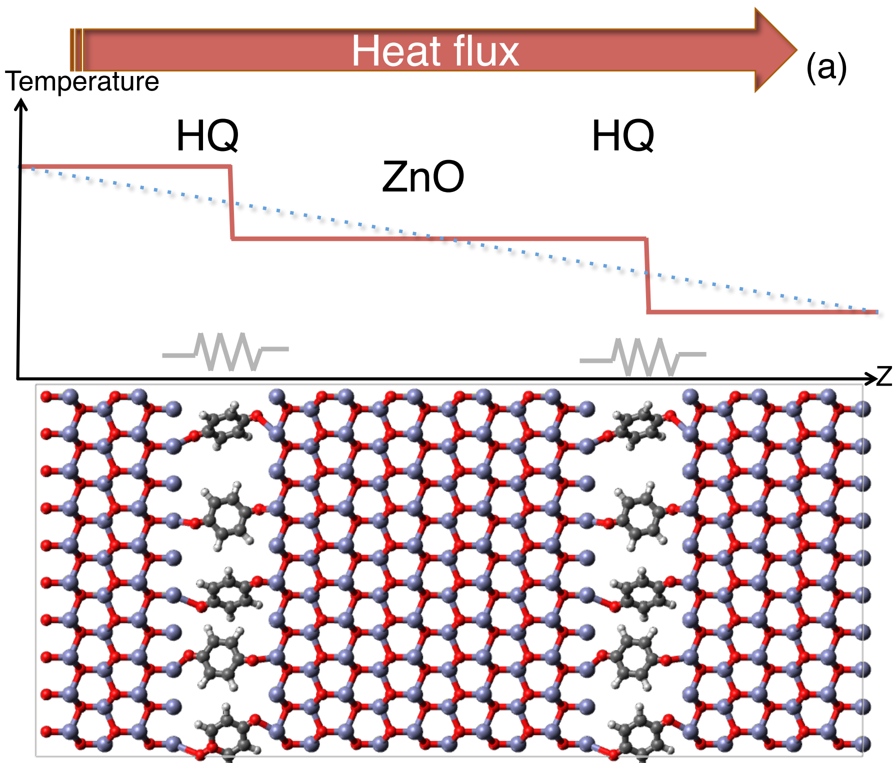
Student: Ashutosh Giri
Collaboration: M. Karppinen (Aalto)

Combined ALD/MLD to reduce κ in oxides

•Molecular interface cases all phonon modes to scatter at boundary (aka: no direct transmission of oxide modes across HQ)



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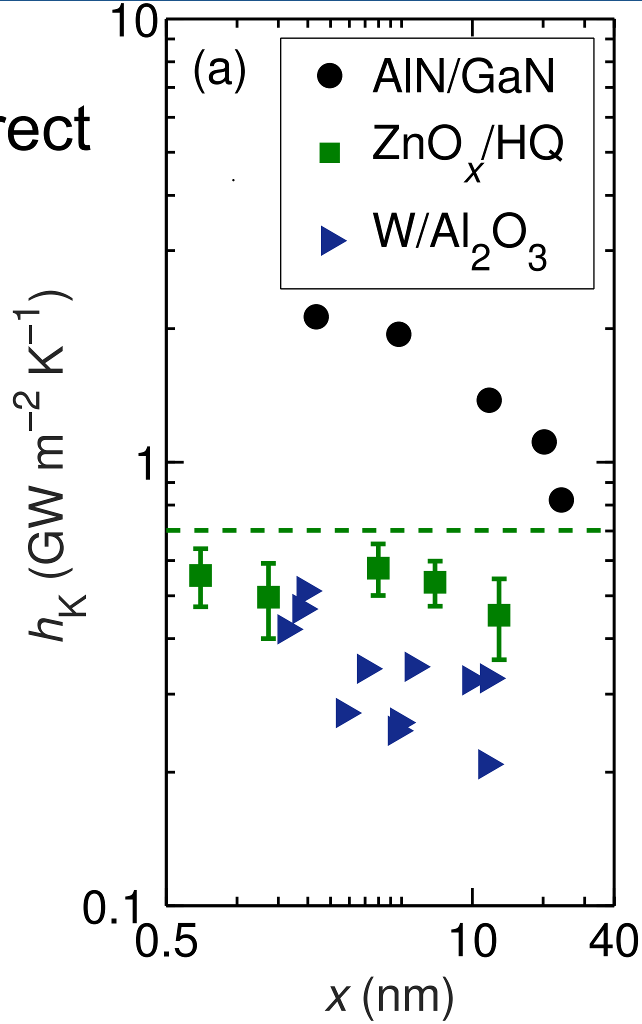

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J. Mat. Chem. A **3**, 11527
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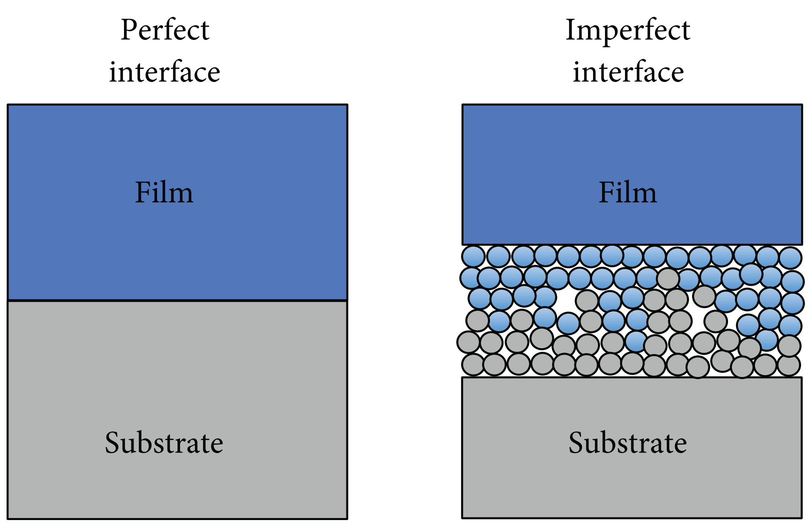
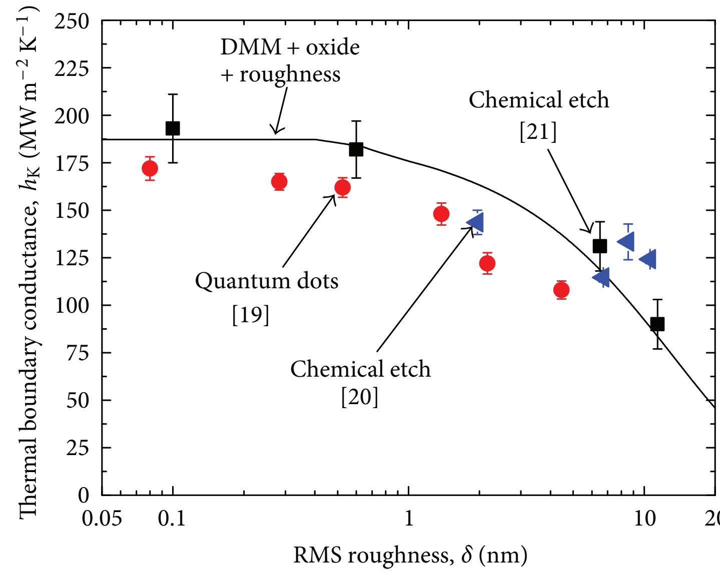
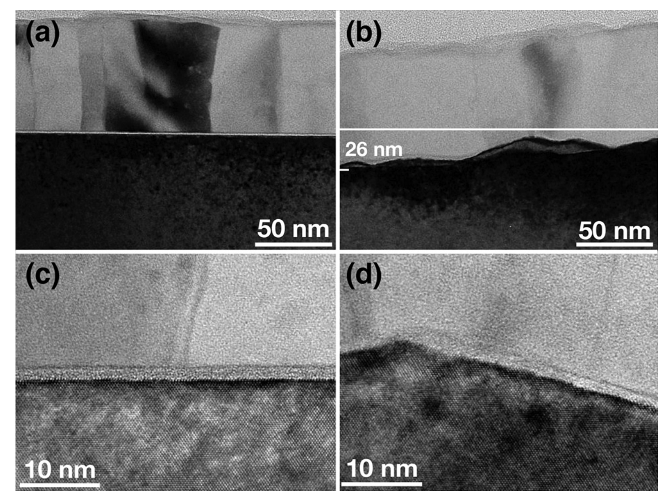
How do we manipulate the thermal boundary conductance?



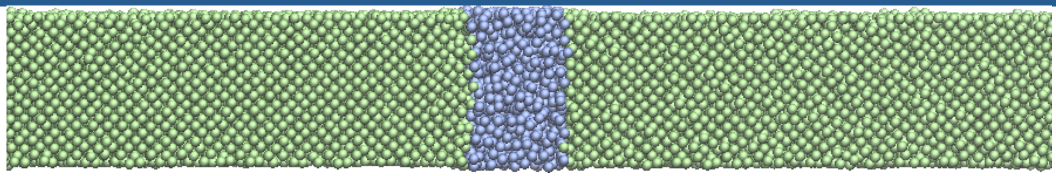


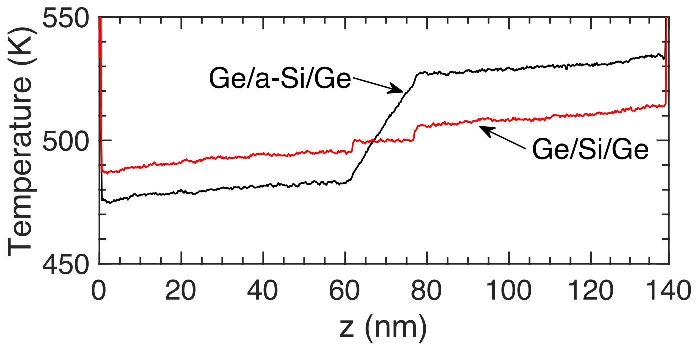


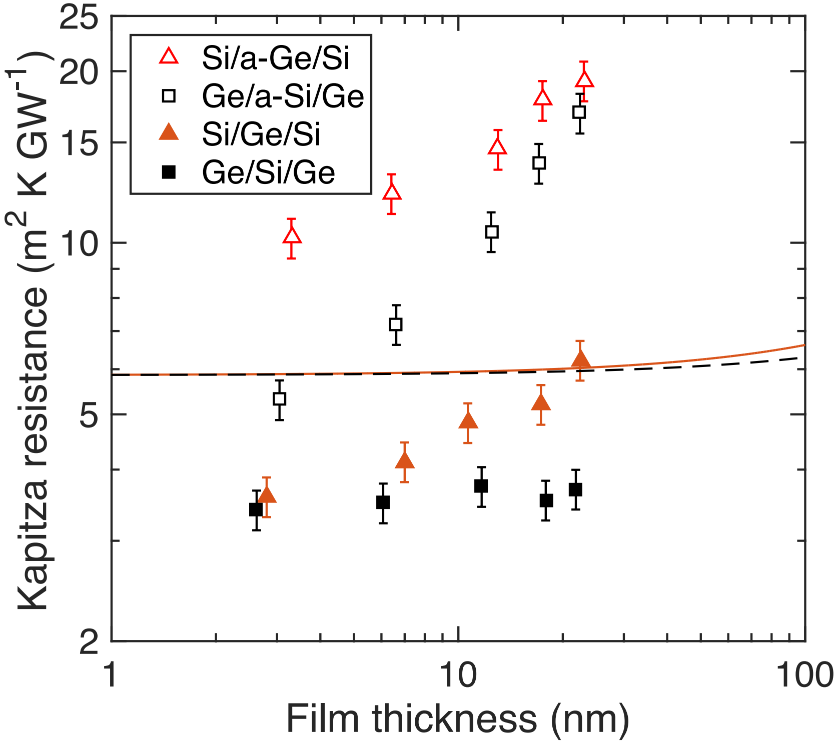
- Defects/imperfections generally thought to decrease h_K.
- How is phonon transmission affected by disordered interfacial films/layers?

Review Article
ISRN Mech. Eng. **2013** 682586 (2013)

How do we manipulate the thermal boundary conductance?







- Heat transfer across interfacial regions related to two things:
    1) Thermal boundary conductance across boundaries
    2) Thermal conductivity of interfacial regions *(ballistic modes can help us here)*

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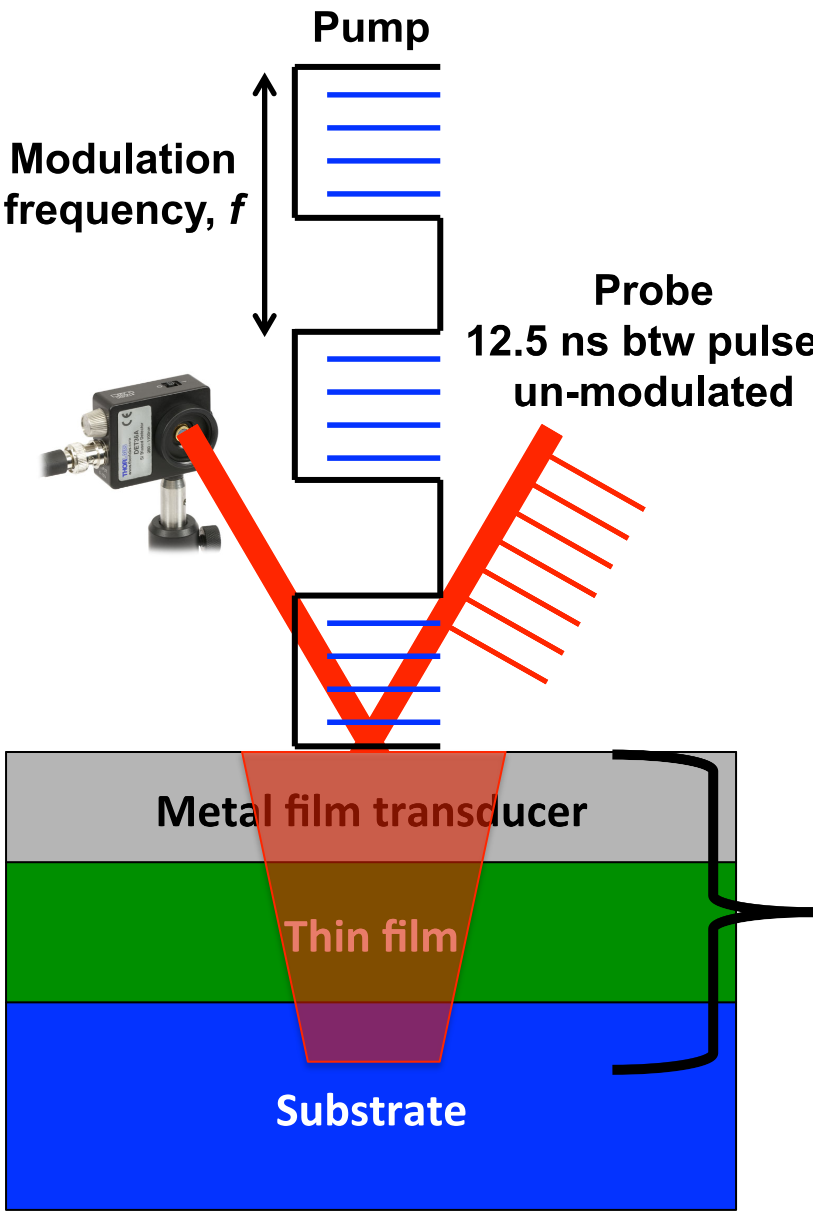
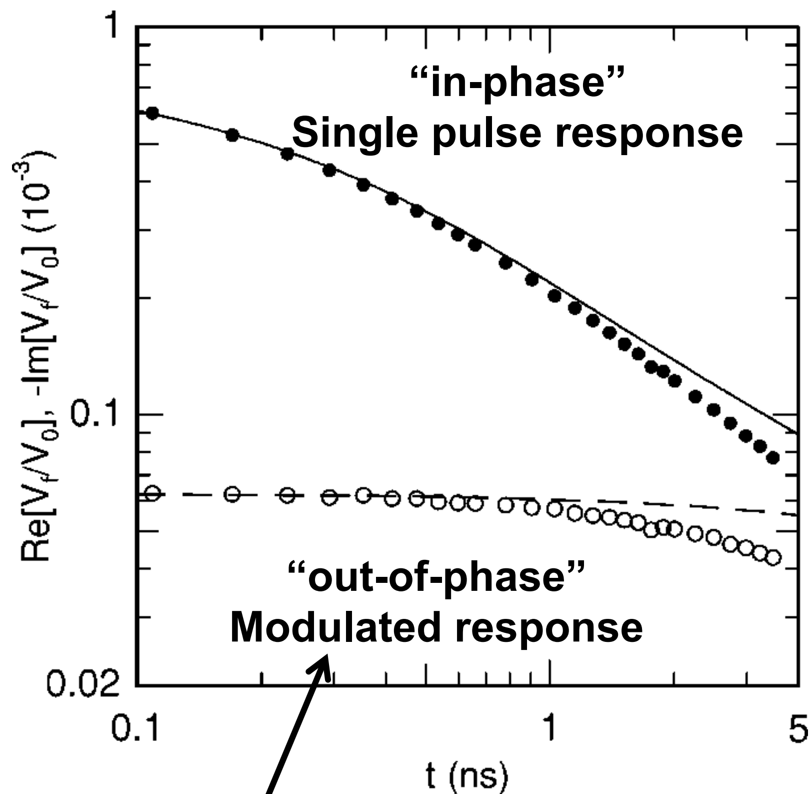
Frequency domain thermoreflectance (FDTR)





Thermal penetration depth
"Measurement volume"

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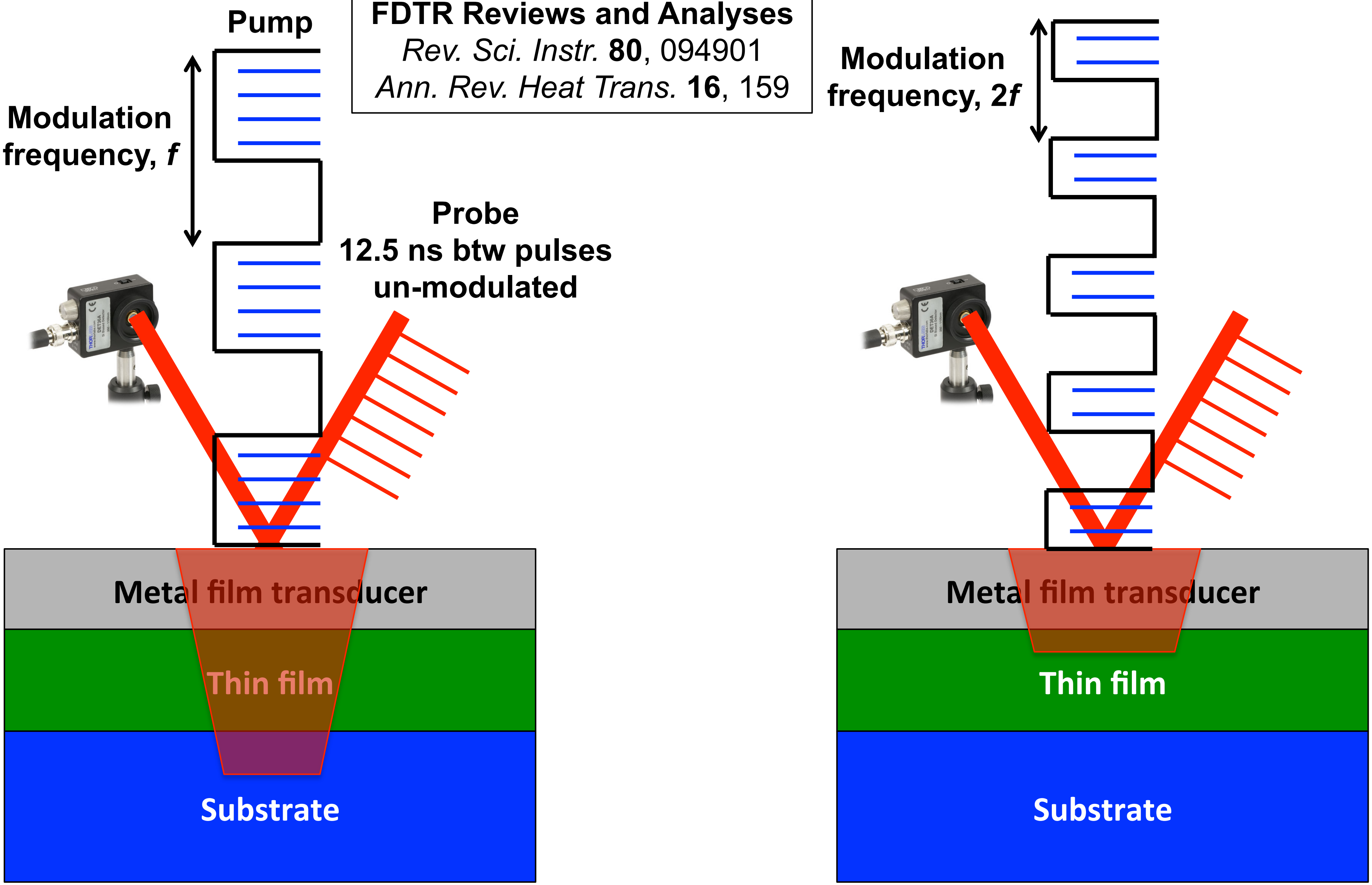
TDTR Reviews and Analyses

Rev. Sci. Instr. **75**, 5119
Rev. Sci. Instr. **79**, 114902
J. Heat Trans. **132**, 081302
Ann. Rev. Heat Trans. **16**, 159

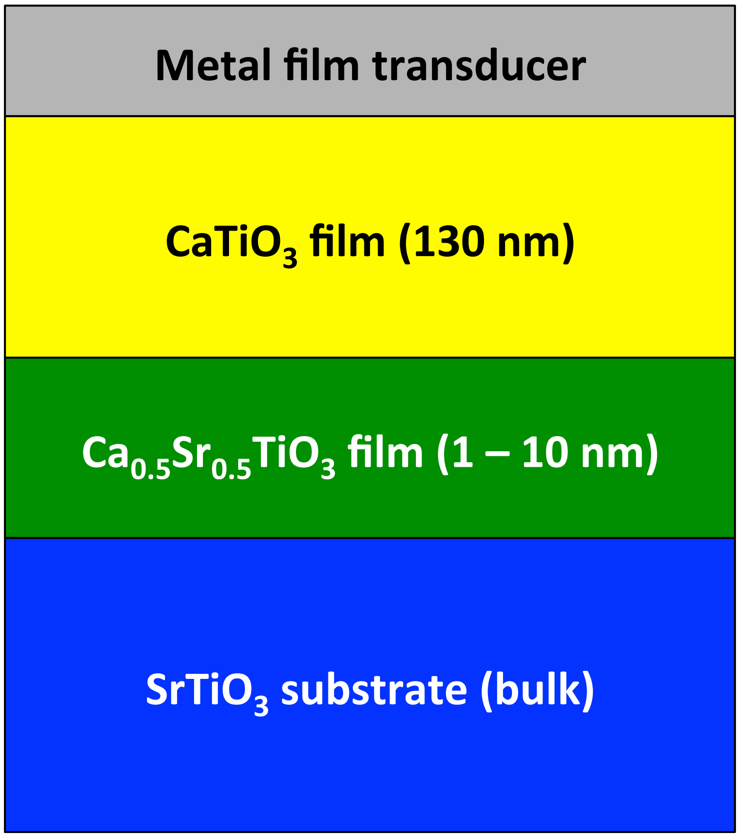
Frequency domain thermoreflectance (FDTR)

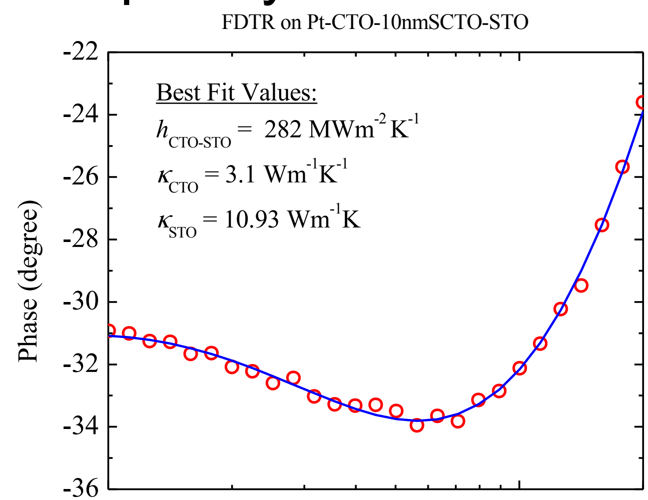
FDTR Reviews and Analyses
Rev. Sci. Instr. **80**, 094901
Ann. Rev. Heat Trans. **16**, 159

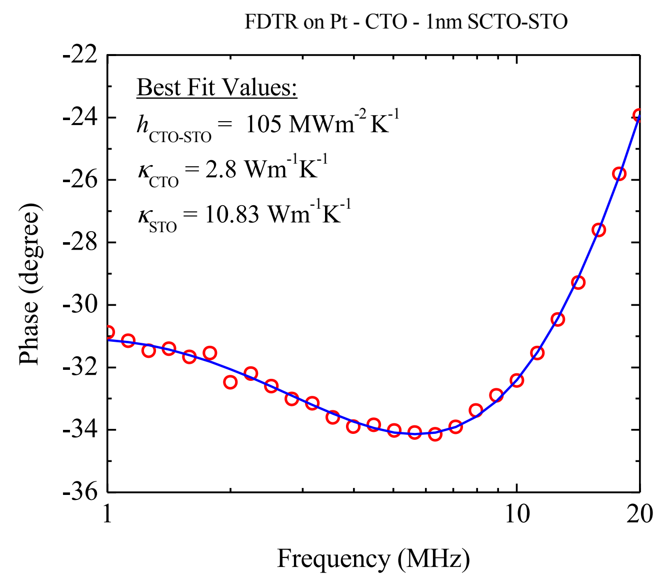


Frequency domain thermoreflectance (FDTR)

With FDTR scans, we can now measure multiple parameters, including thermal boundary conductance across buried interfaces (depth profiling) and thermal conductivity of multiple layers at once







PRL **109** 195901

Student: Ramez Cheaito, Brian Foley

Collaboration: J. Ihlefeld (SNL)

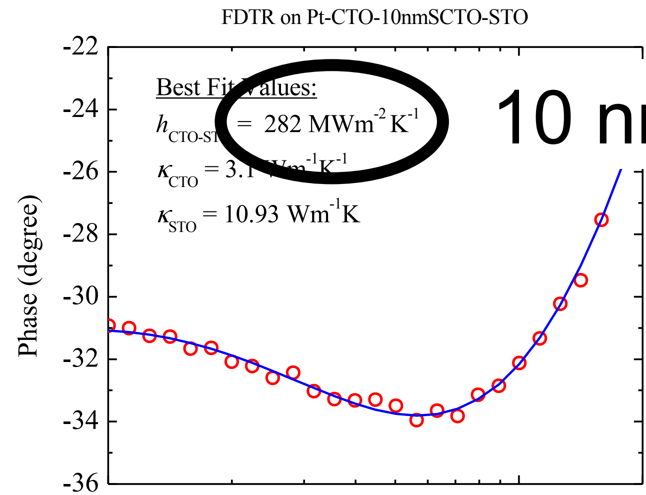
Frequency domain thermoreflectance (FDTR)

- Thicker alloys ***increase*** the thermal boundary conductance across $CaTiO_3$/alloy/$SrTiO_3$ interfacial region

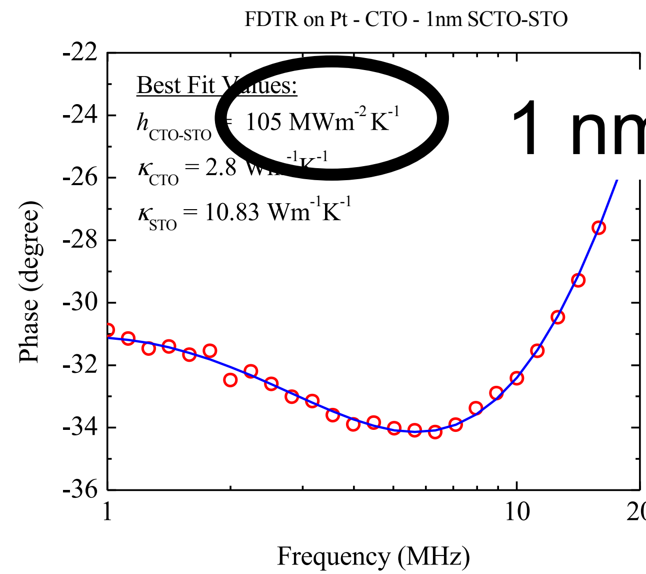
- **In other words: ADDING MATERIAL DECREASES RESISTANCE?**

<u>Possibility</u>

- Alloy thermal conductivity increasing with thickness?



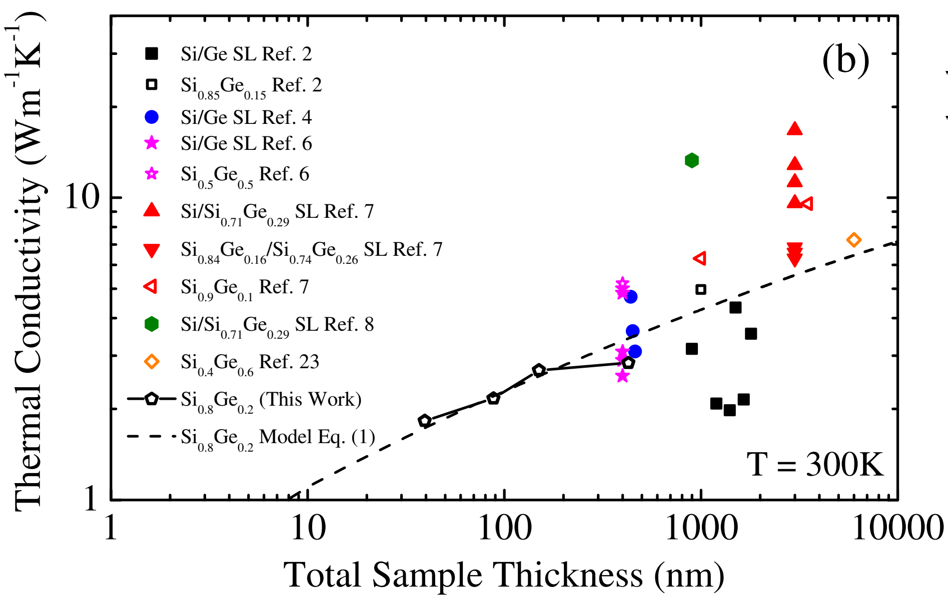
10 nm alloy

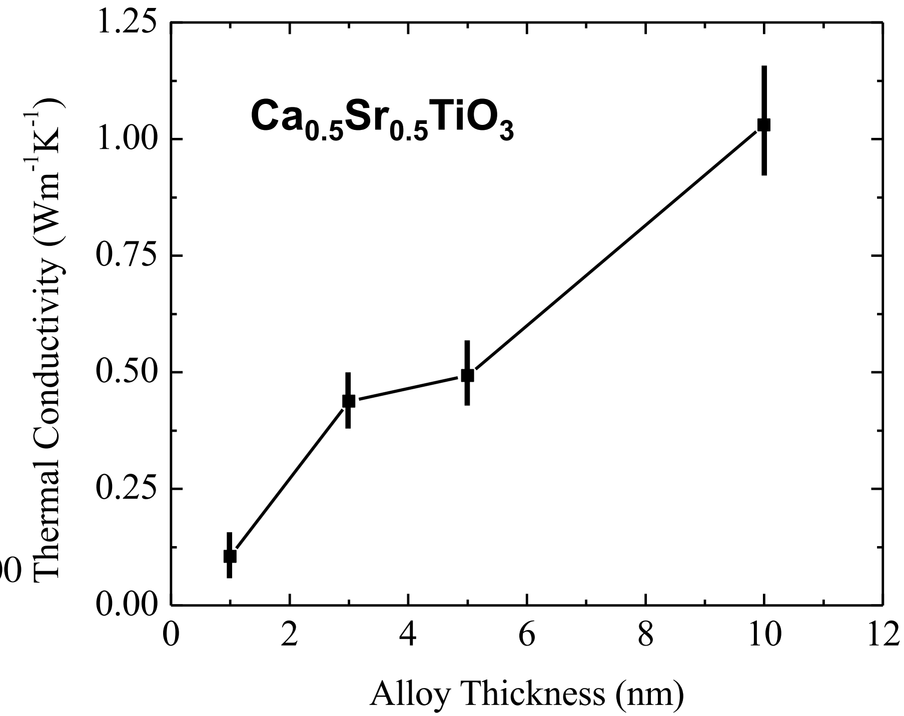


1 nm alloy

Size effects in the thermal conductivity of alloys

- Long wavelength modes carry most of the heat in disordered alloys due to mass impurity scattering
- Thicker alloy: more ballistically traveling “phonons” (propagons) to carry the heat
- Means we can decrease thermal resistances at interfaces by **adding disordered alloys** to interfaces





PRL **109** 195901
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Conclusions

Through intimate control during growth and fabrication, oxide materials offer new directions and regimes for phonon thermal transport