UVA | SCHOOL of ENGINEERING & APPLIED SCIENCE

Changing the nature and behavior of electron and phonon thermal transport with nanoscale interfaces

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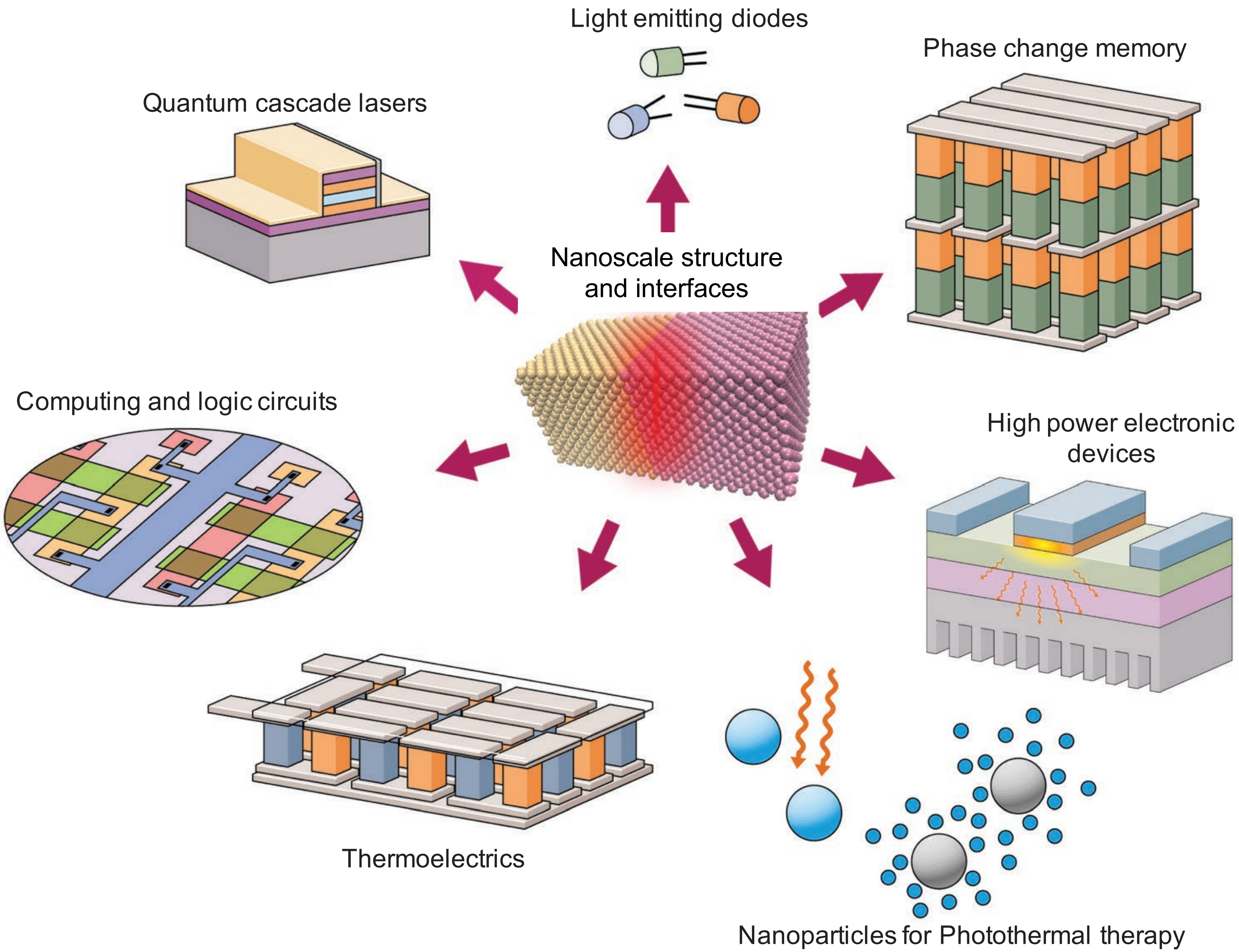
ExSITE AT THE UNIVERSITY OF VIRGINIA

University of Virginia, Charlottesville, VA

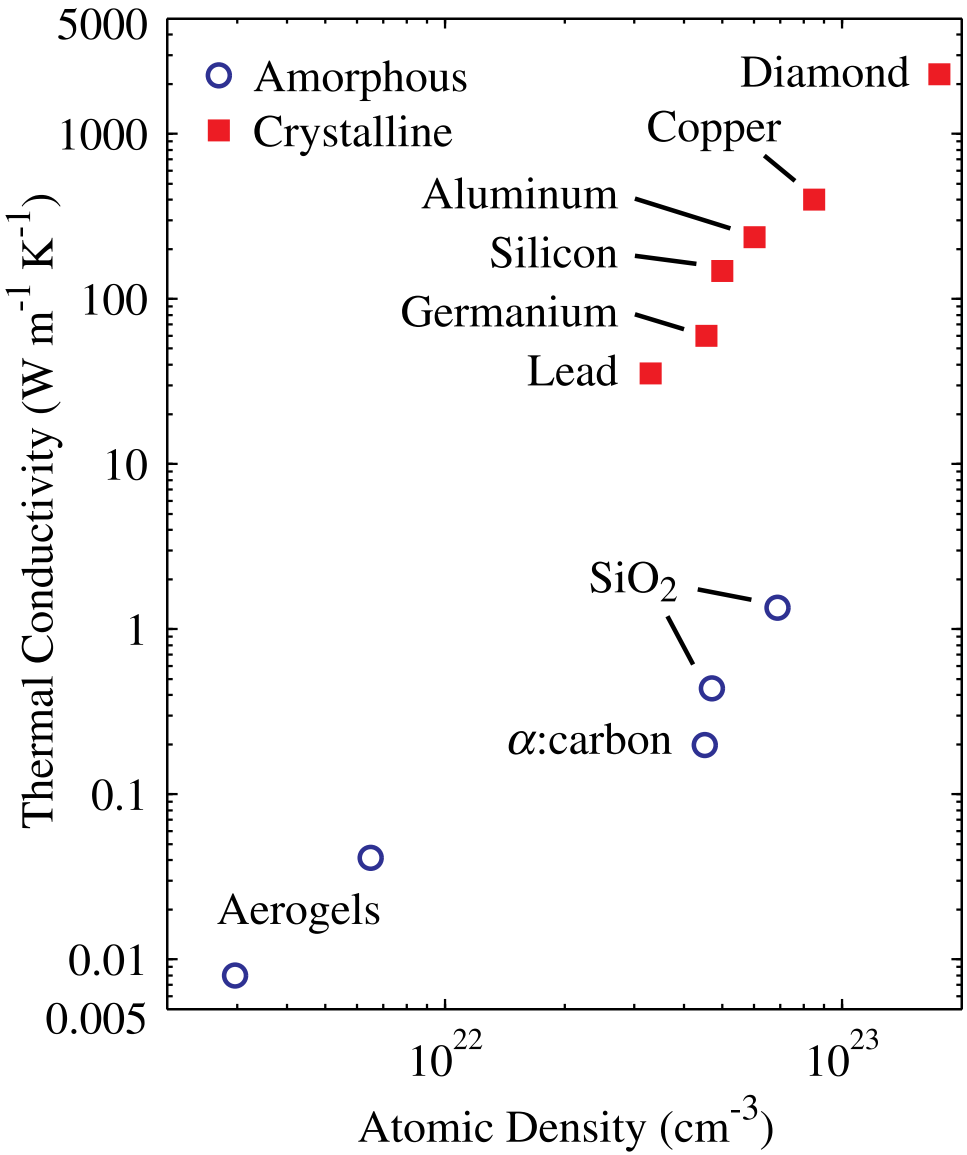
Home to Thomas Jefferson
3rd US president
founder of UVA

ExSiTE Lab: Experiments & Simulations in Thermal Engineering



Giri and Hopkins, *Adv. Funct. Mat.* **30**,1903857 (2020)

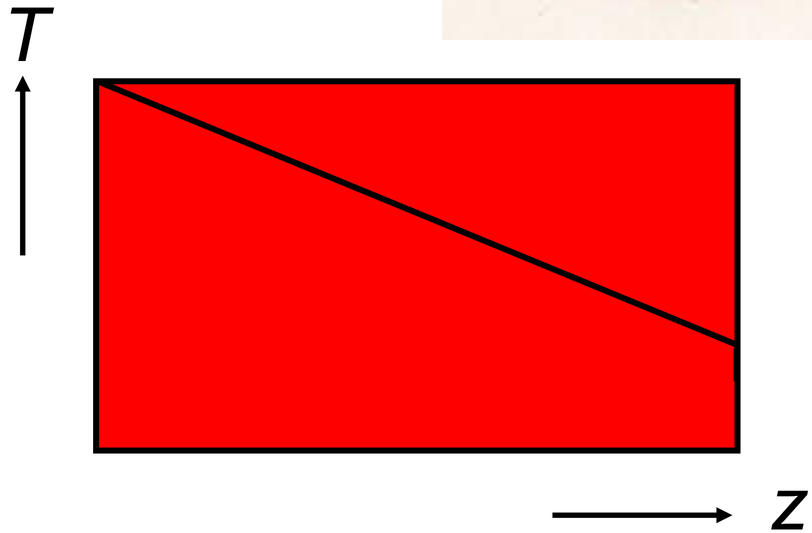
Thermal conductivity of materials – Macro/Microscopic



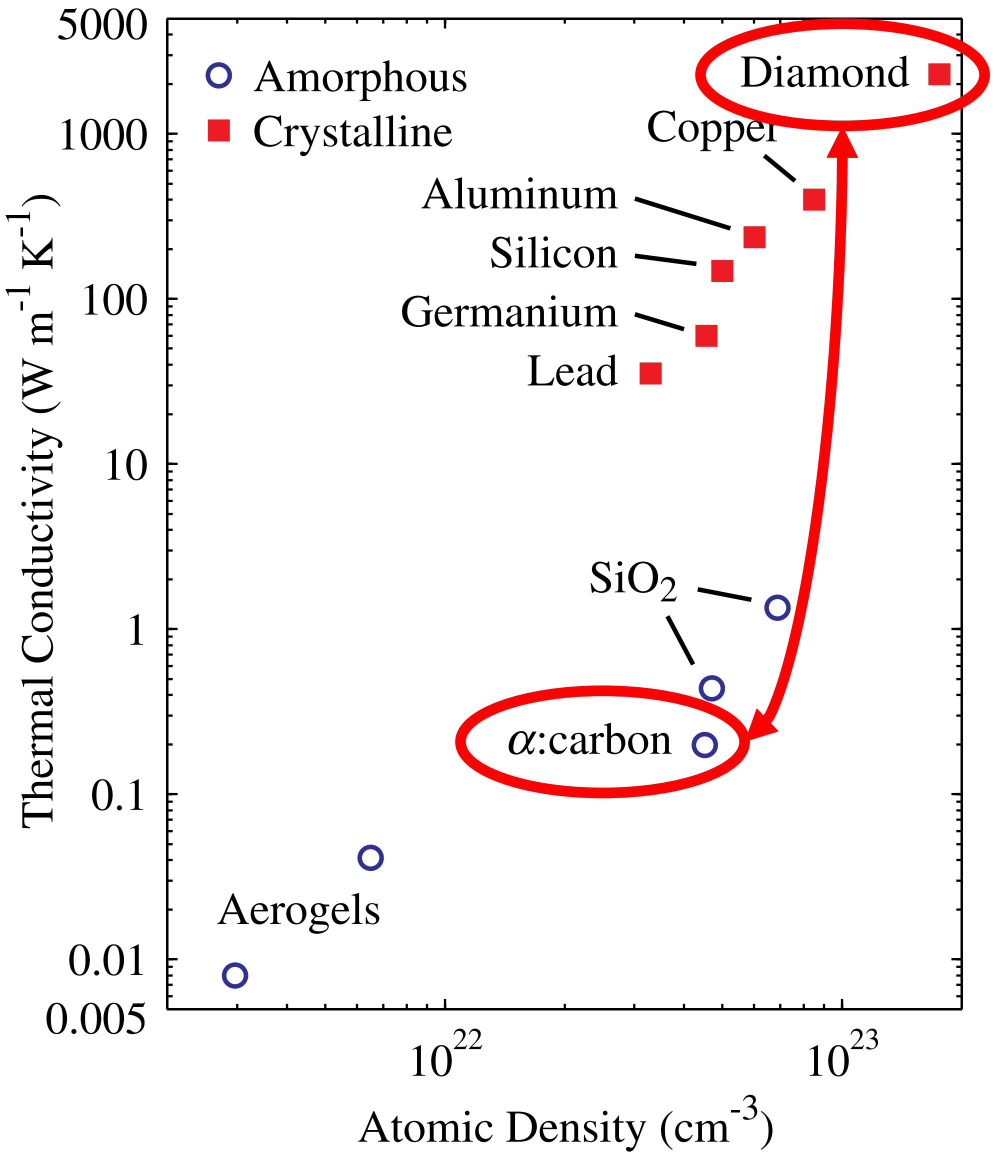
PRL **110**, 015902 (2013)

The Fourier Law

$$q = -\kappa \frac{\partial T}{\partial z}$$



Thermal conductivity of materials – Macro/Microscopic



PRL **110**, 015902 (2013)

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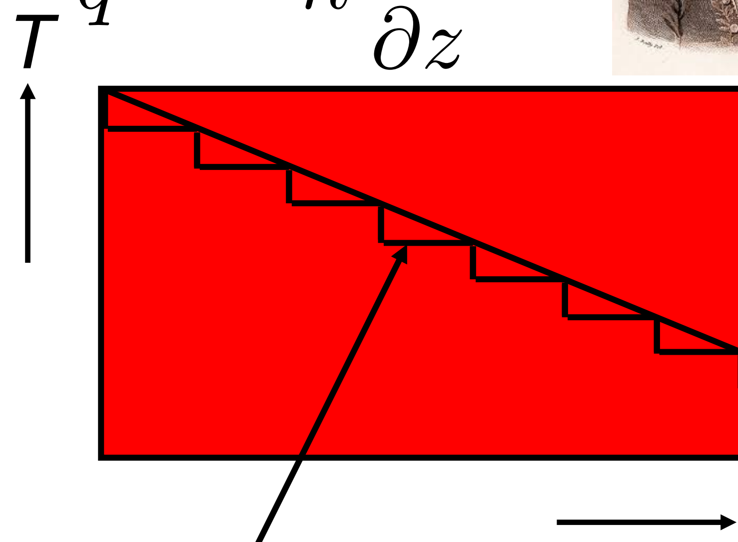


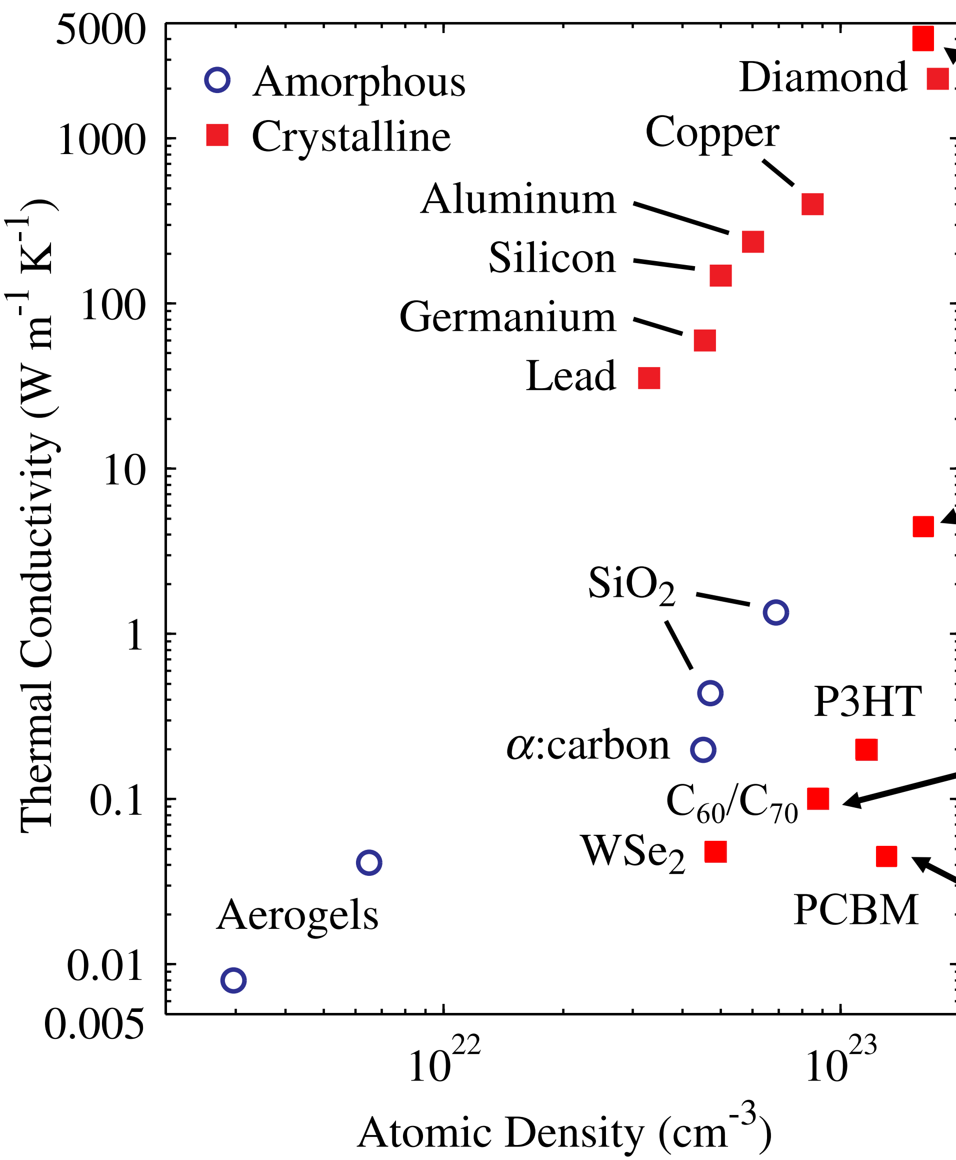
λ = Mean free path

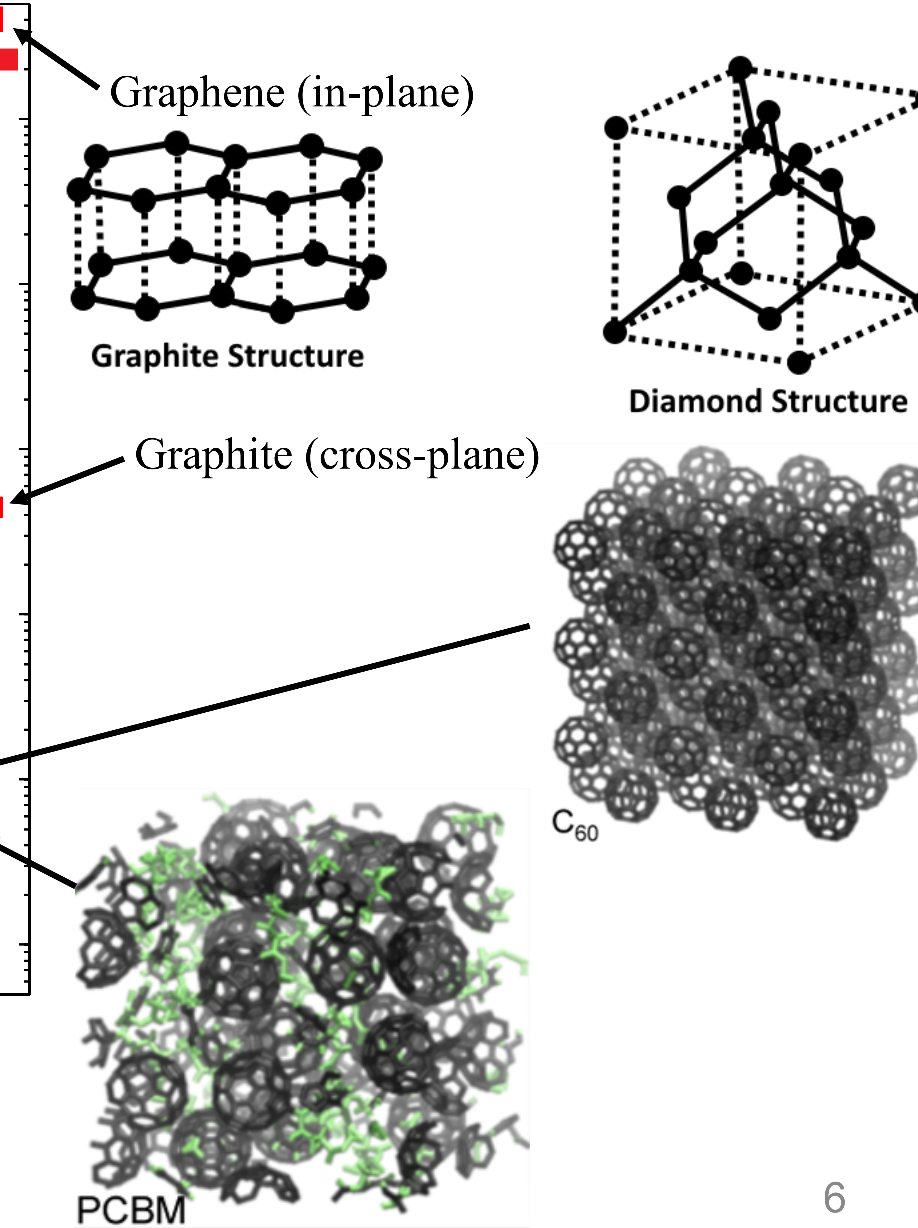
$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

Heat capacity

Velocity

Thermal conductivity of materials – Nanoscopic

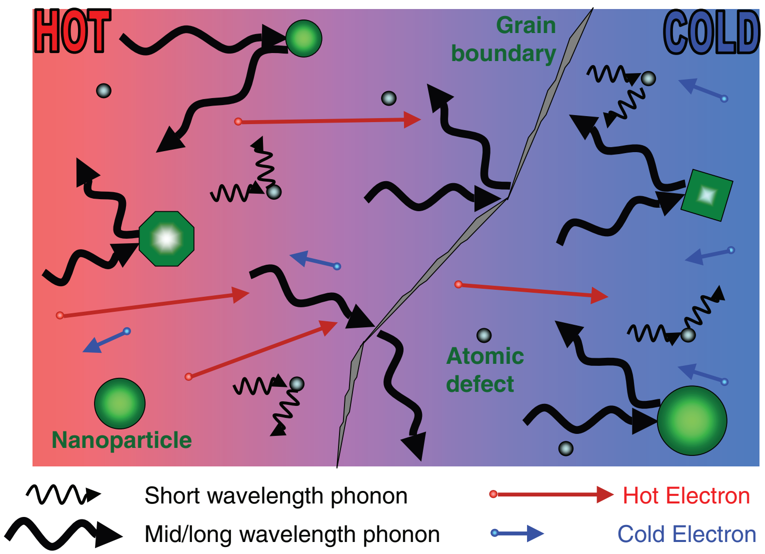




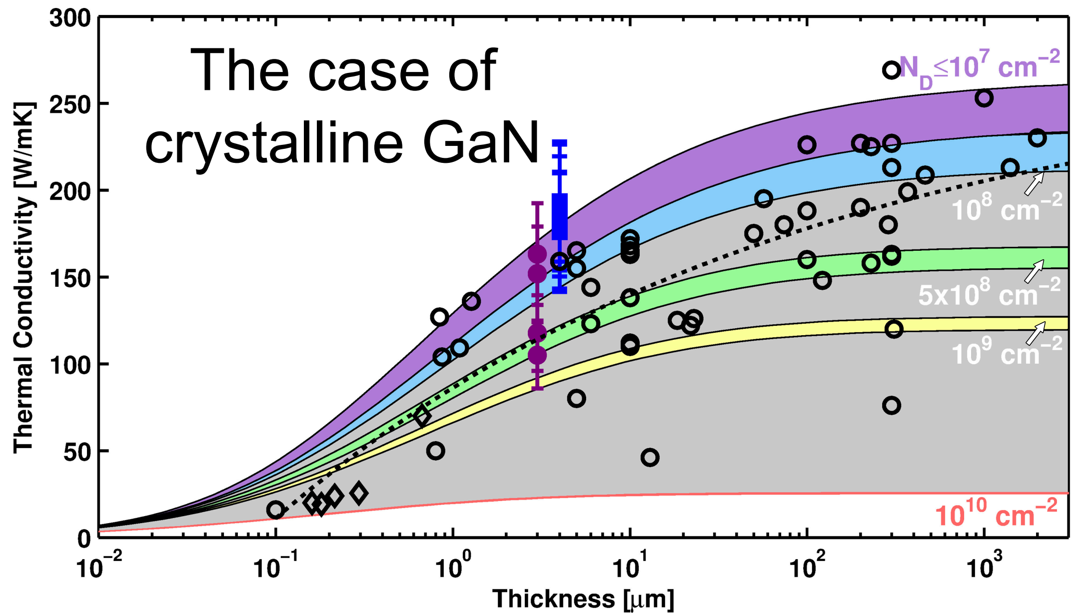
PRL **110**, 015902 (2013)

Thermal conductivity of materials – Nanoscale behavior

Well controlled and prescribed inclusions, defects, or **interfaces** change thermal conductivity based on manipulating the behavior of electrons and phonons



Adv. Mat. **22**, 3970

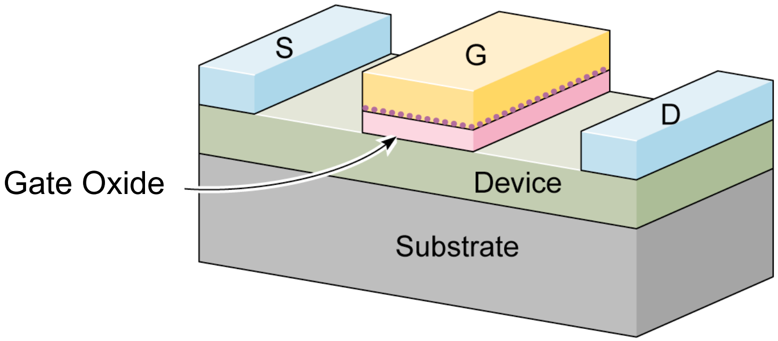


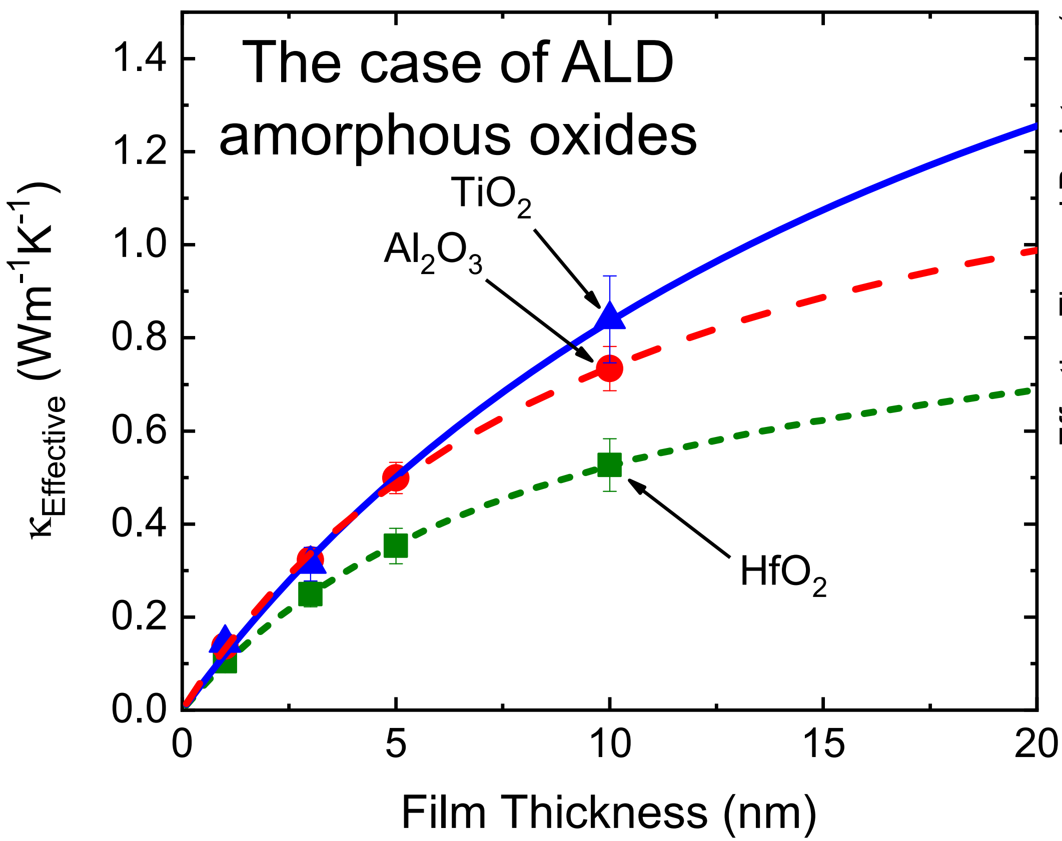
J. Appl. Phys. **120**, 095104

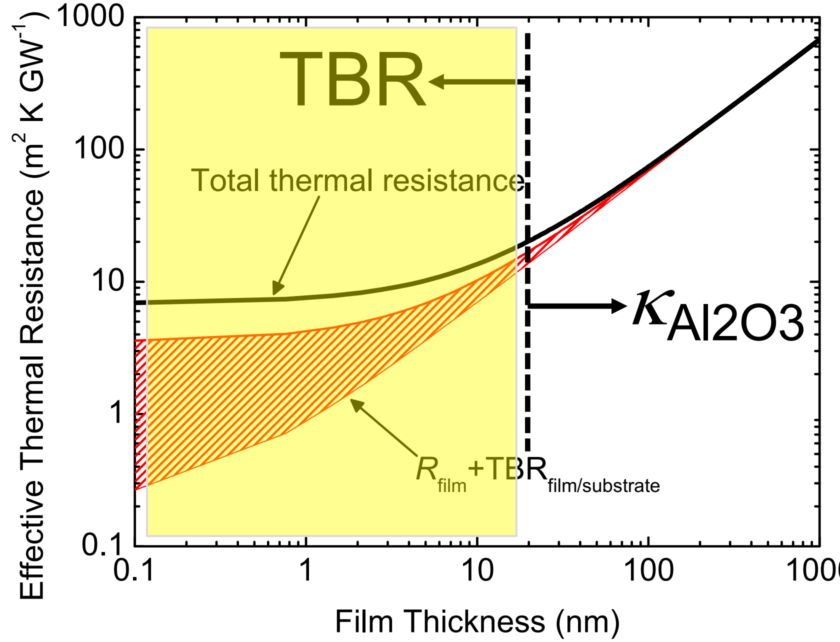
$$\kappa = \frac{1}{3} C v \lambda$$

Interfaces critical when thickness < λ

Thermal conductivity of materials – Nanoscale behavior



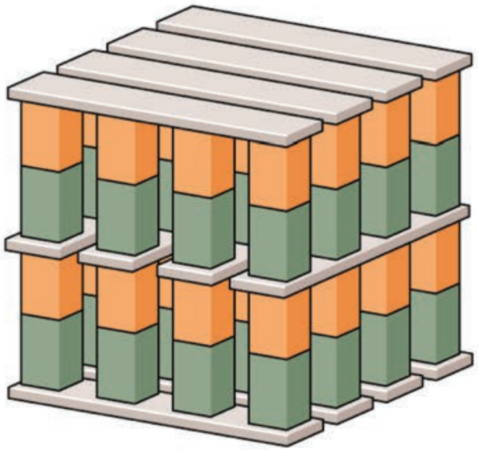


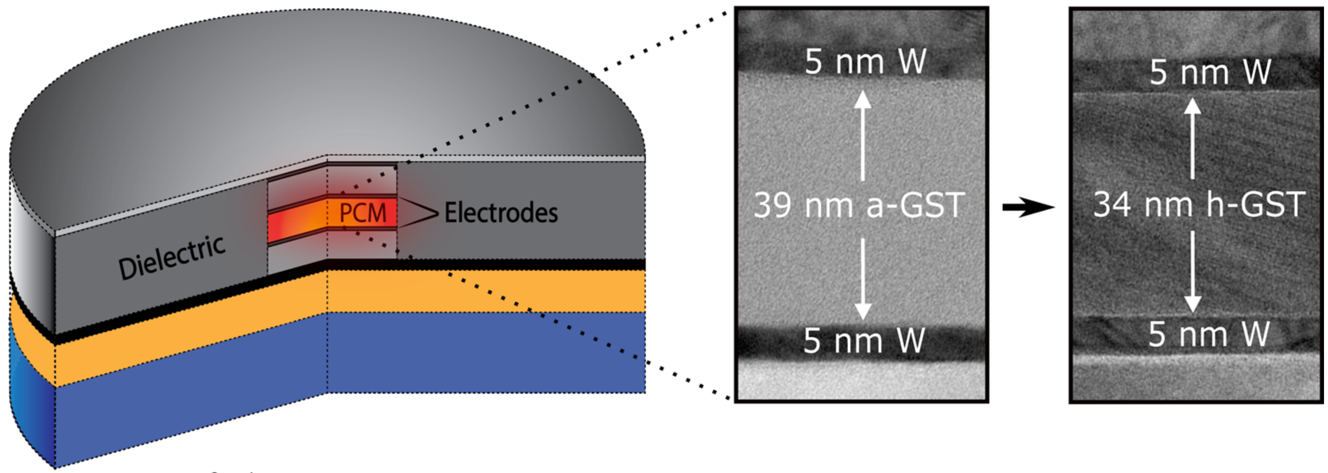


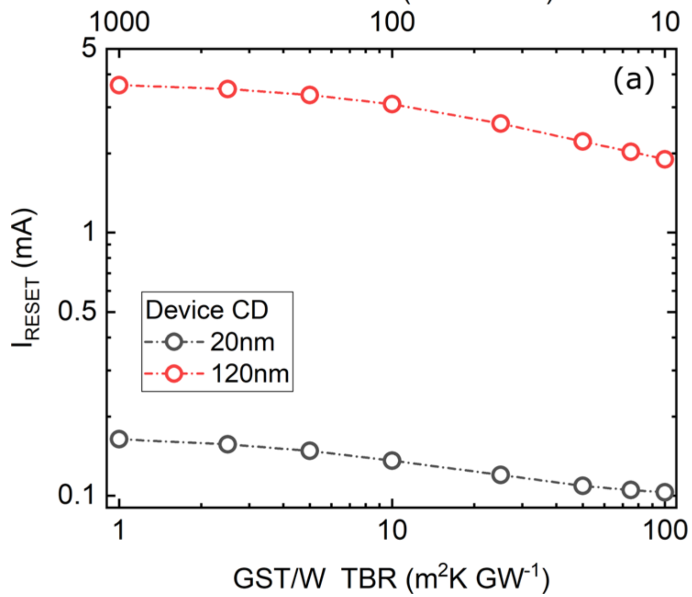
APL Materials **6**, 058302

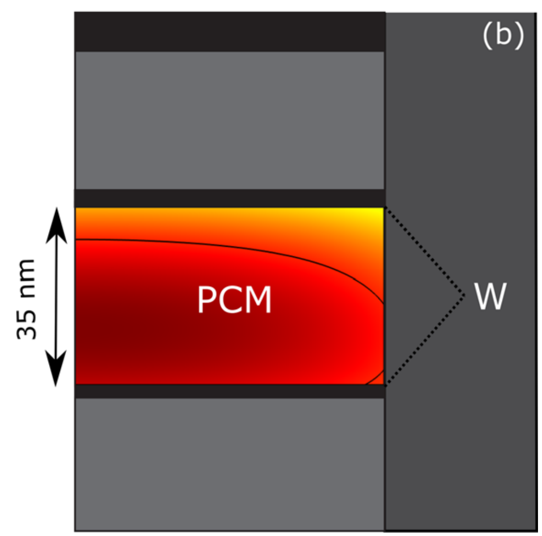
Nanoscale behavior impacts device functionality

Phase change memory





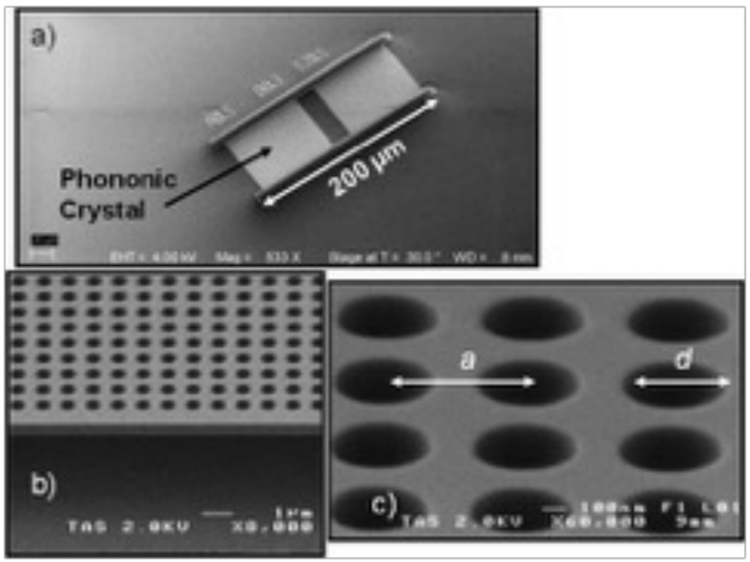




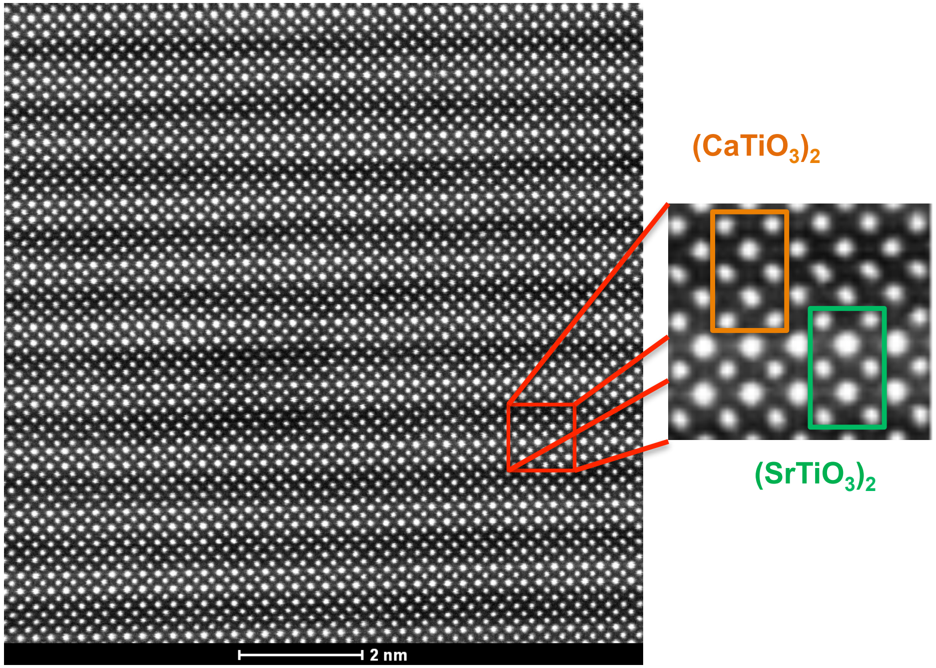
Aryana *et al. Nature Comm.* **12**, 774 (2021)

Thermal conductivity of materials – Nanoscale nature

Well controlled and ***ordered*** inclusions, defects, or ***interfaces*** change thermal conductivity based on manipulating the ***wave nature*** of electrons and phonons



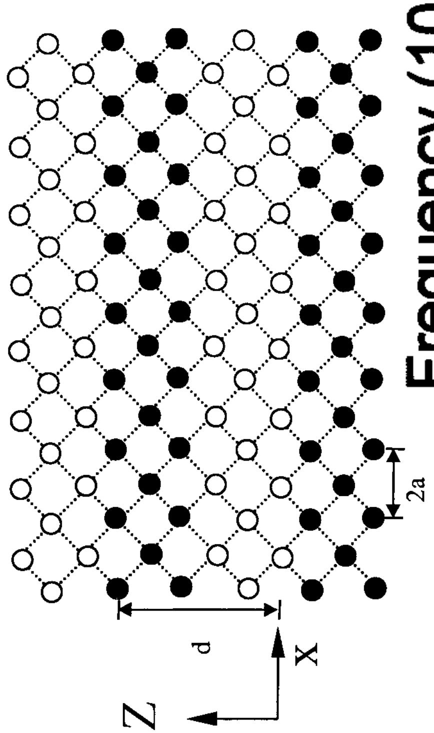
Nano Lett. **11**, 107 (2011)

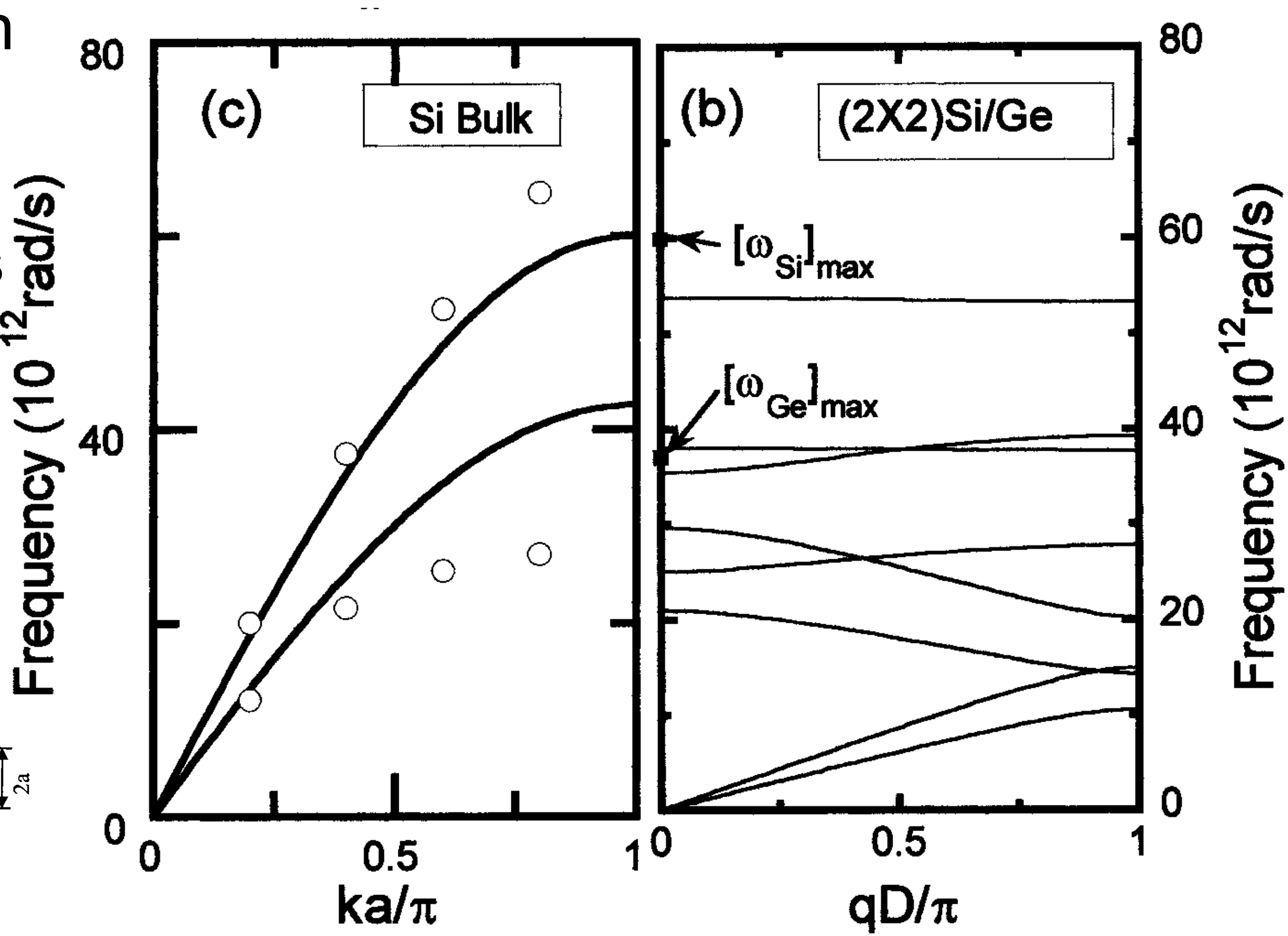


Nature Materials **13**, 168 (2013)

Thermal conductivity of materials – Nanoscale nature

Ex: SLs can change phonon dispersions





Yang and Chen, *Microscale Thermophysical Engineering* **5**, 107 (2001)

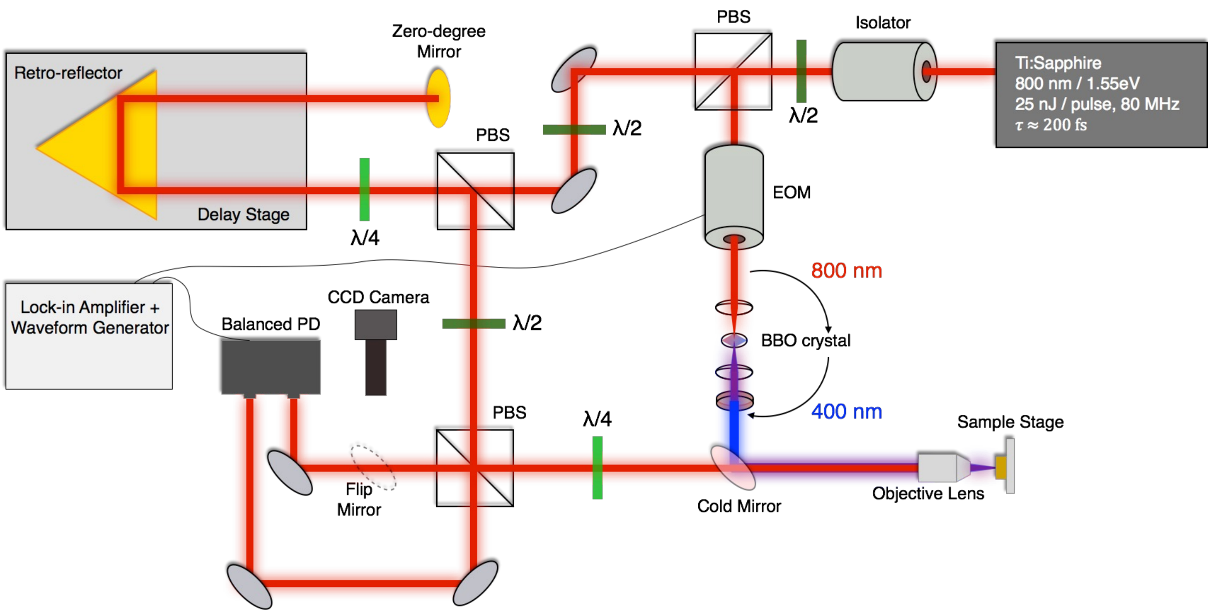
Outline

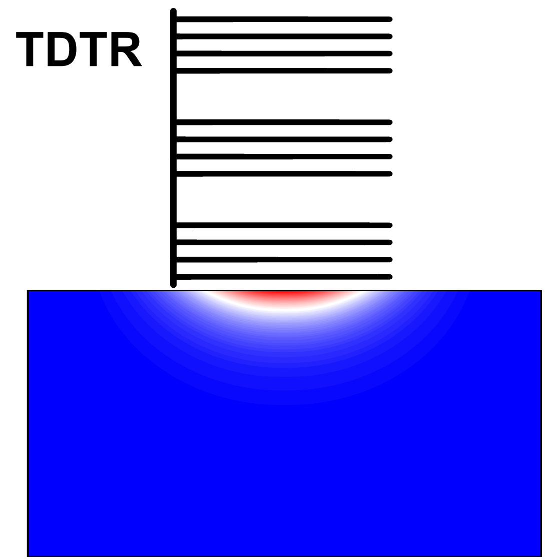
Theme: Atomic properties at interfaces can change the nature and behavior of heat transfer via phonons, electrons and photons

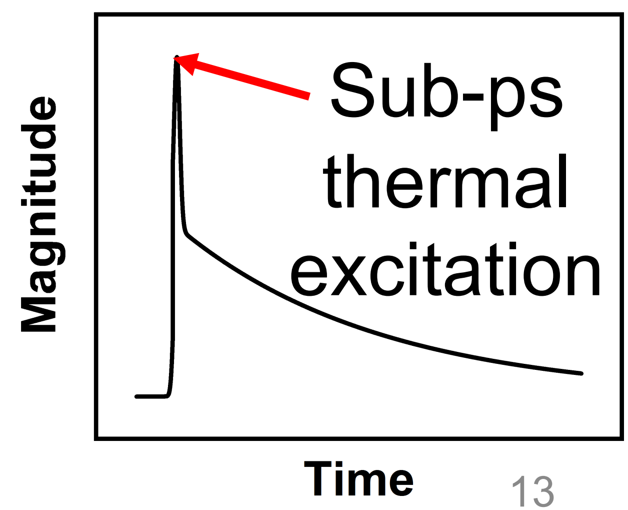
- Thermal boundary conductance
  - Overview
  - How we measure (thermoreflectance)
- Phonon coherence in the thermal conductivity of oxide superlattices
- Electron and phonon thermal resistance at interfaces in thin film phase change materials (GST, GSST)
- Interfacial heat transfer control of the IR properties of solids: long lived plasmon modulation

How do we measure the thermal properties? TDTR

Thin film or "near surface" measurements



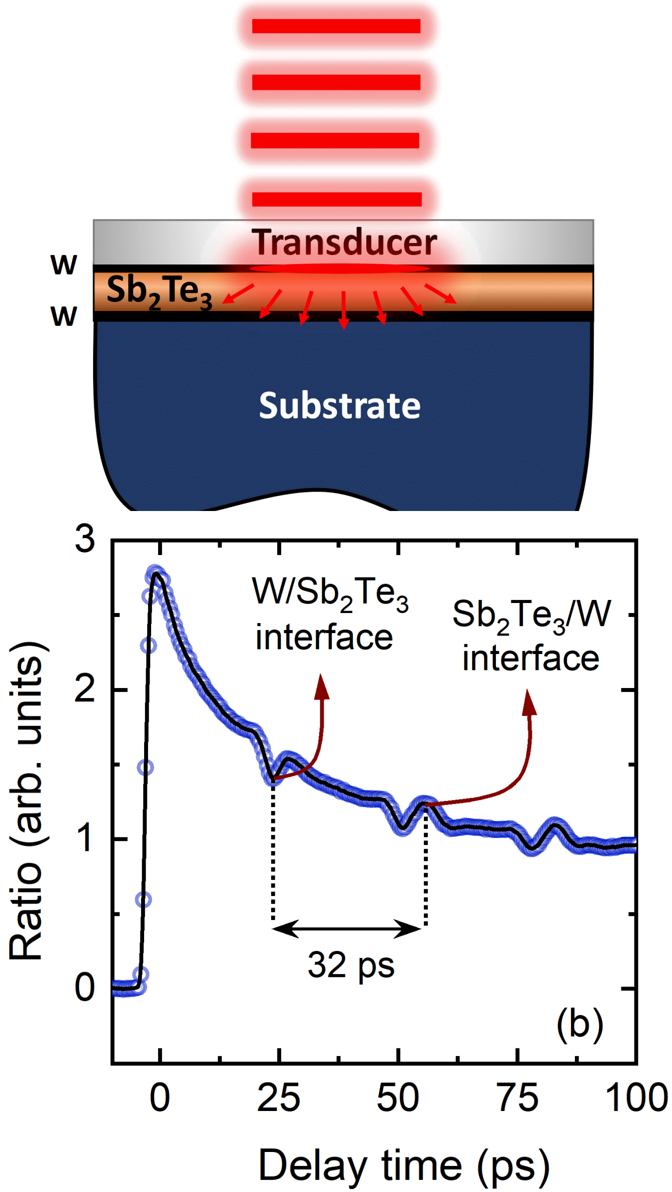


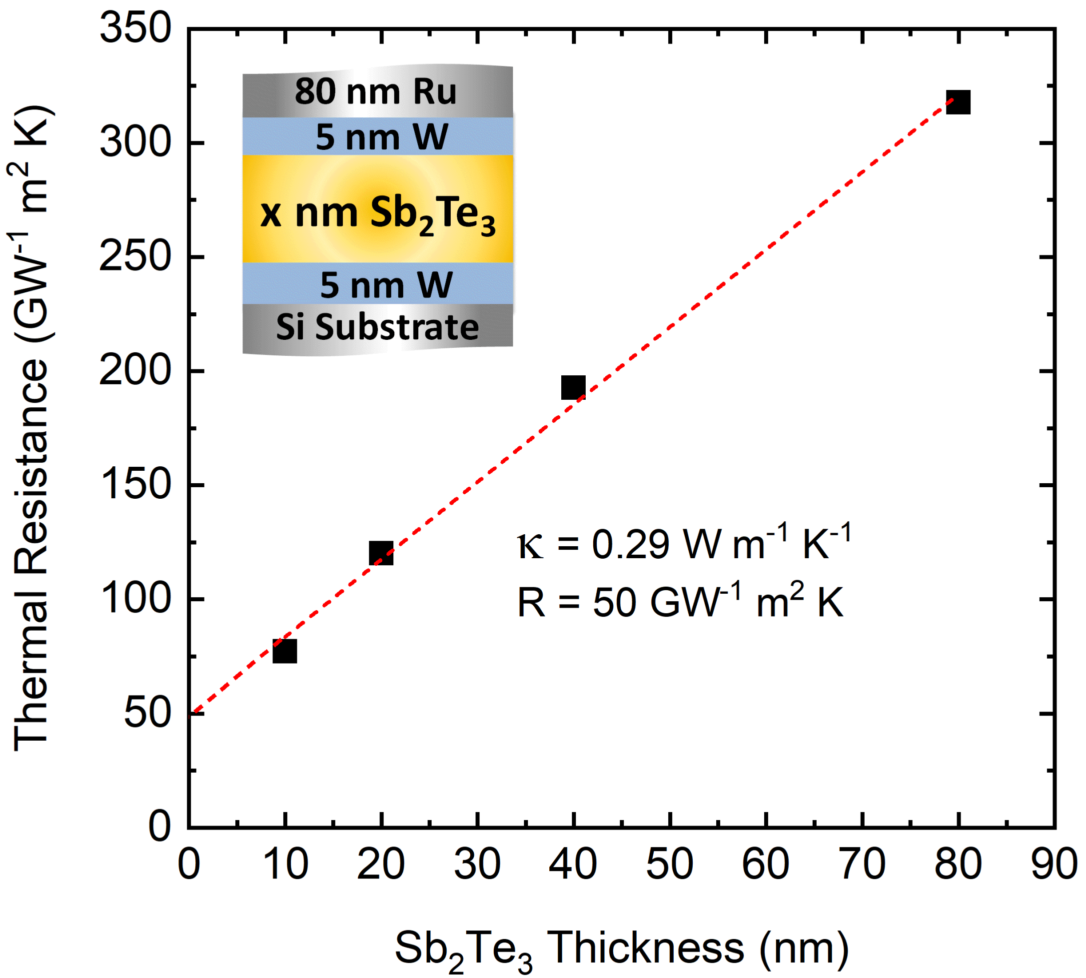


TDTR Reviews and Analyses

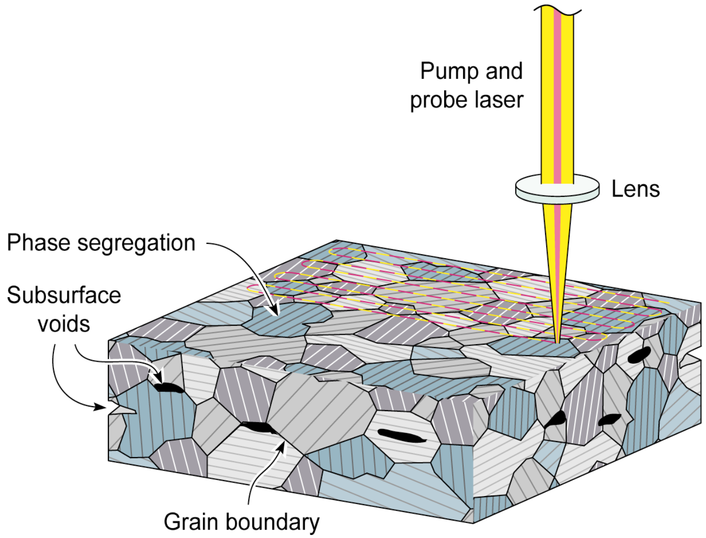
Rev. Sci. Instr. **75**, 5119;
Rev. Sci. Instr. **79**, 114902
J. Heat Trans. **132**, 081302;
Ann. Rev. Heat Trans. **16**, 159

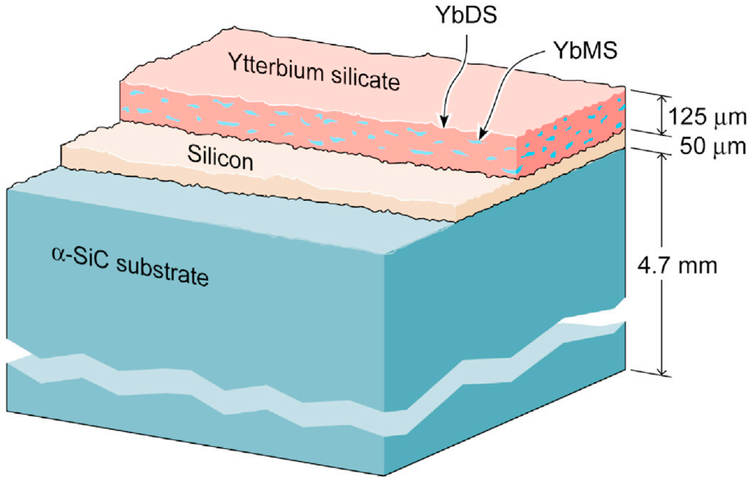
Collaboration w/ Van Dyck and Detavernier

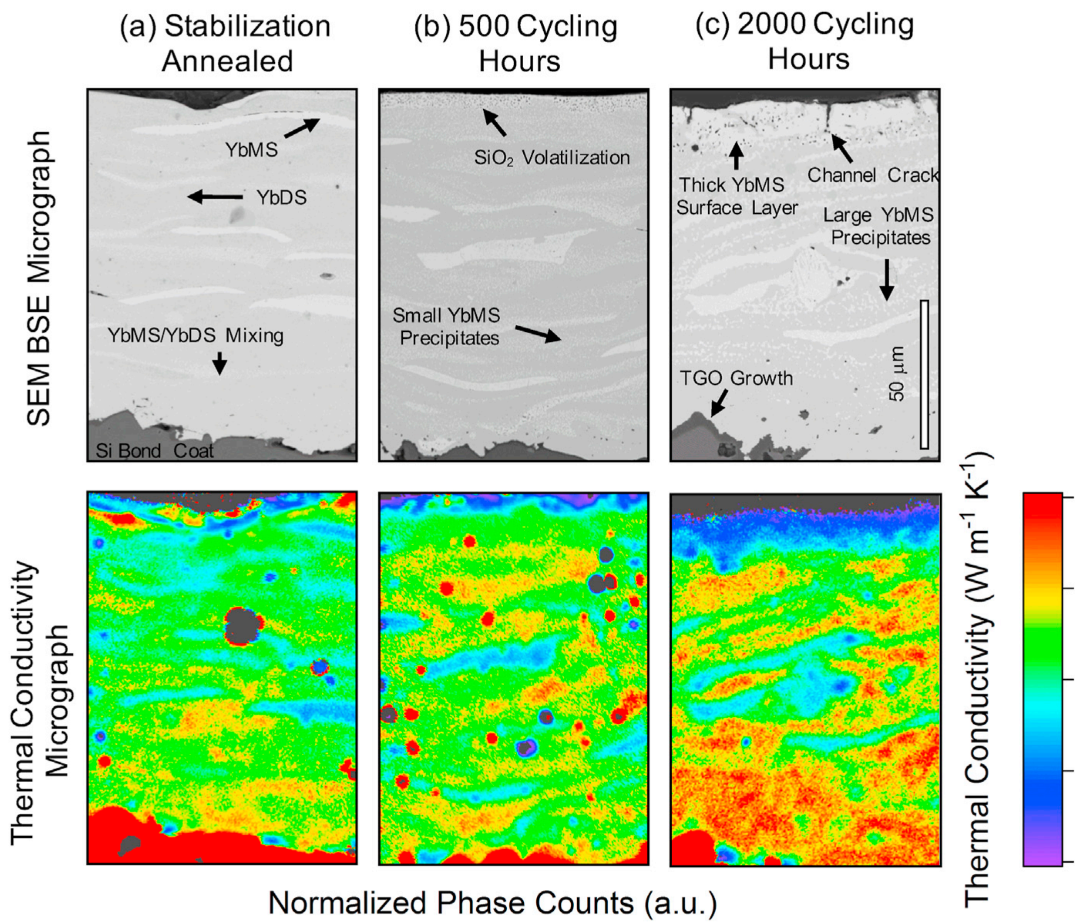




Local thermal conductivity measurements and spatial maps

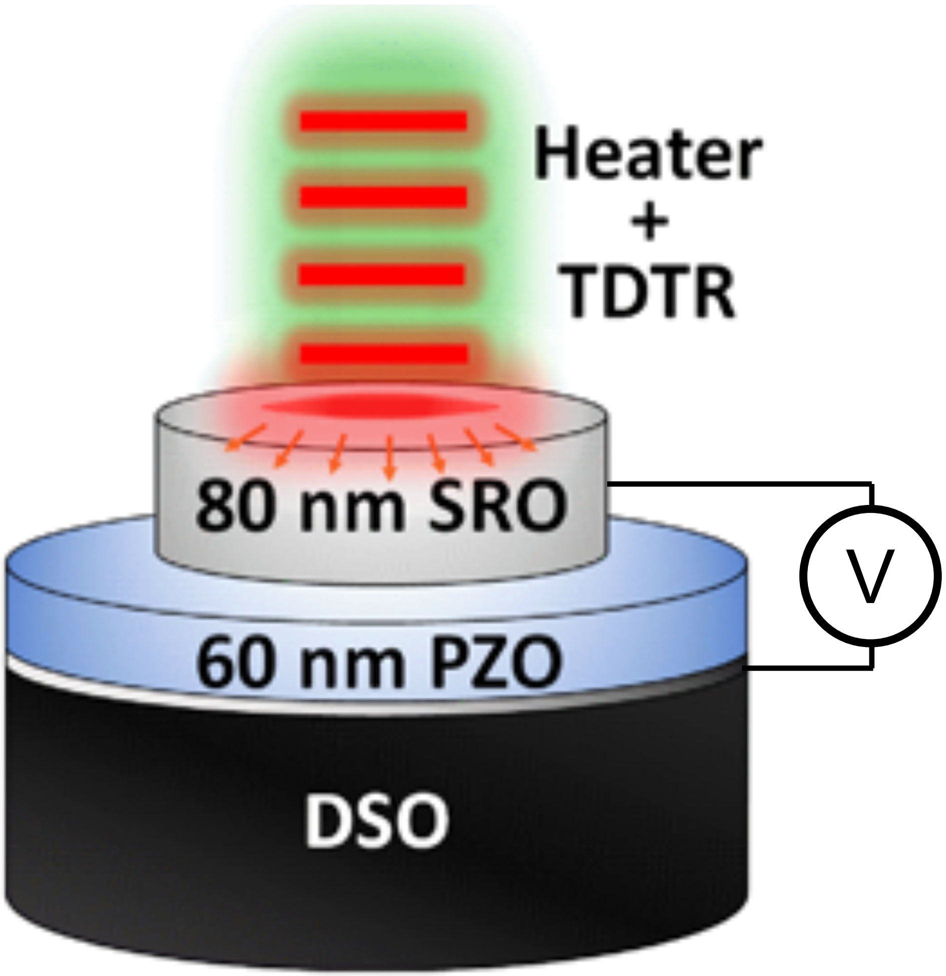


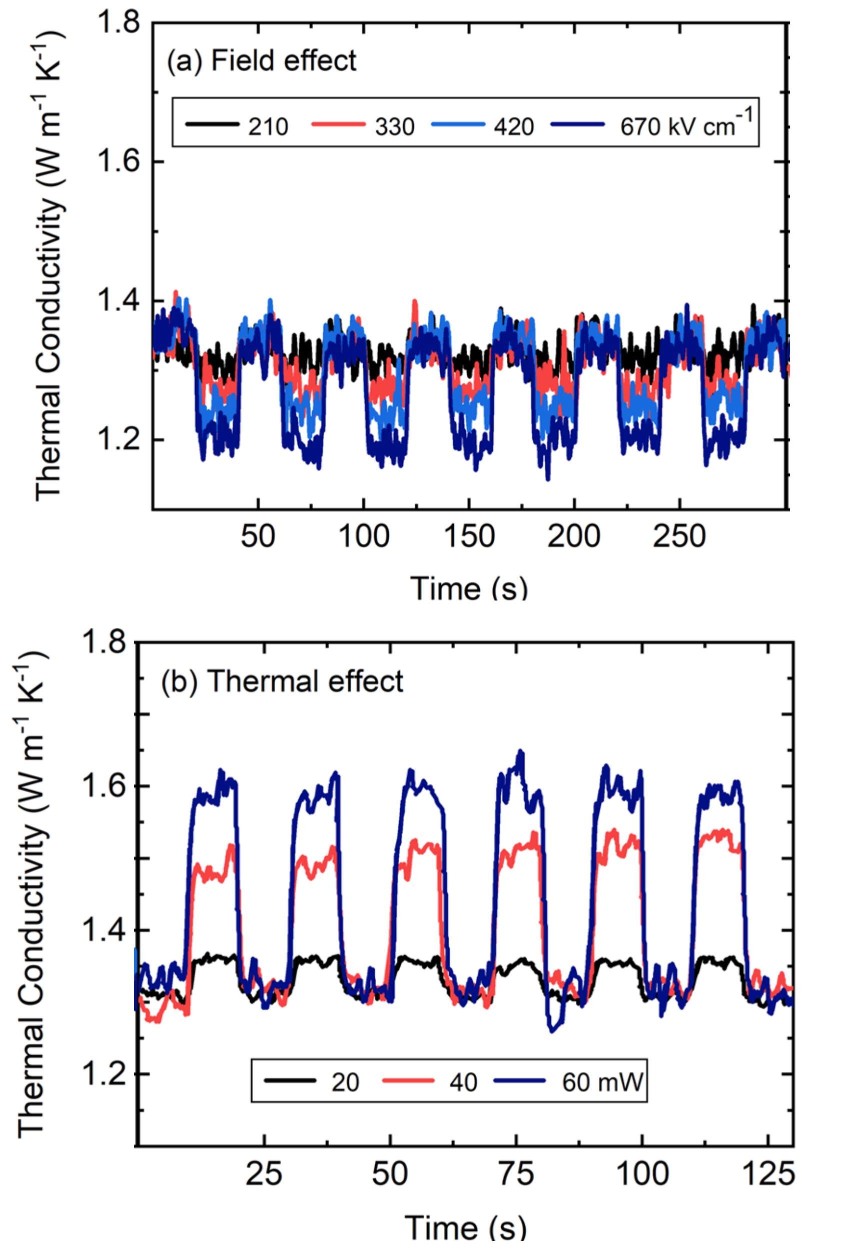




Olson *et al., Materials Today Phys.* **17**, 100304 (2021)

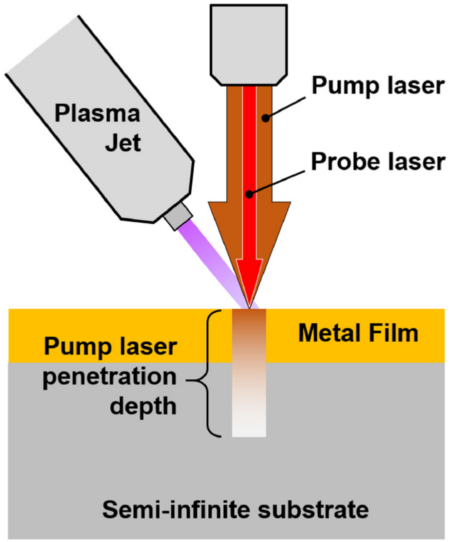
Actively switching thermal conductivity w/ FE/AFE domains

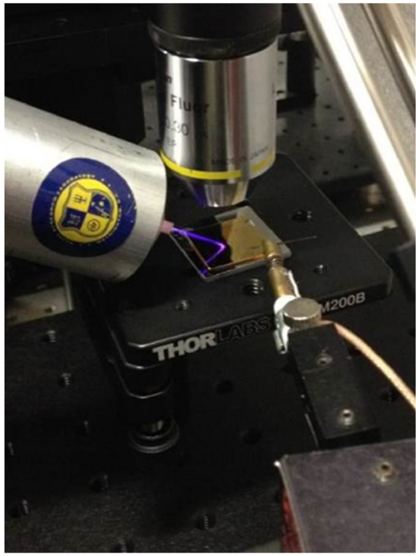


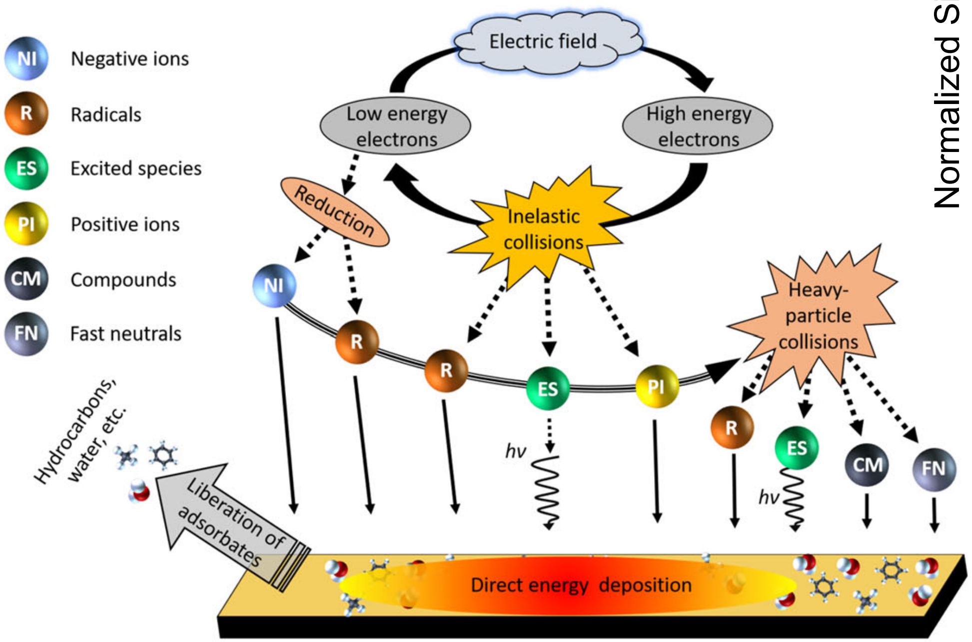


Aryana *et al.*, *Nat. Comm.* **13**, 1573 (2022)

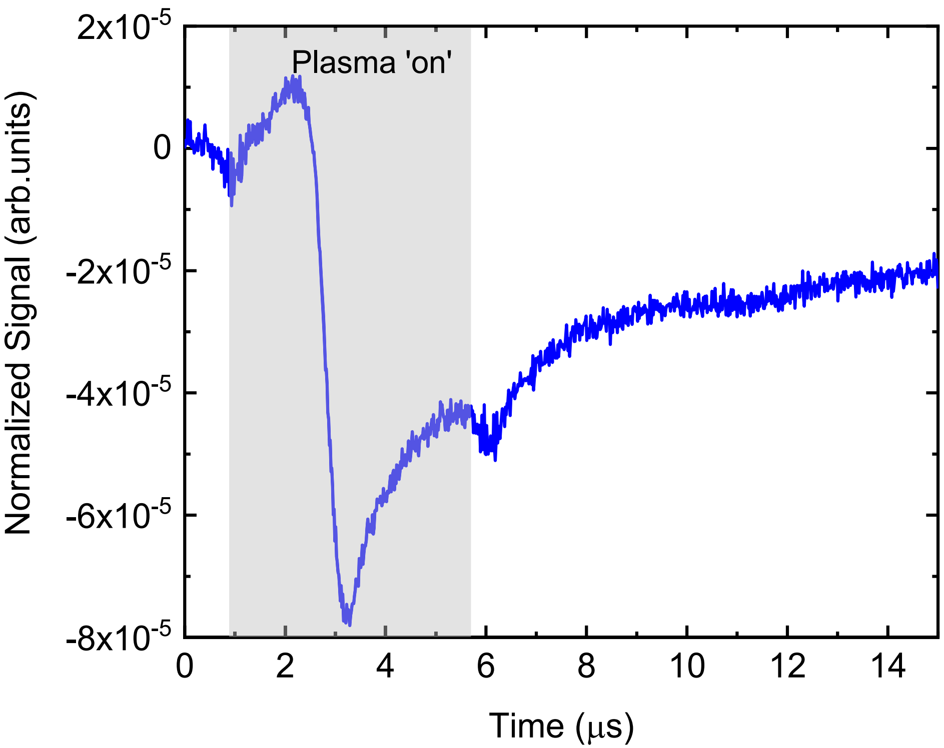
Plasma-surface interactions and heat transfer





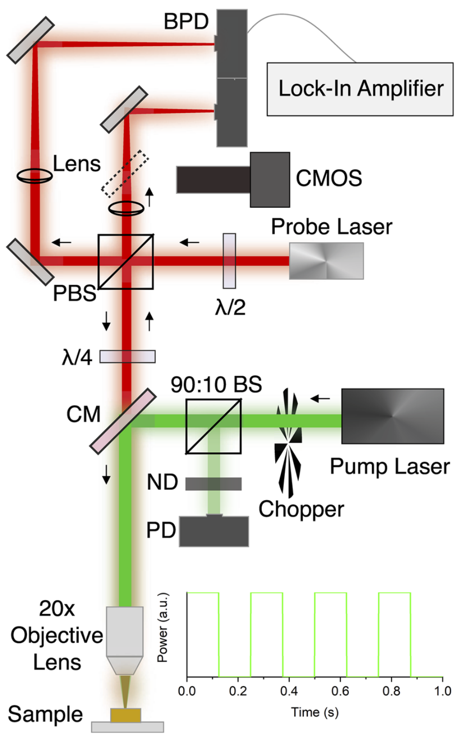


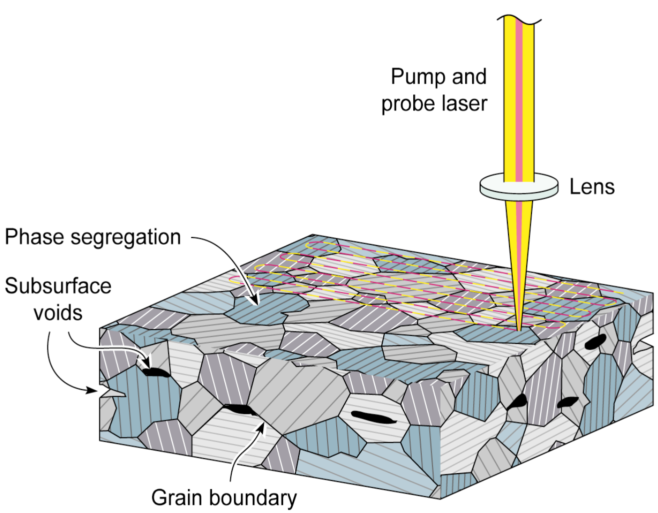
Plasma cooling!

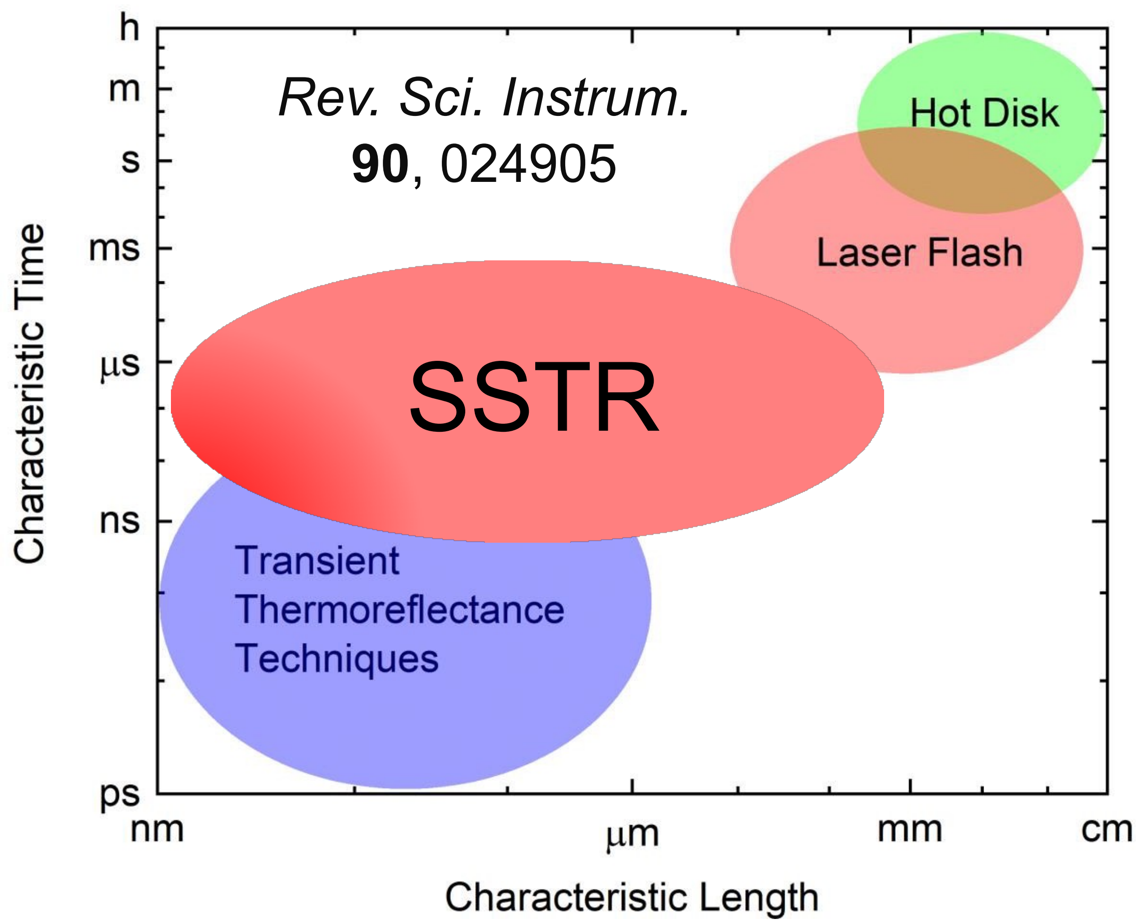


Tomko *et al.*, *Nat. Comm.* **13**, 2623 (2022)

But how do we measure nano to macro HX processes?







Spatially resolved thermoreflectance techniques for thermal conductivity measurements from the nanoscale to the mesoscale

Cite as: J. Appl. Phys. **126**, 150901 (2019); doi: 10.1063/1.5120310
Submitted: 17 July 2019 · Accepted: 29 September 2019 ·
Published Online: 16 October 2019

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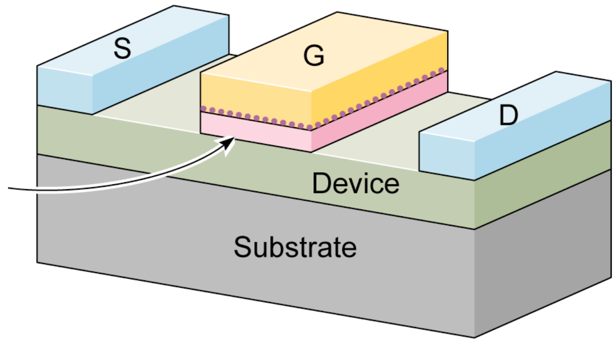
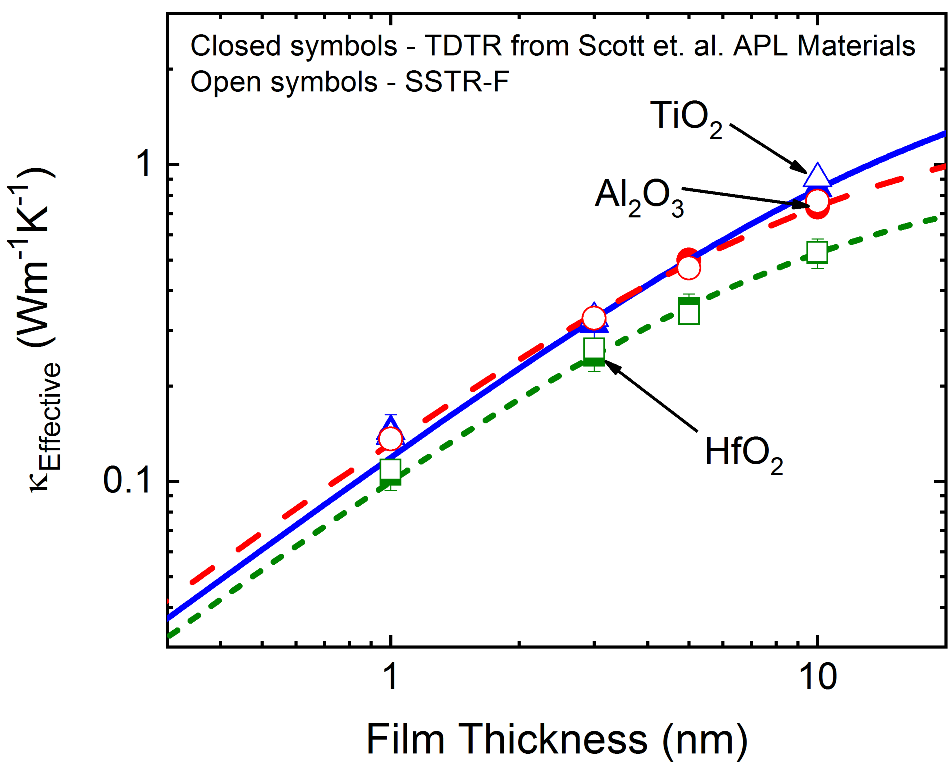
David H. Olson,[1] Jeffrey L. Braun,[1] and Patrick E. Hopkins[1,2,3,a)]

SSTR: Capabilities for thermal conductivity measurements

Thermal conductivity of dielectric films as thin as 1 nm



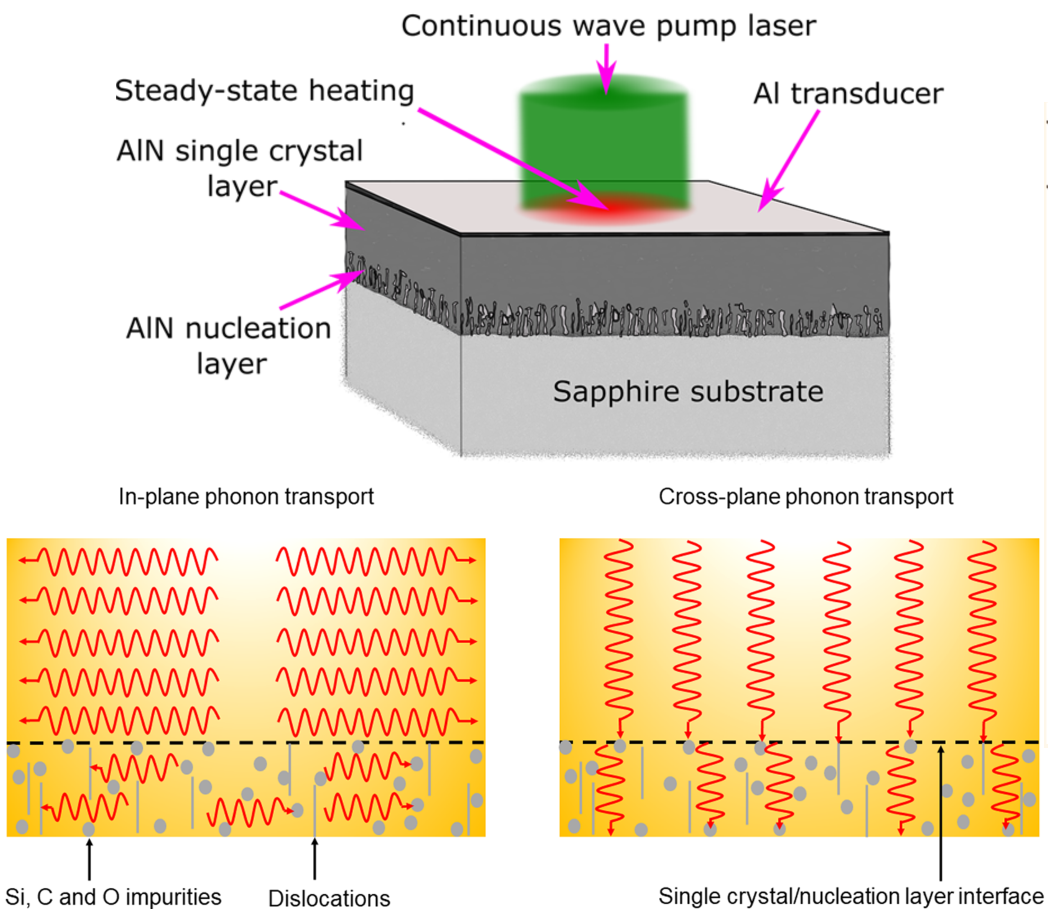


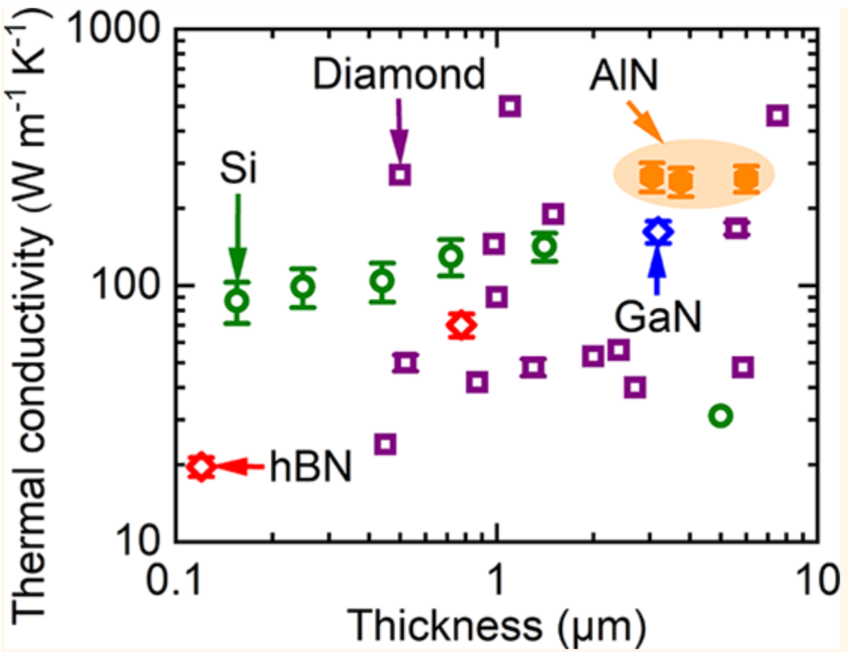
- Verified over three materials systems using SSTR-F
- Matches existing TDTR measurements
- Measuring resistance from interfaces and from material resistance in this case

APL Materials **6**, 058302 (2018)

SSTR: Capabilities for thermal conductivity measurements

In-plane thermal conductivity of thin films i.e., anisotropy effects in AlN thin films

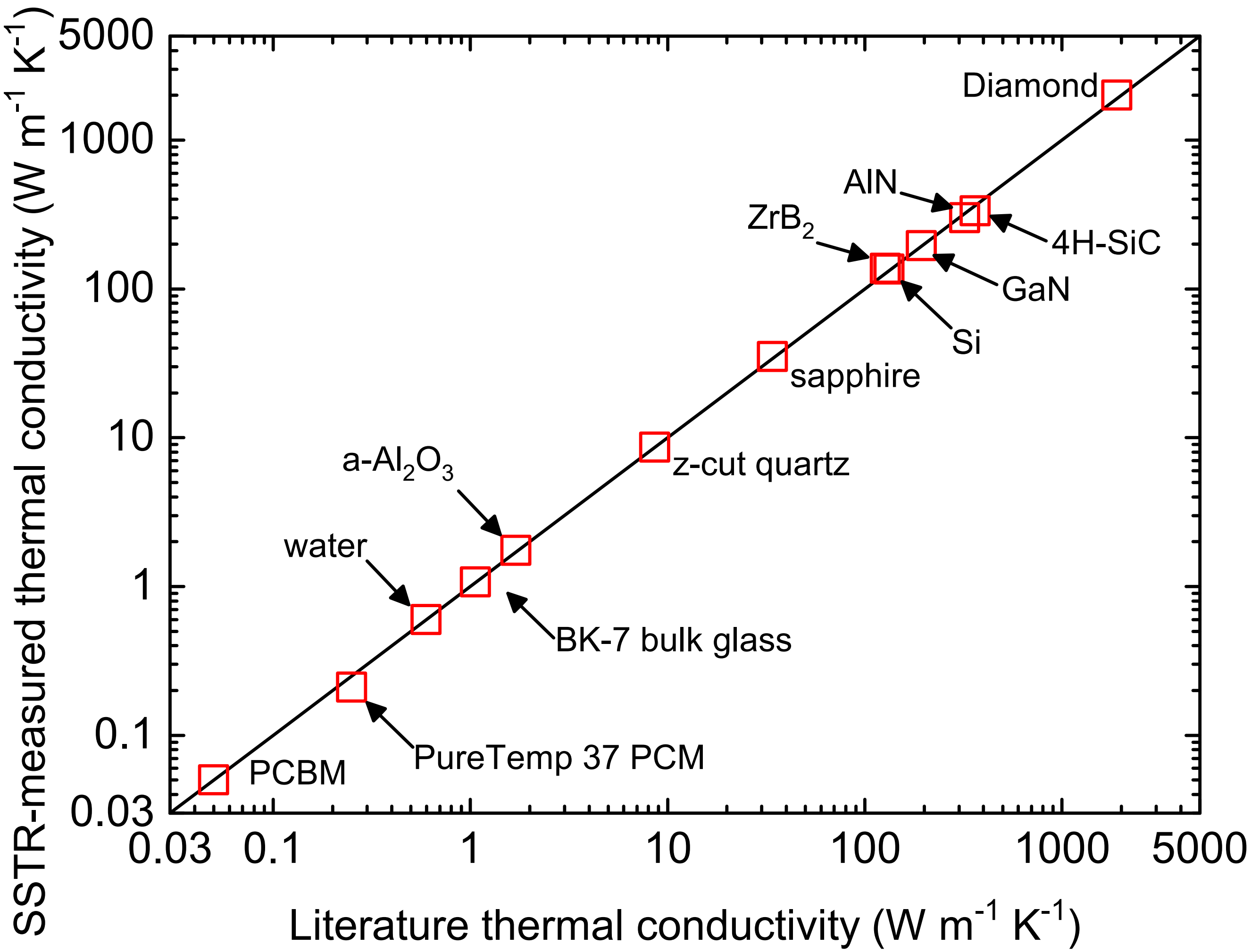




ACS Nano **15**, 9588

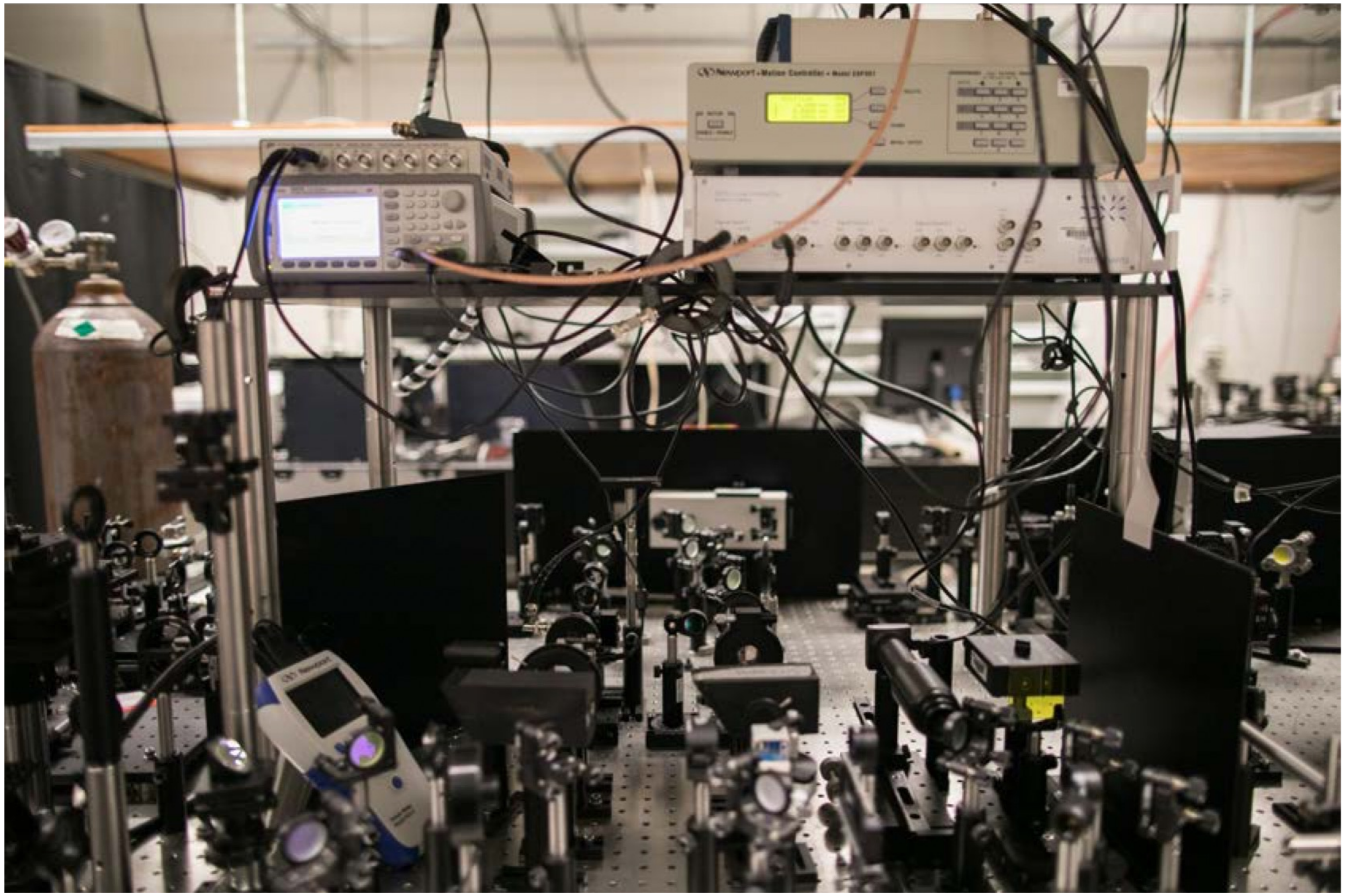
SSTR: Capabilities for thermal conductivity measurements

Extremely conductive (diamond) and insulative (PCBM) materials



SSTR-F: Recently commercialized for turn-key, fiber-optically integrated thermal conductivity microscope

The typical thermoreflectance set up

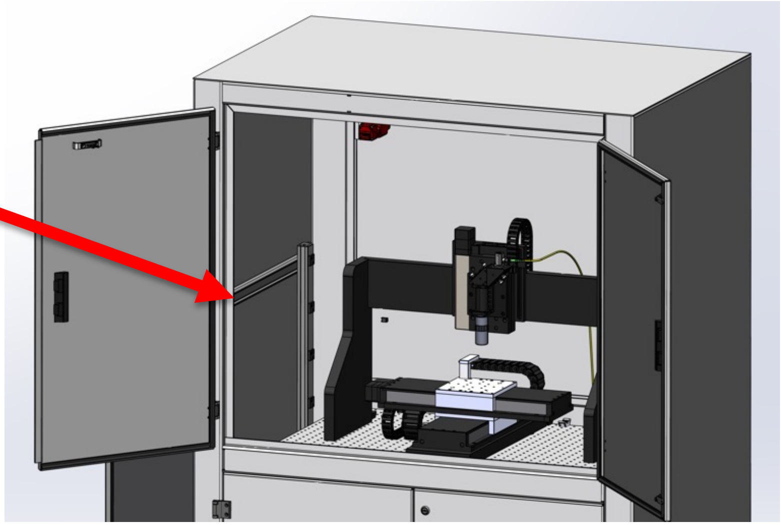


A LOT of optics, upkeep and expertise for analysis

SSTR-F: Commercialized for turn-key thermal conductivity microscope for bulk materials, thin films and interfaces

https://Laserthermal.com

LASER THERMAL



Laser Thermal, Inc. will be exhibiting at ALD/ALE 2022 next month!

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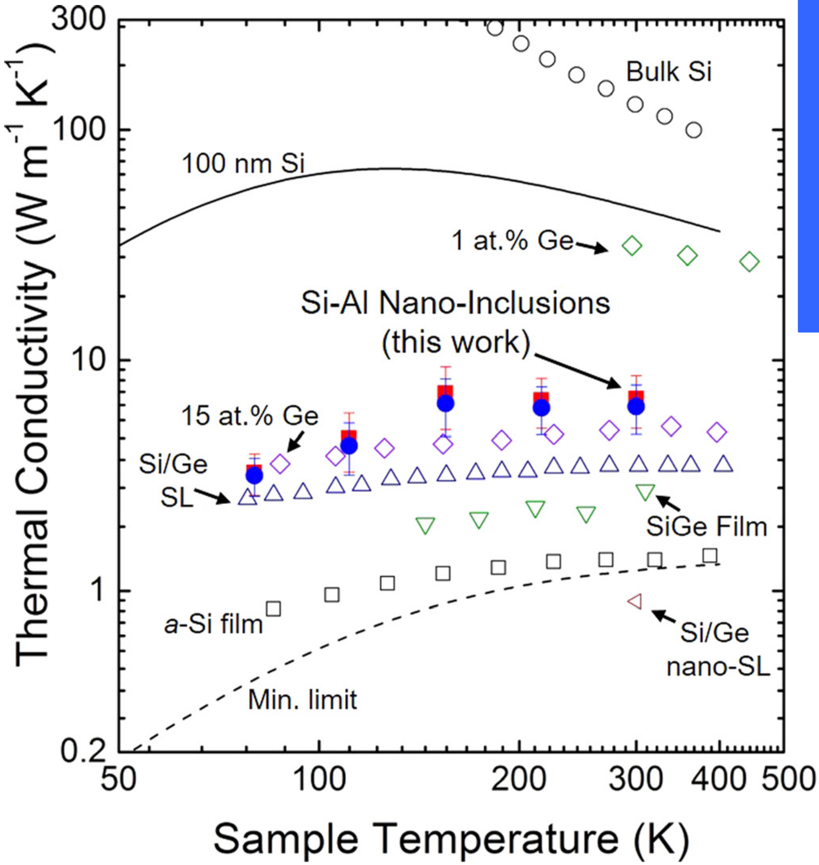
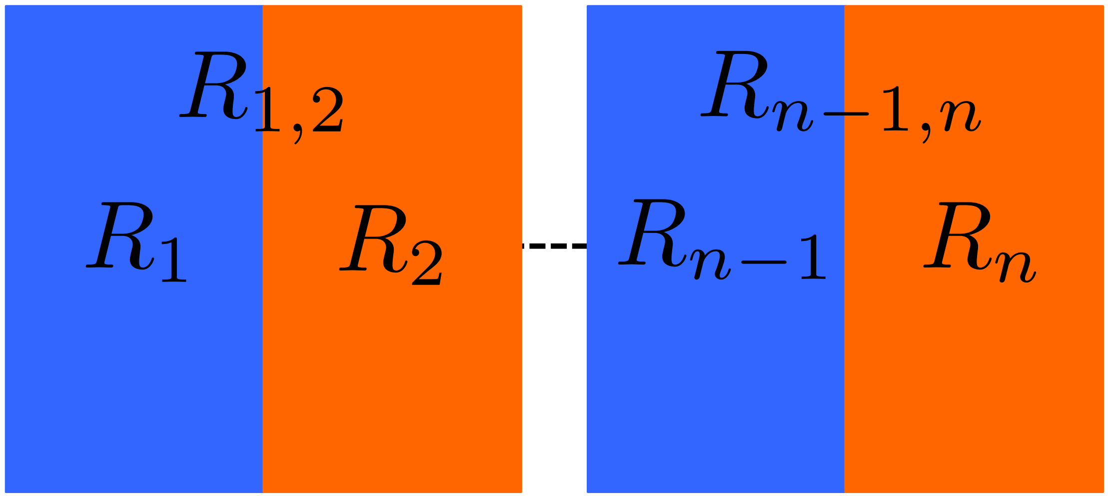
Phonon thermal conductivity in superlattices: incoherent



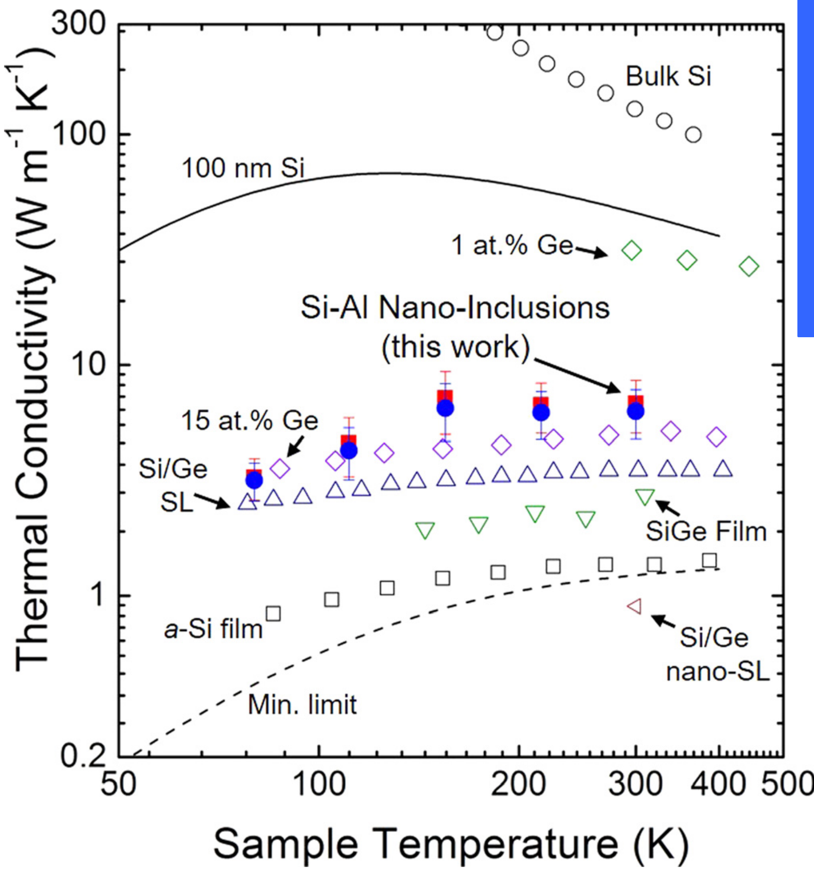
APL **112**, 213103



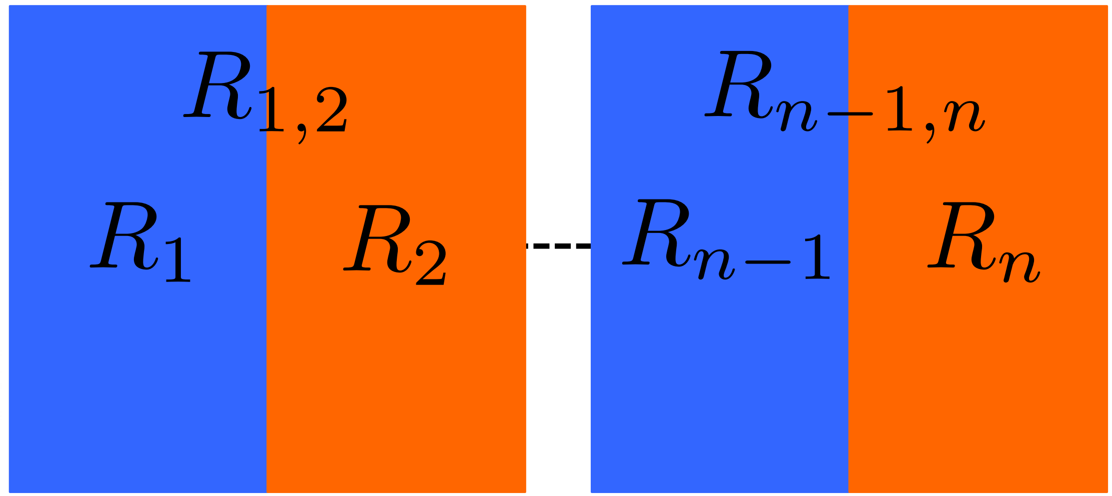
$$1/\kappa \propto 1/h = \sum_n R_j$$

Phonons scatter at every interface, and thus each interface offers a resistance to the overall thermal conductivity

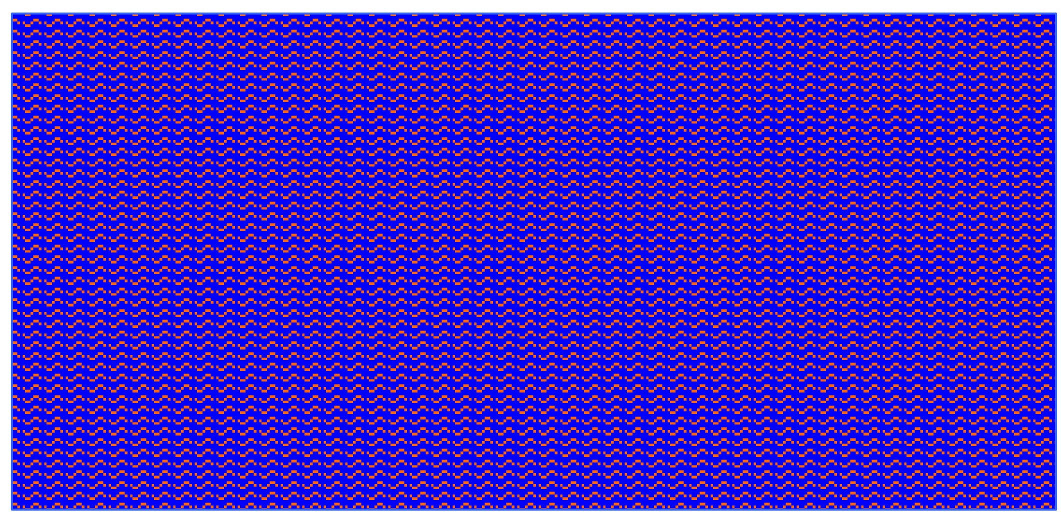
Phonon thermal conductivity in superlattices: coherent



APL **112**, 213103



What if layers are “linked”?
– coherent transport



The minimum thermal conductivity of superlattices

PHYSICAL REVIEW B VOLUME 25, NUMBER 6 15 MARCH 1982

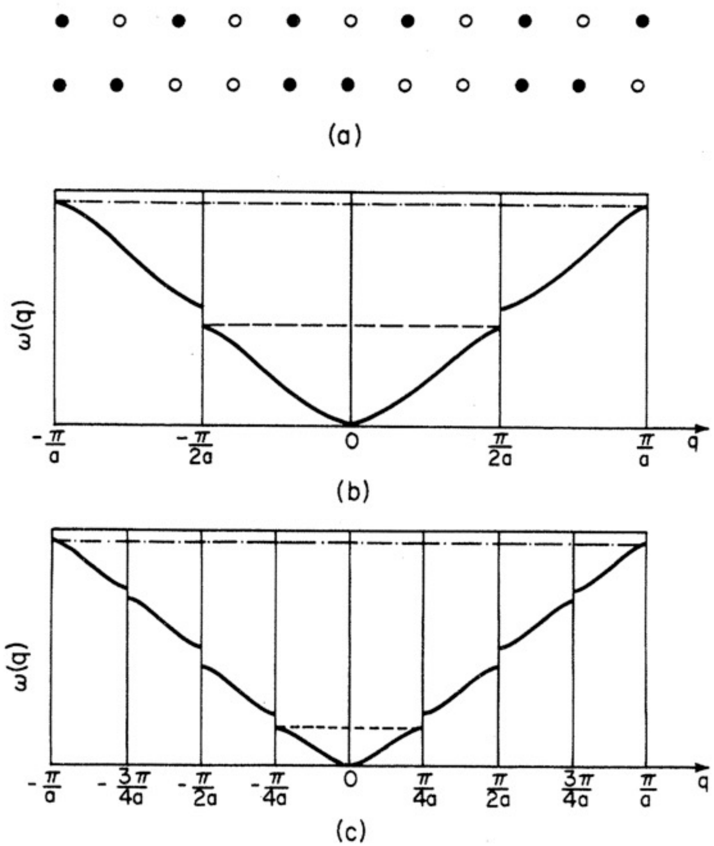
Thermal conductivity of superlattices

Shang Yuan Ren* and John D. Dow
Department of Physics and Coordinated Science Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
(Received 21 September 1981)

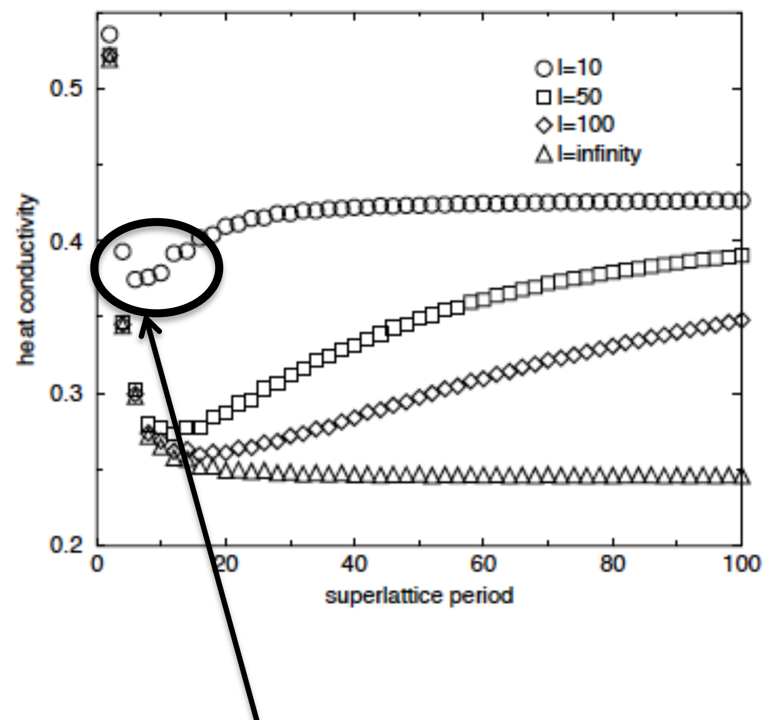
VOLUME 84, NUMBER 5 PHYSICAL REVIEW LETTERS 31 JANUARY 2000

Minimum Thermal Conductivity of Superlattices

M. V. Simkin and G. D. Mahan
Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1200 and Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831
(Received 23 July 1999)



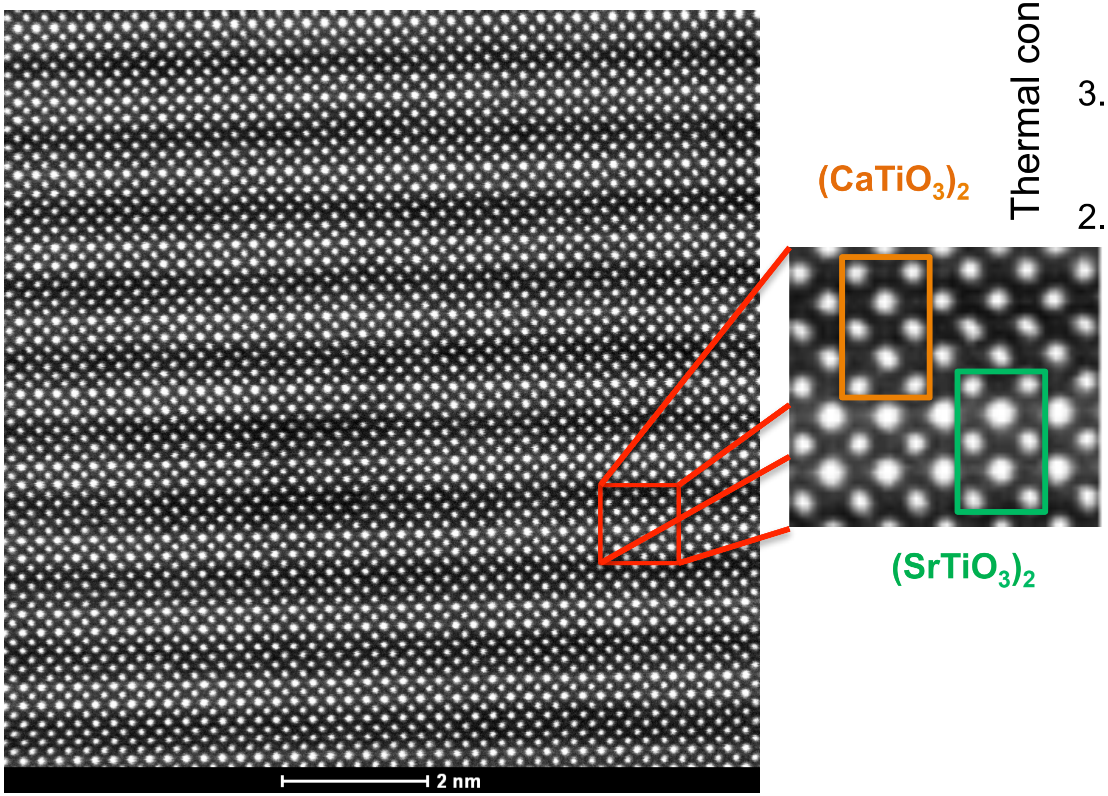
Interfacial periodicity can lead to "mini-band" formation

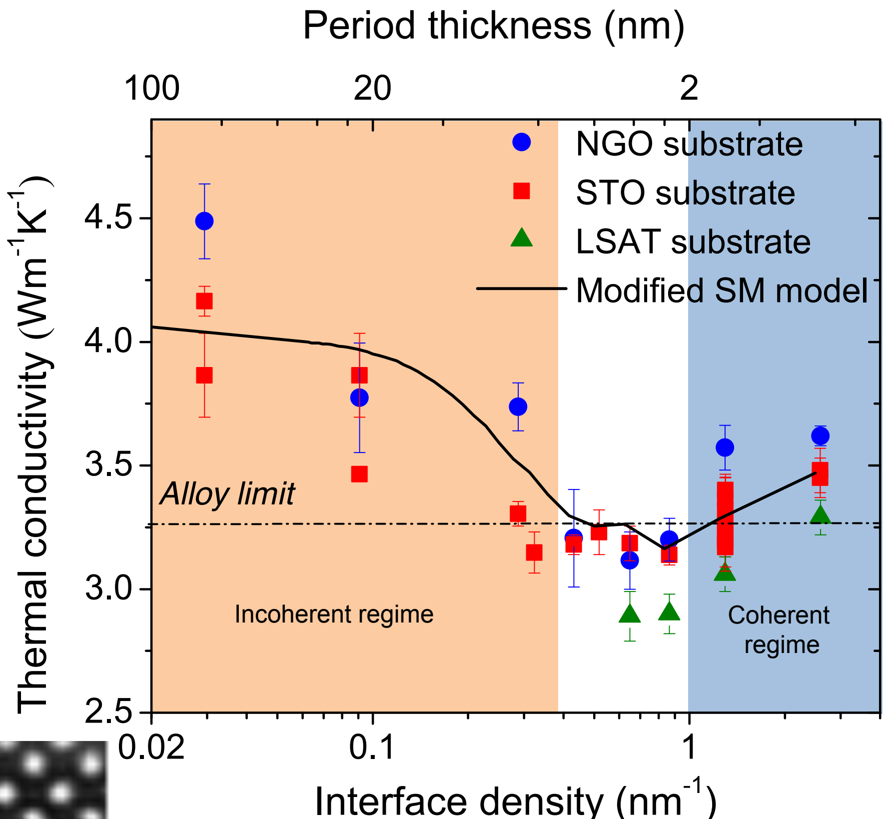


Mini-band formation leads to a minimum in the superlattice thermal conductivity

Experimental evidence of minimum thermal conductivity

Nature Materials **13**, 168 (2013)

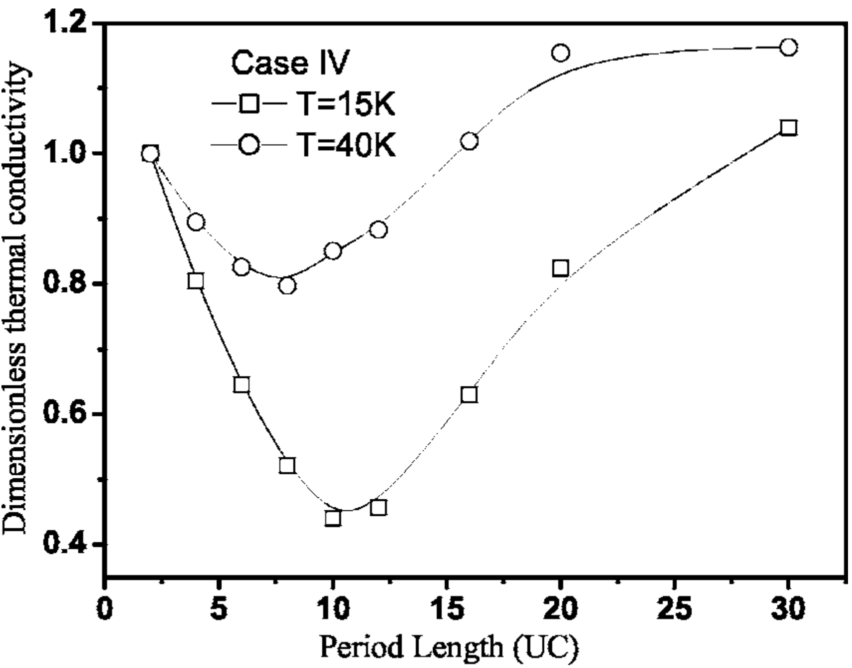


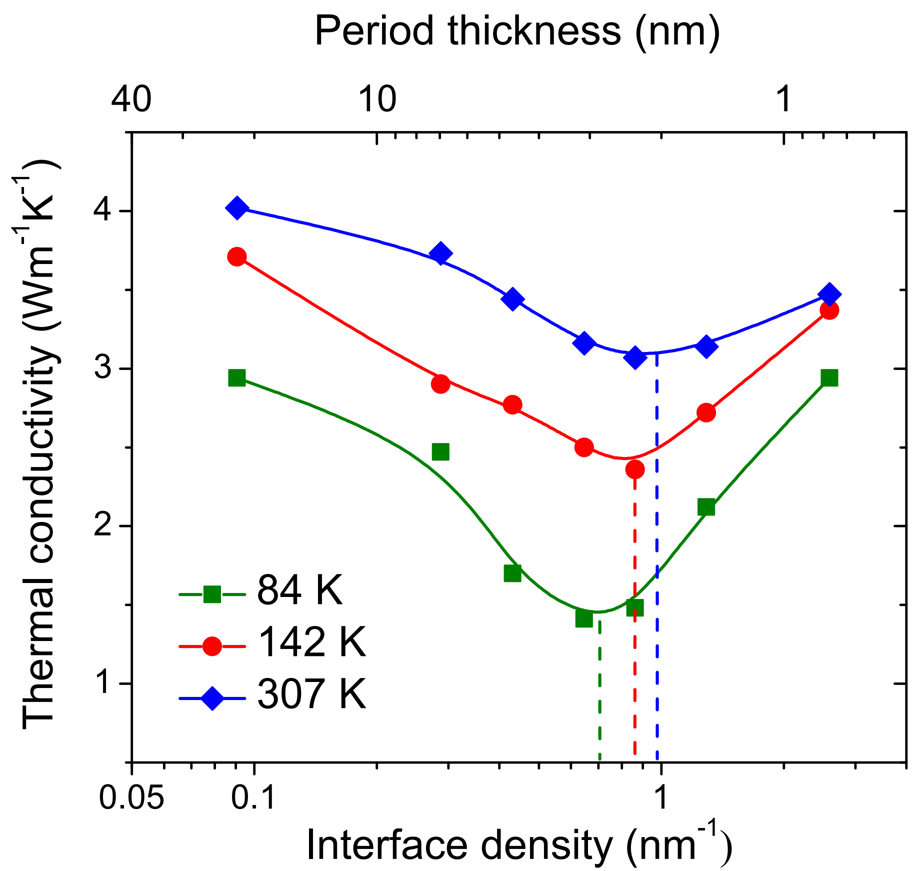


Growth PLD:
J. Ravichandran
A. Yadav
R. Ramesh
A. Majumdar

Experimental evidence of minimum thermal conductivity

- More pronounced minimum at low T, thermal conductivity measurements show trends of mini-band formation
- MD simulation (left), mini-band = phonon bandgap (PRB **72**, 174302)

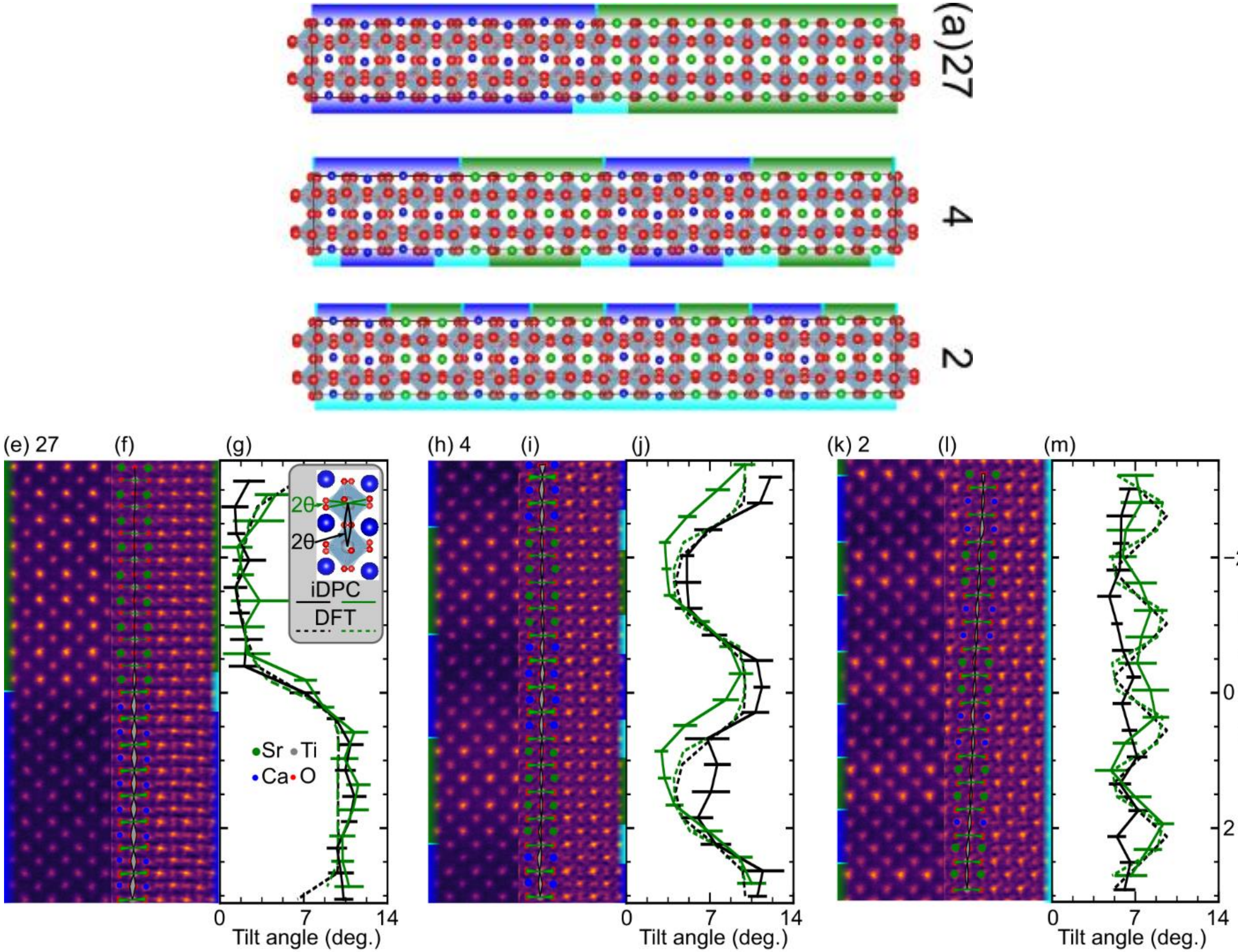




SL design to manipulate coherent phonon transport

Ravichandran *et al. Nature Materials* **13**, 168 (2013)

Experimental evidence of phonon coherence



Hoglund *et al.* *Nature* **601**, 556 (2022)

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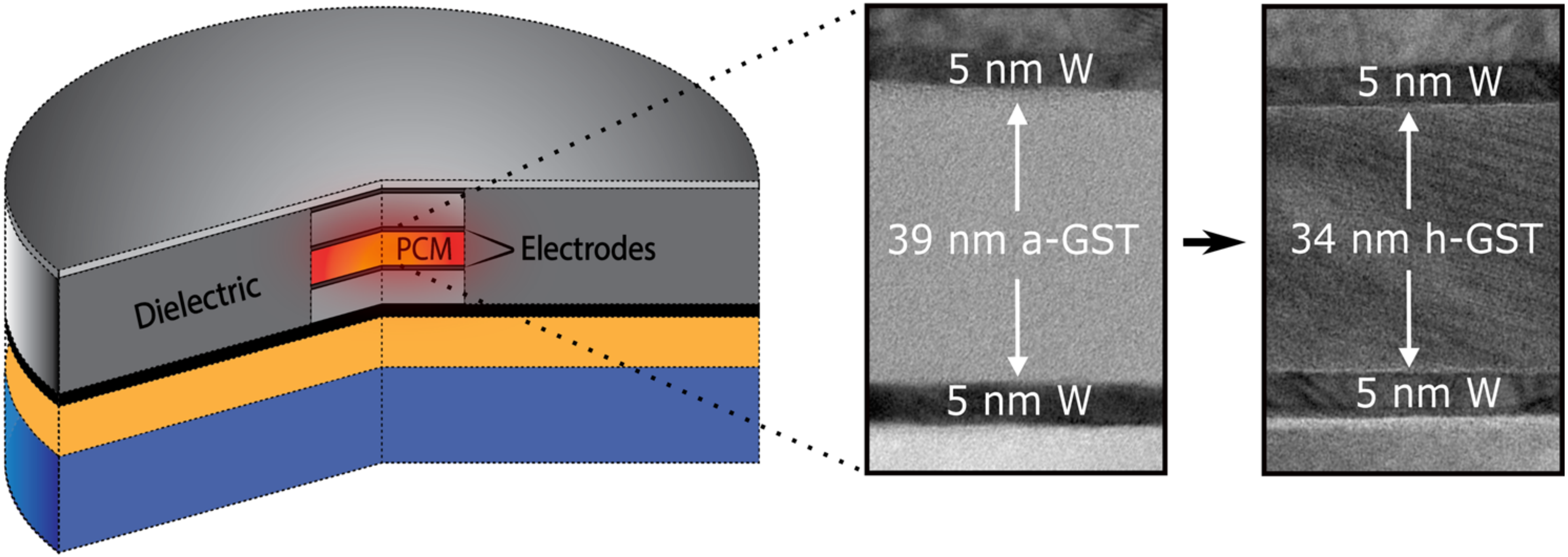
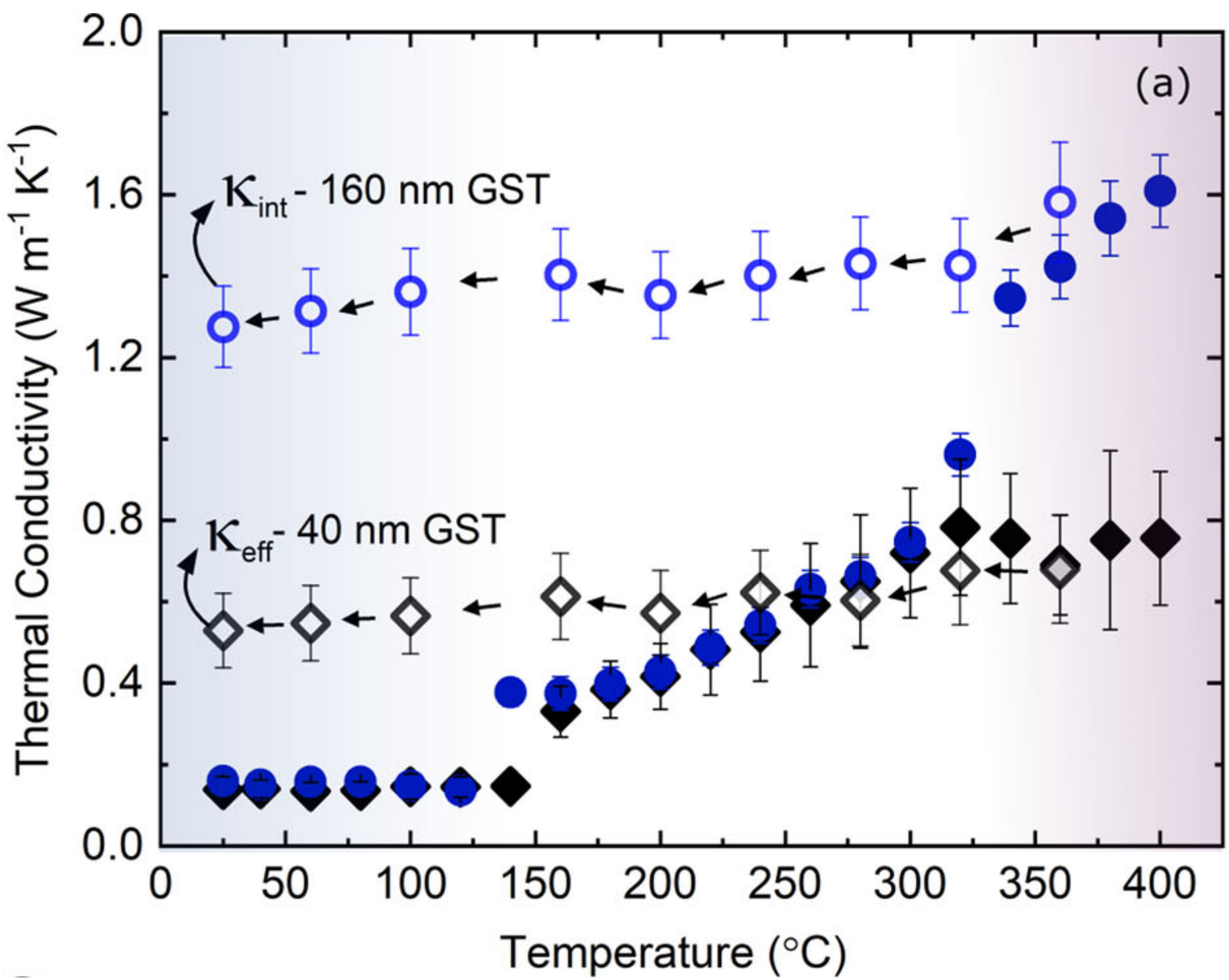
Heat conduction processes in ultrathin GST



What happens as the thickness of the GST decreases down to length scales of electron and phonon mean free paths?

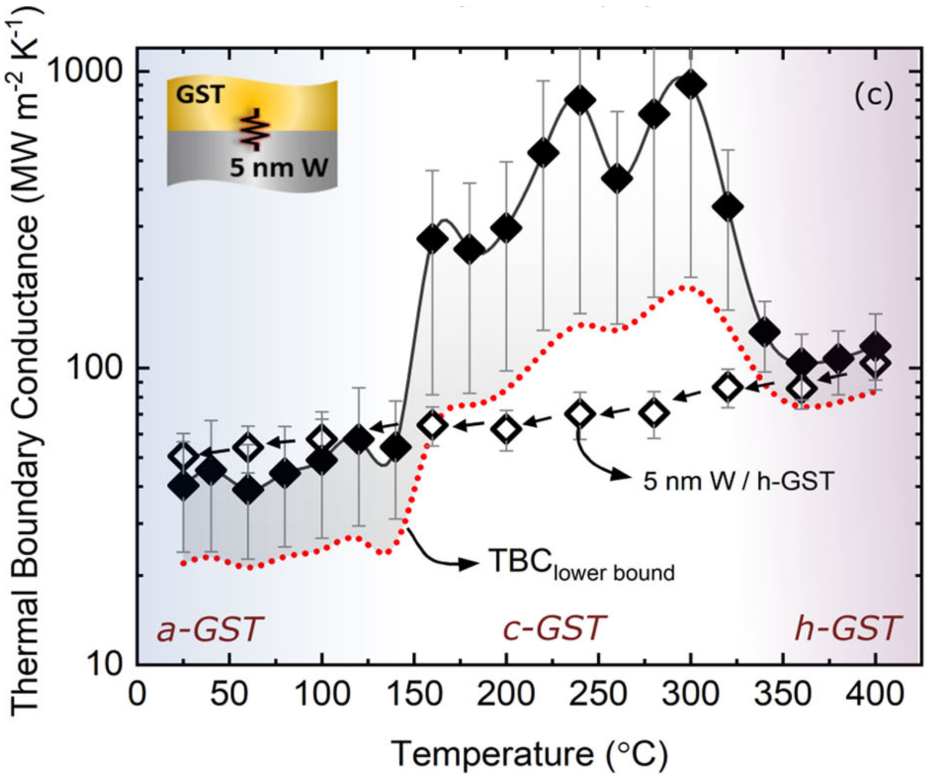
Aryana *et al. Nature Comm.* **12**, 774 (2021)

Heat conduction processes in ultrathin GST



Aryana *et al. Nature Comm.* **12**, 774 (2021)

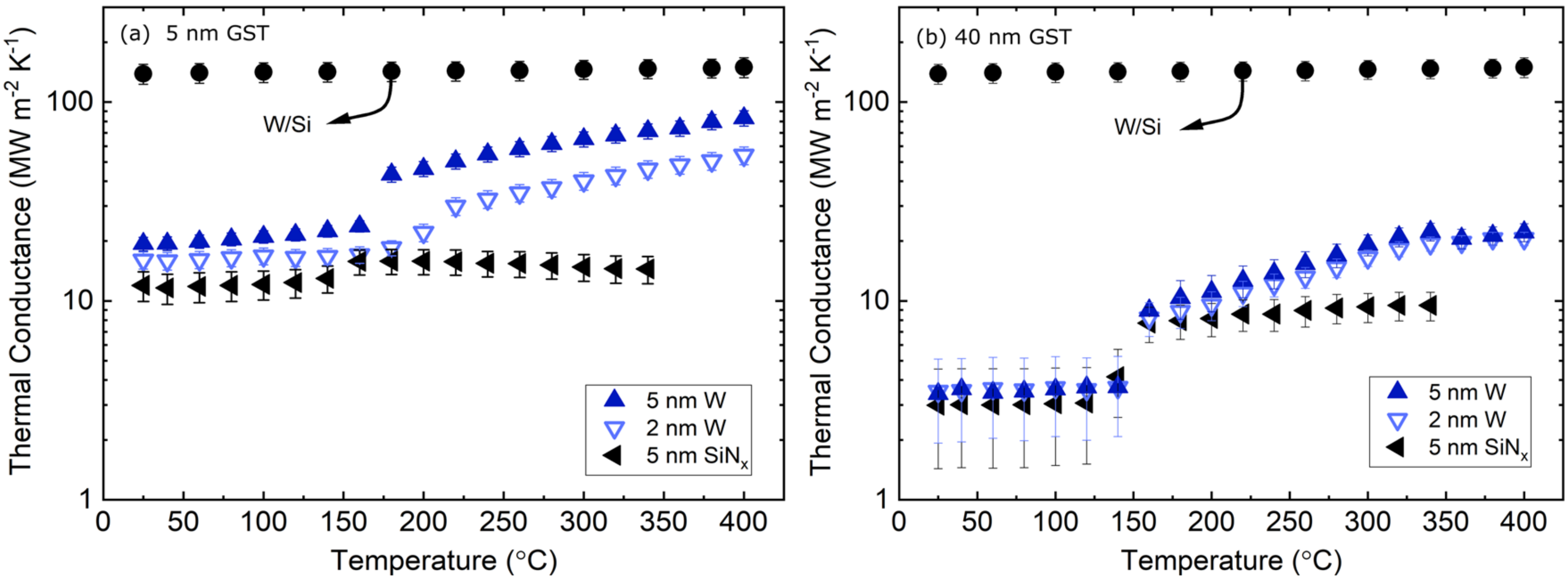
Phase dependence thermal boundary conductance



- Thermal boundary conductance across contact interfaces drive overall thermal transport as thickness decreases
- TBC dependent on GST phase, much like κ

Aryana *et al. Nature Comm.* **12**, 774 (2021)

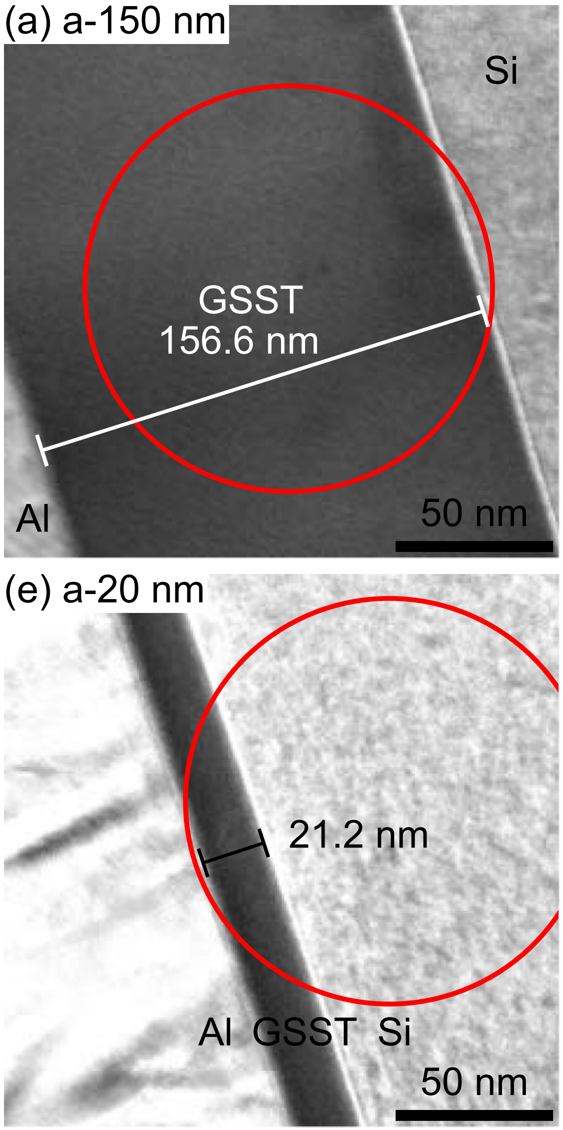
Ballistic electron transport across GST

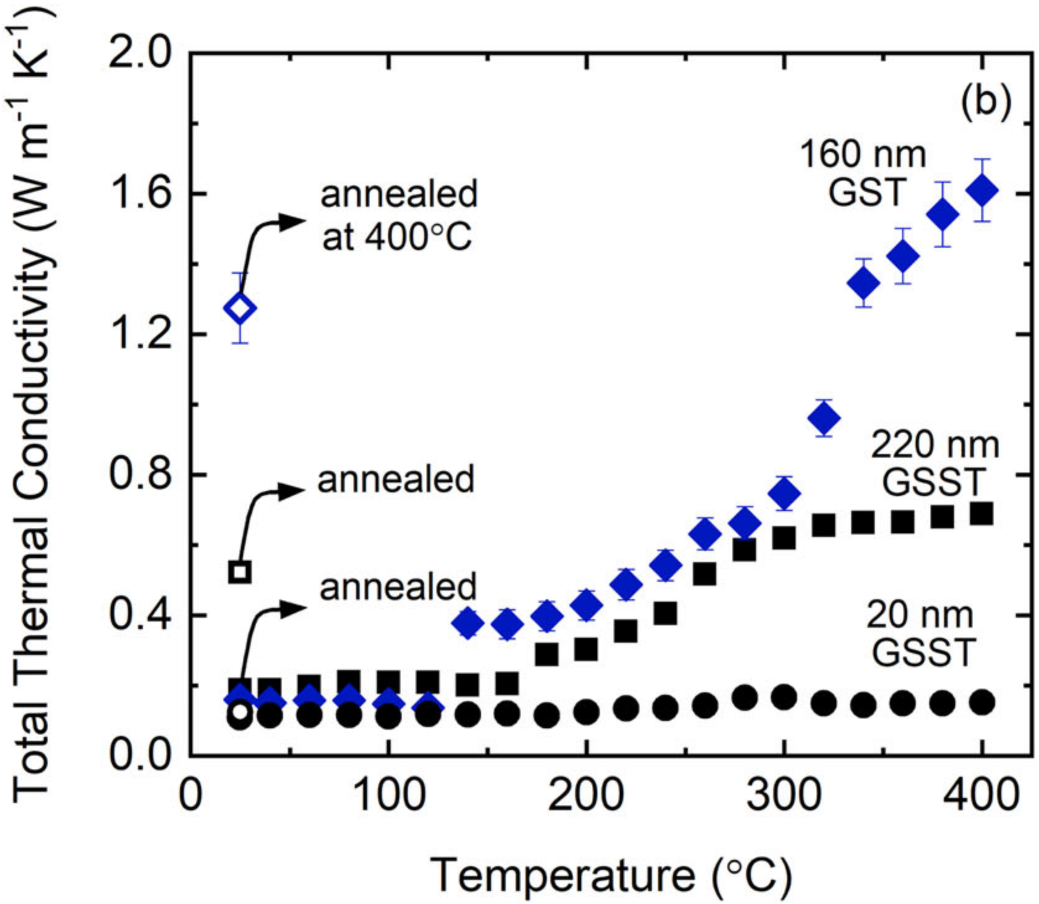


- Overall conductance *higher* for thin GST film (5 nm)
- Ballistic thermal conductance of electrons from contact to contact (i.e., the electrons don't "see" the GST and it's just a metal/metal TBC)

Aryana *et al. Nature Comm.* **12**, 774 (2021)

Suppressing electron transport: Add in Se! (GSST)





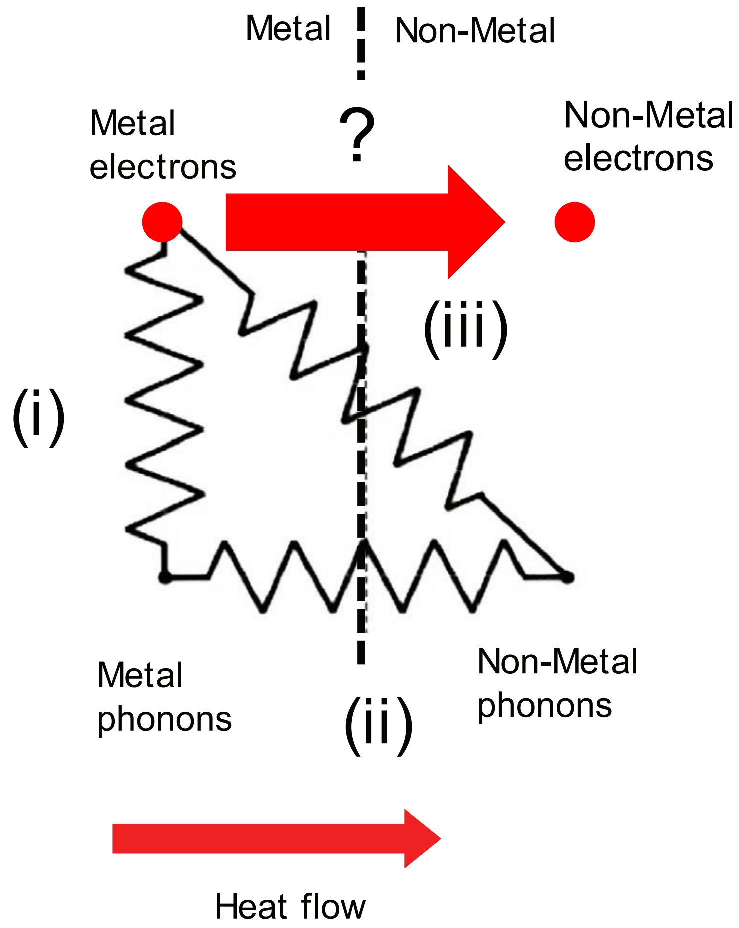
Aryana *et al. Nature Comm.* **12**, 7187 (2021)

Outline

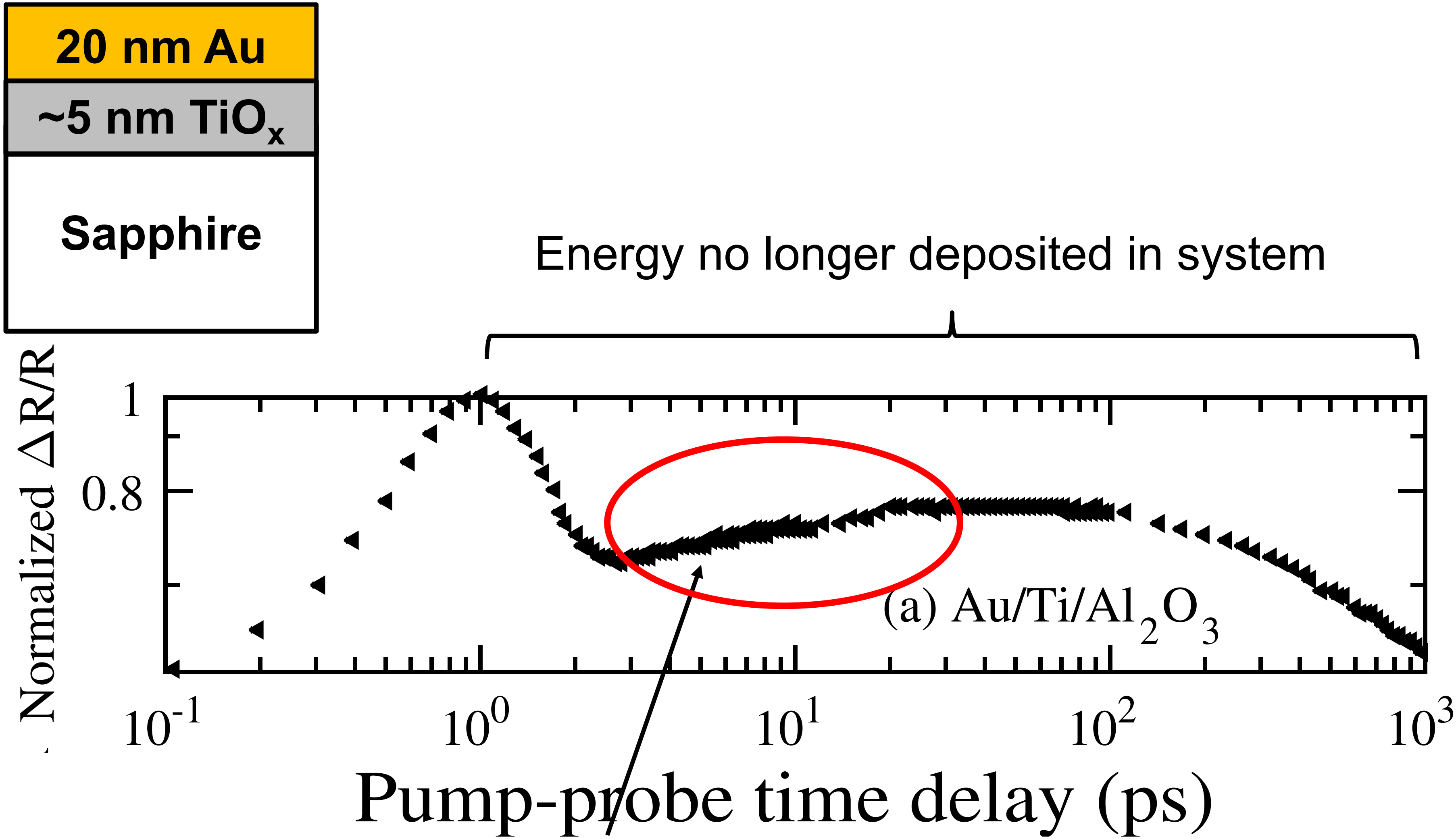
Theme: Atomic properties at interfaces can change the nature and behavior of heat transfer via phonons, electrons and photons

- Thermal boundary conductance
  - Overview
  - How we measure (thermoreflectance)
- Phonon coherence in the thermal conductivity of oxide superlattices
- Electron and phonon thermal resistance at interfaces in thin film phase change materials (GST, GSST)
- Interfacial heat transfer control of the IR properties of solids: long lived plasmon modulation

Electron energy transfer at metal/nonmetal interfaces



Ultrafast pump-probe to measure EP coupling

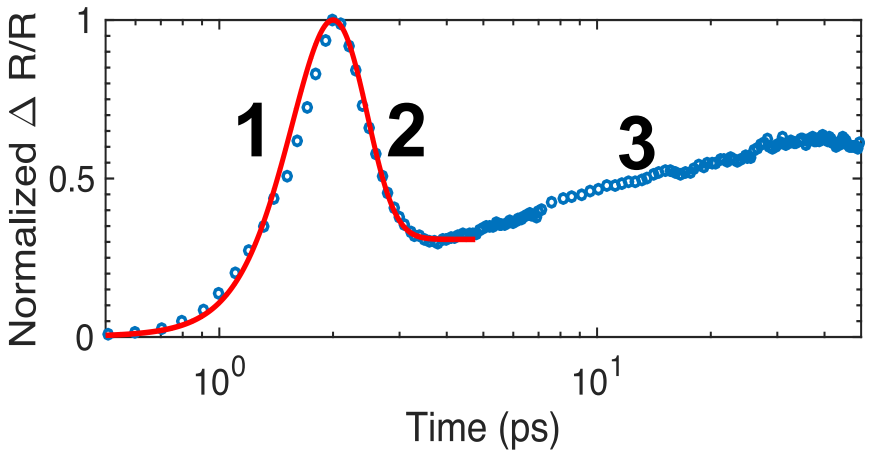


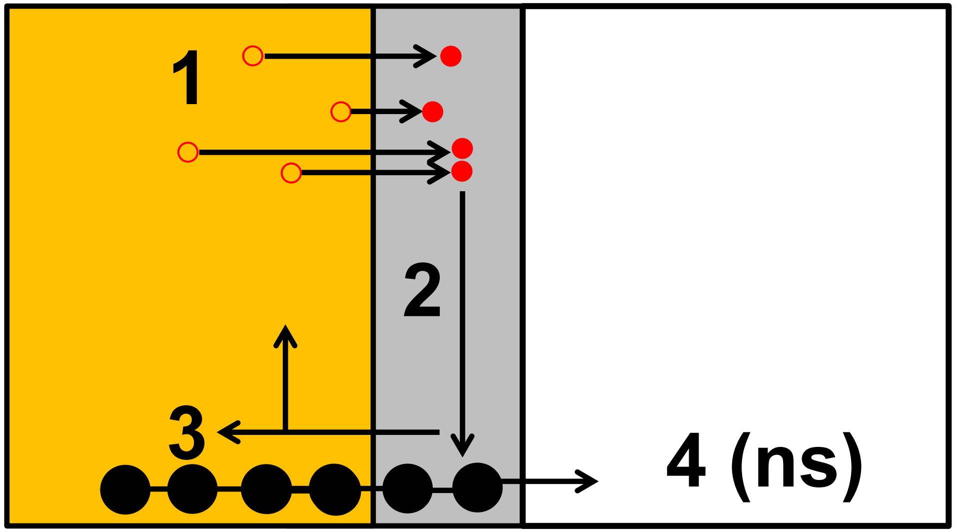
So why does temperature at surface increase when no energy is deposited in the system?

JAP **117**, 105105

Ballistic thermal injection

- Excited electrons in metal from pulse do not thermalize with lattice and deposit their energy to lattice in sub-surface layer
- Ballistic transport of electron energy through gold into titantium

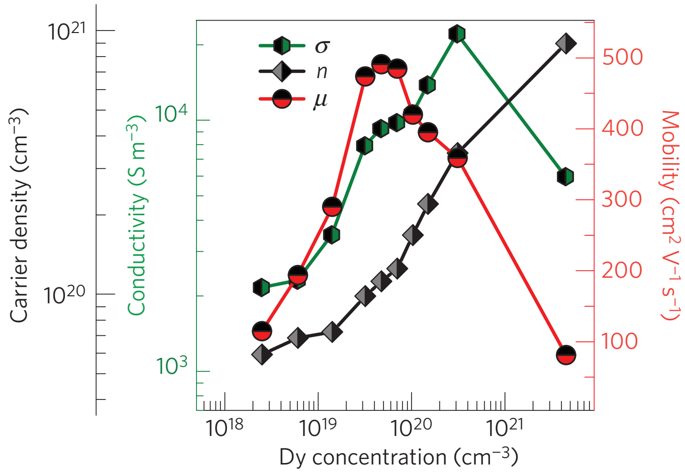


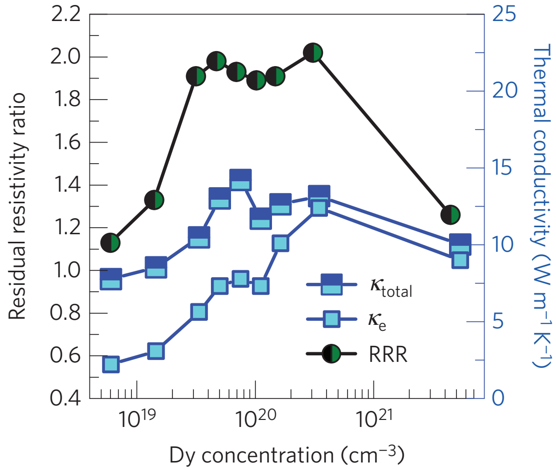


<u>When would we see this effect?</u>

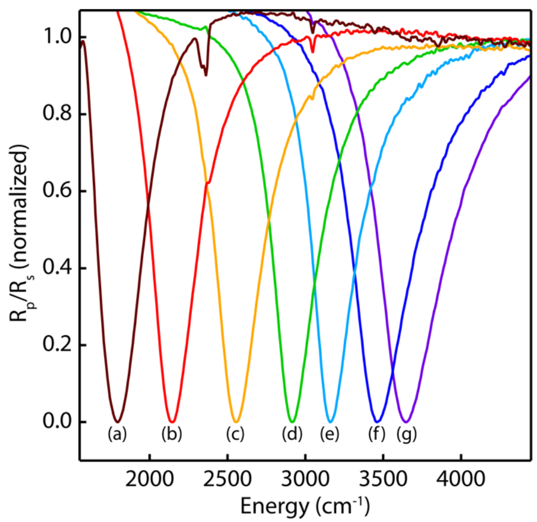
1. Metal/metal or metal/non-metal interfaces with large differences in electron-phonon coupling factor
2. Films with thicknesses less than electron-phonon mean free path
3. Interfaces with very little electron-electron thermal resistance

CdO – a gateway for mid-IR plasmonics





Nat. Mat. **14**, 414
Appl. Phys. Lett. **108**, 021901

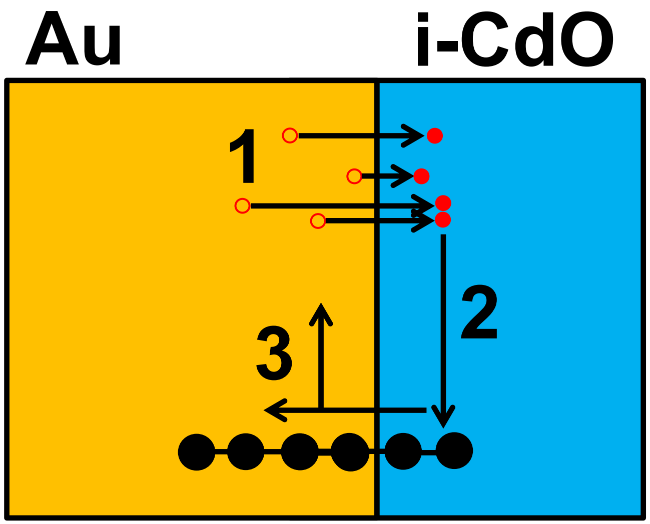


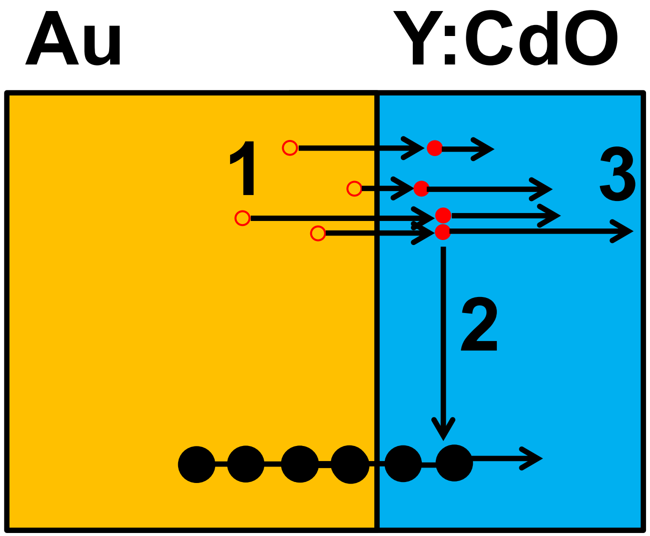
ACS Photonics **4**, 1885

- Large electron mobility in CdO results in large electronic thermal conductivity
- Doping concentration tunes electronic conductivity and IR absorption

Nonequilibrium processes at Au/CdO interfaces

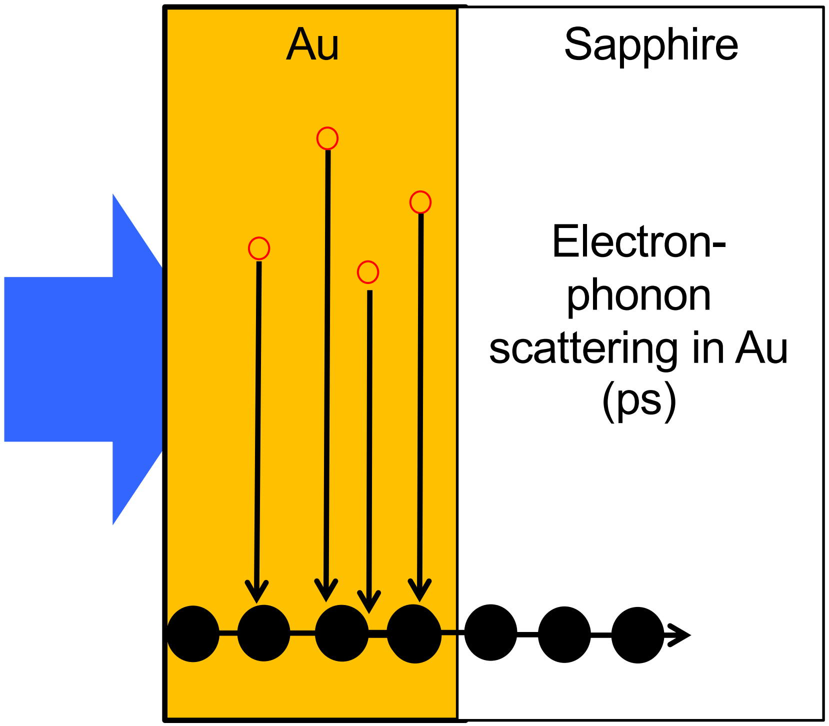
Doping will control electron-electron TBC and electron thermal conductivity in CdO, vary “back heating”

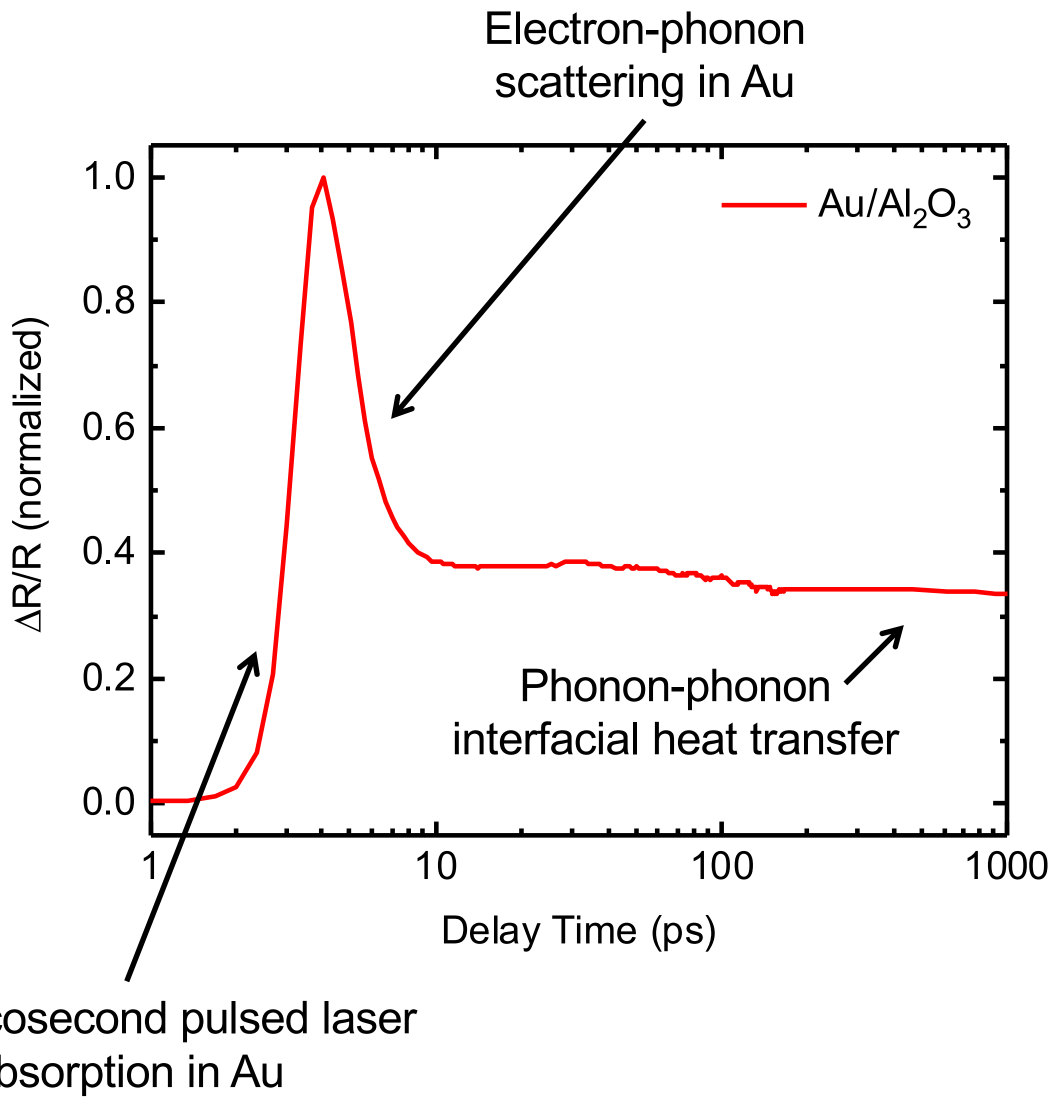




Tomko *et al. Nature Nano.* **16**, 47 (2021)

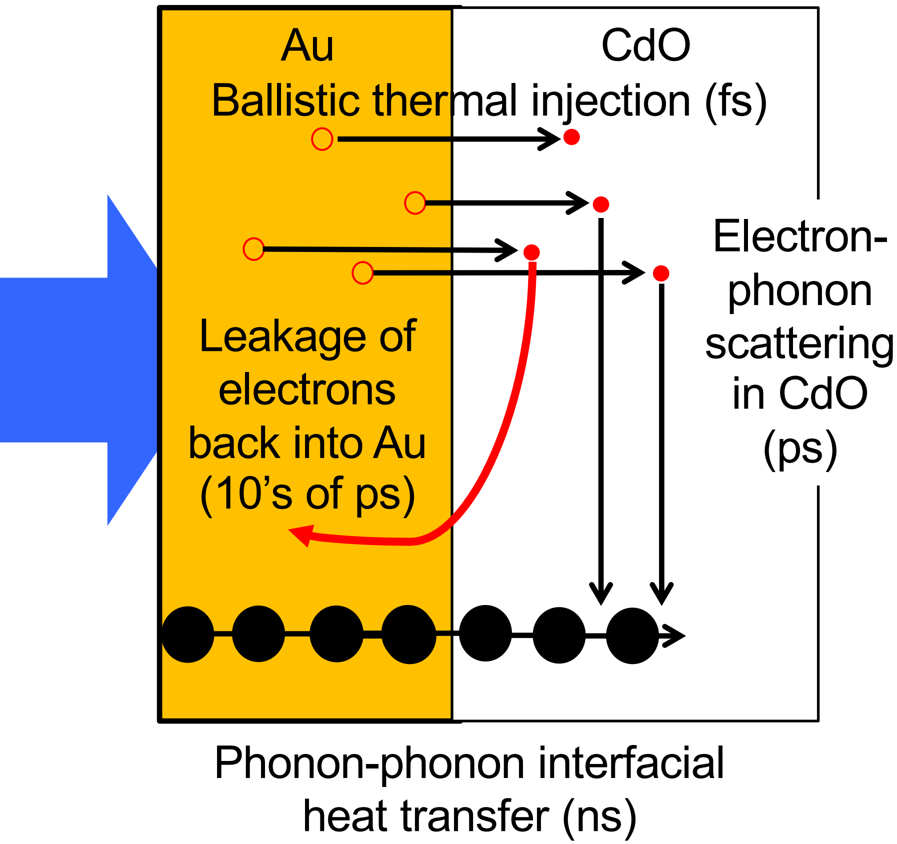
Nonequilibrium processes at Au/CdO interfaces

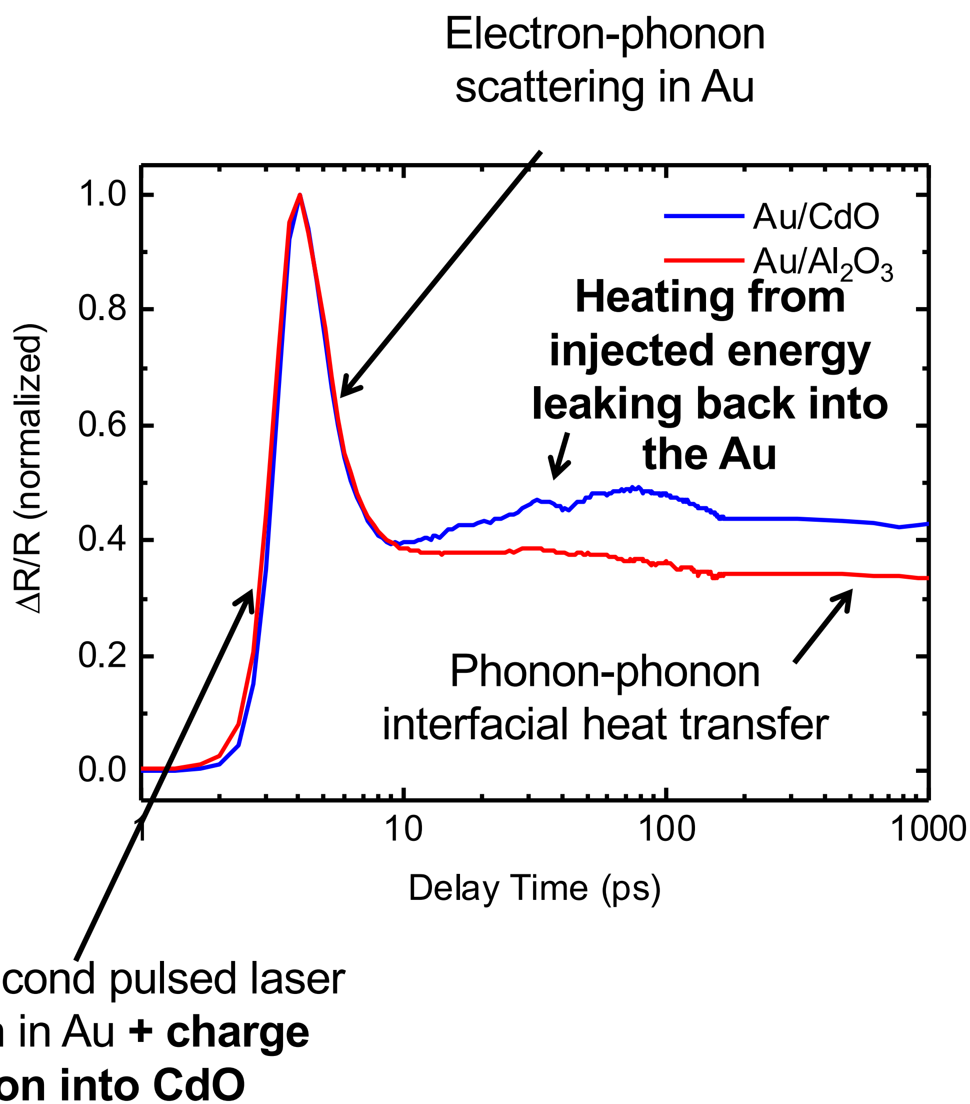




Tomko *et al. Nature Nano.* **16**, 47 (2021)

Nonequilibrium processes at Au/CdO interfaces





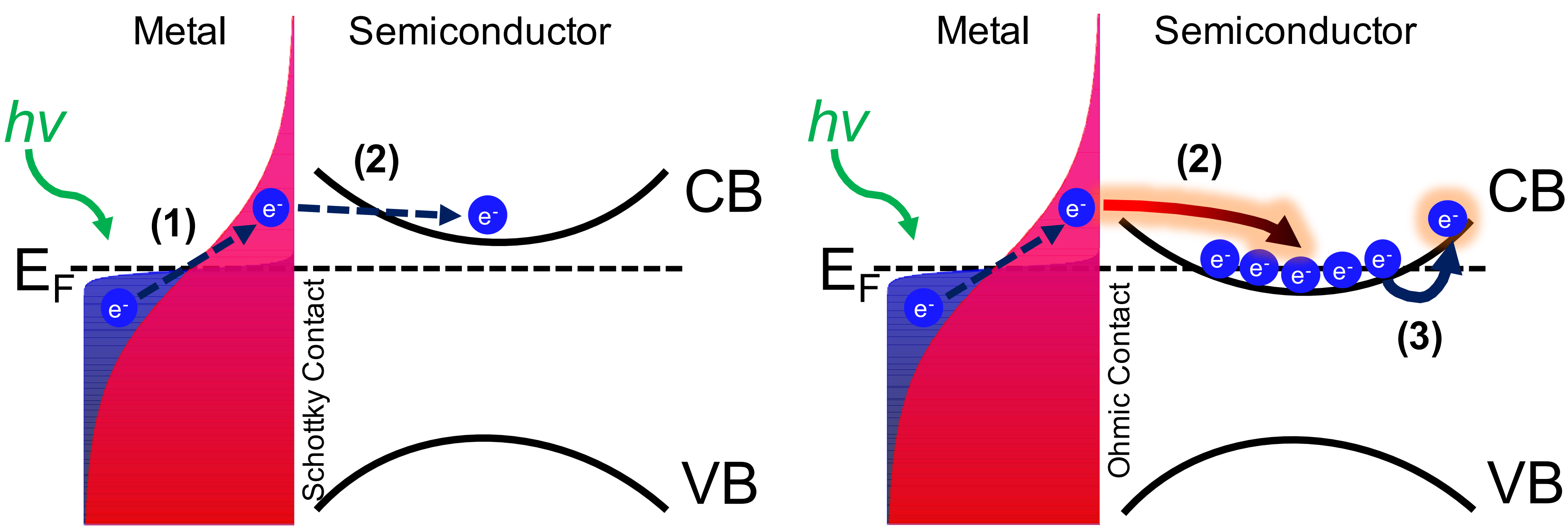
Tomko *et al. Nature Nano.* **16**, 47 (2021)

Ballistic thermal injection

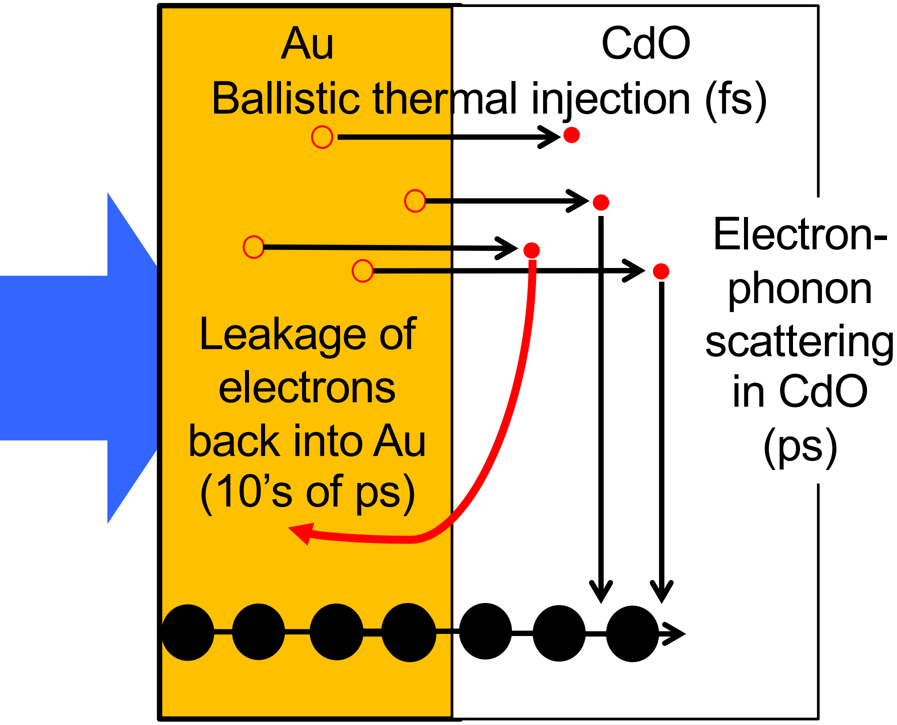
- Can enable a "transient thermal diode" effect
- Energy easily transmitted across interface when traveling ballistically
- Slowly "goes back" across the interface when diffusive
- Is this just hot electron injection (charge)?
  - Too slow of process
  - Can further rule this out by monitoring CdO plasmon response

a) Hot electron injection (Charge transfer)

b) Ballistic thermal injection (Energy transfer)



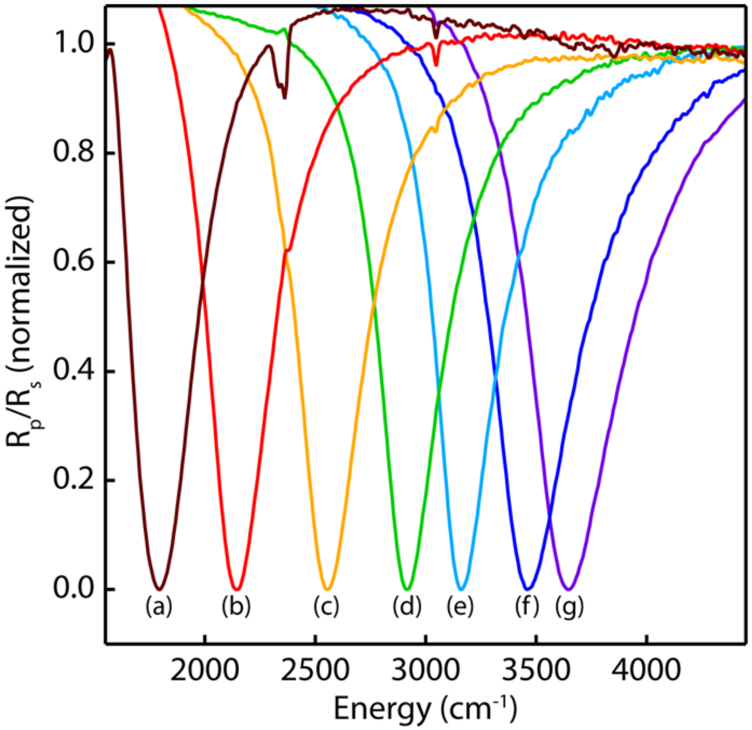
Nonequilibrium electrons to control CdO plasmons



Phonon-phonon interfacial heat transfer (ns)

+

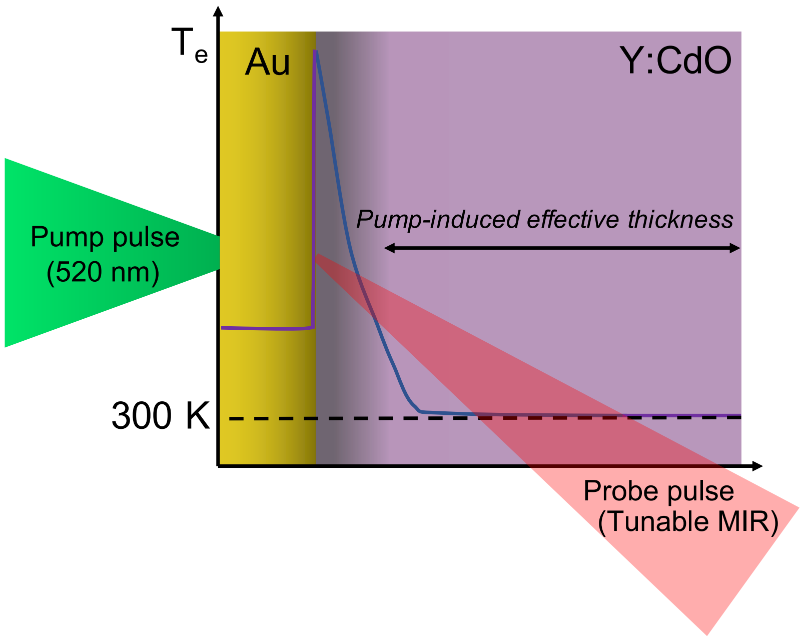
5 μm 3.3 μm 2.5 μm



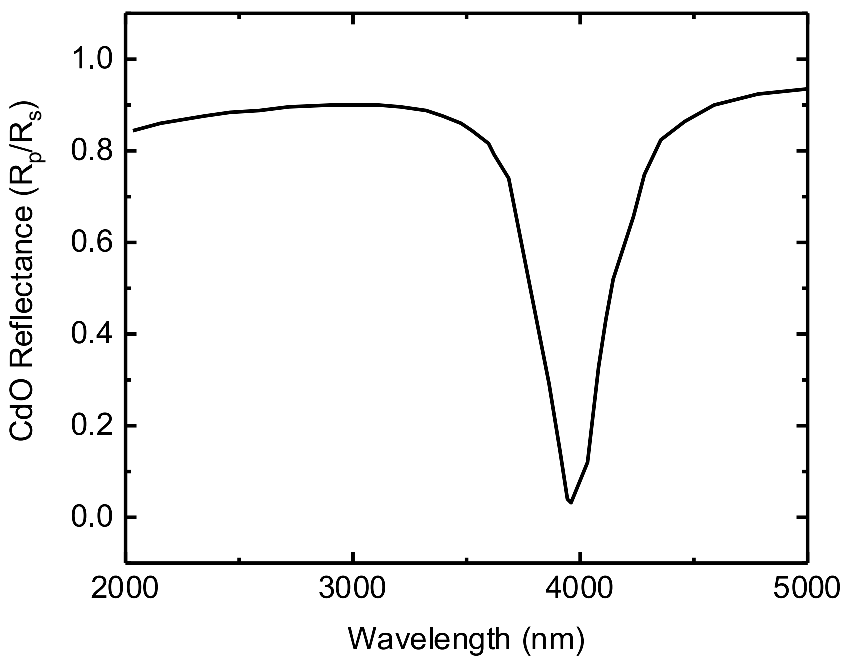
Increasing carrier concentration

Pump electrons in Au, probe plasmon in CdO

How is the IR plasmon response of CdO impacted by ballistic thermal injection?



Au/CdO/sapphire absorption response

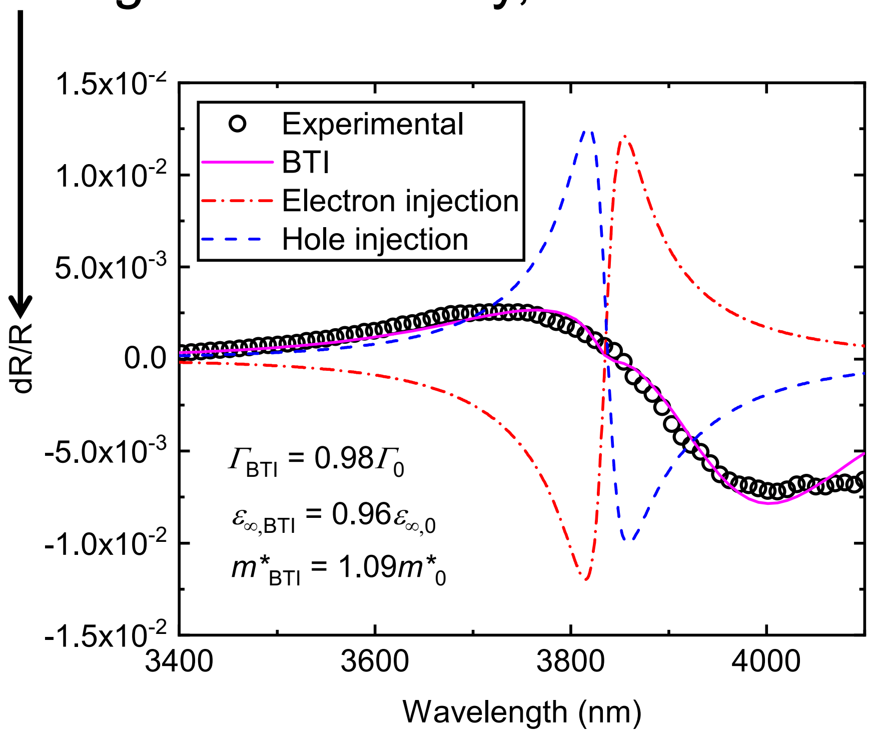


Tomko *et al. Nature Nano.* **16**, 47 (2021)

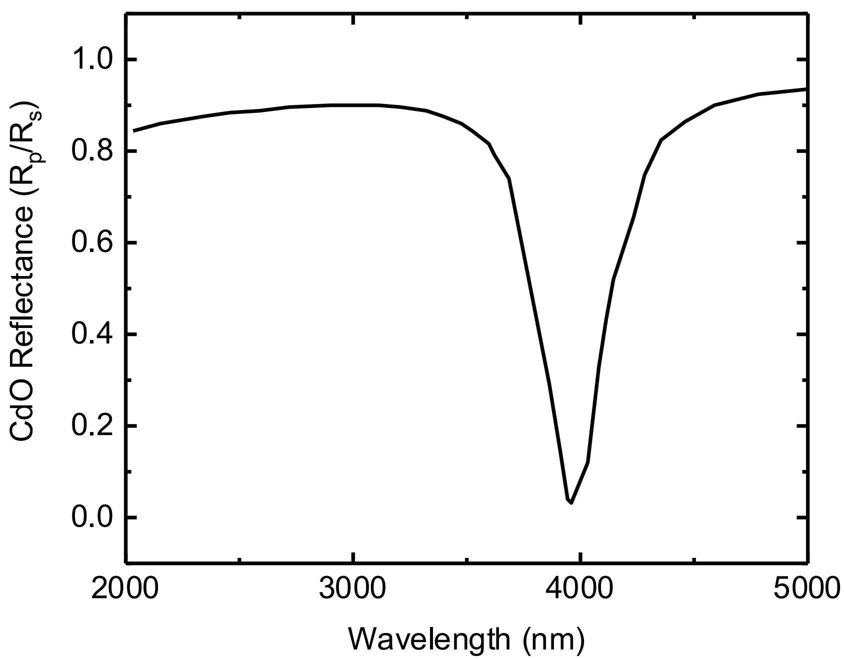
Pump electrons in Au, probe plasmon in CdO

Asymmetric red shift in ENZ plasmon mode due to BTI

Note we are measuring *change* in reflectivity, dR



Au/CdO/sapphire absorption response



Tomko *et al. Nature Nano.* **16**, 47 (2021)

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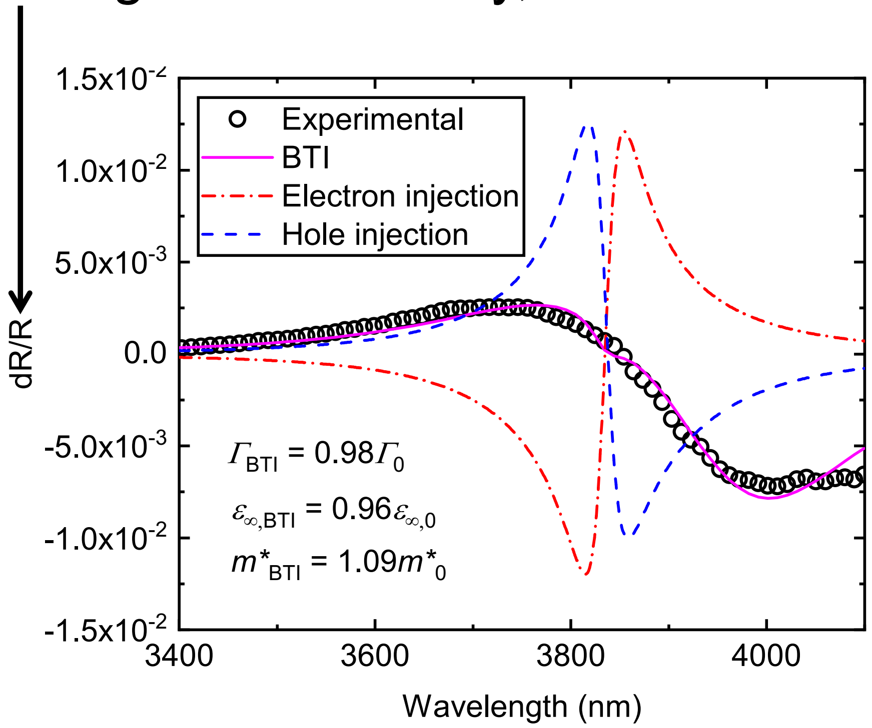
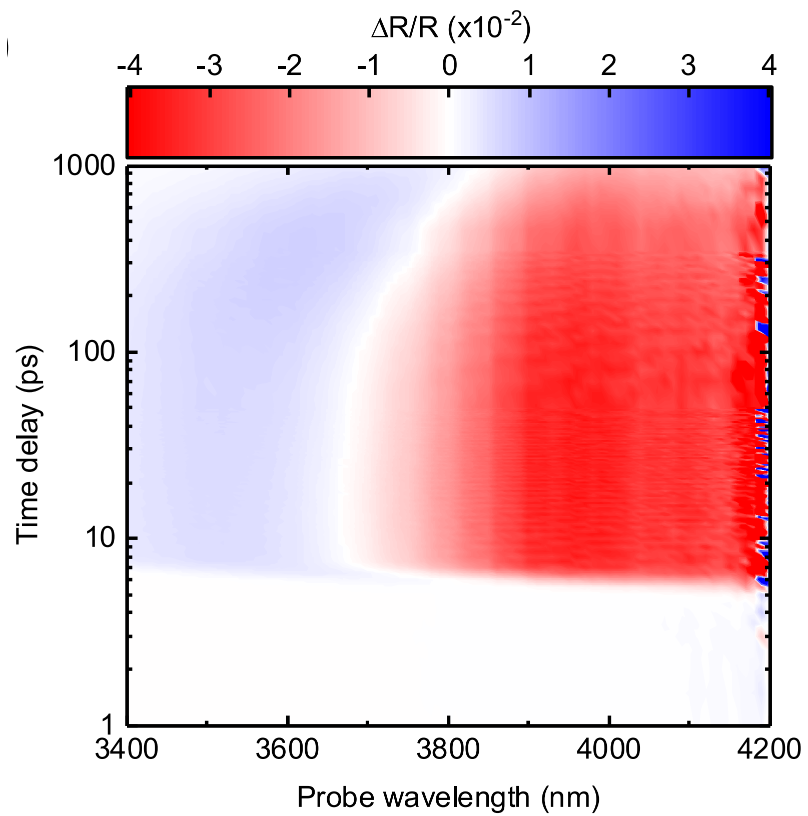
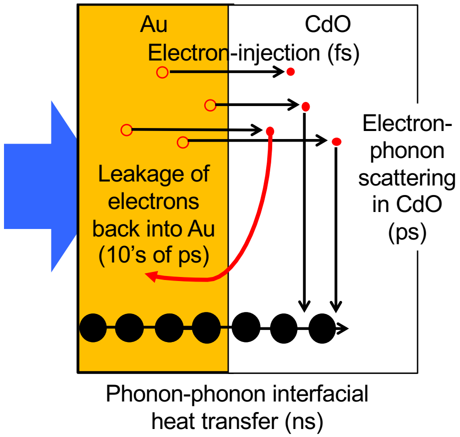


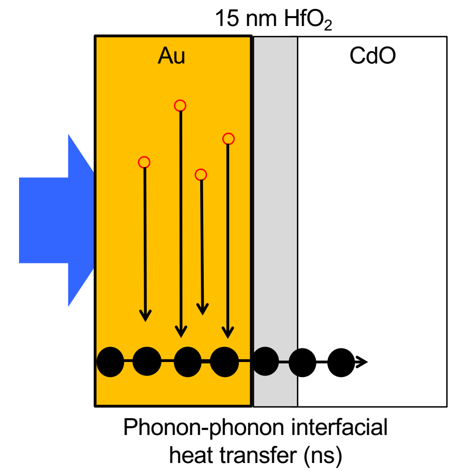


Tomko *et al. Nature Nano.* **16**, 47 (2021)

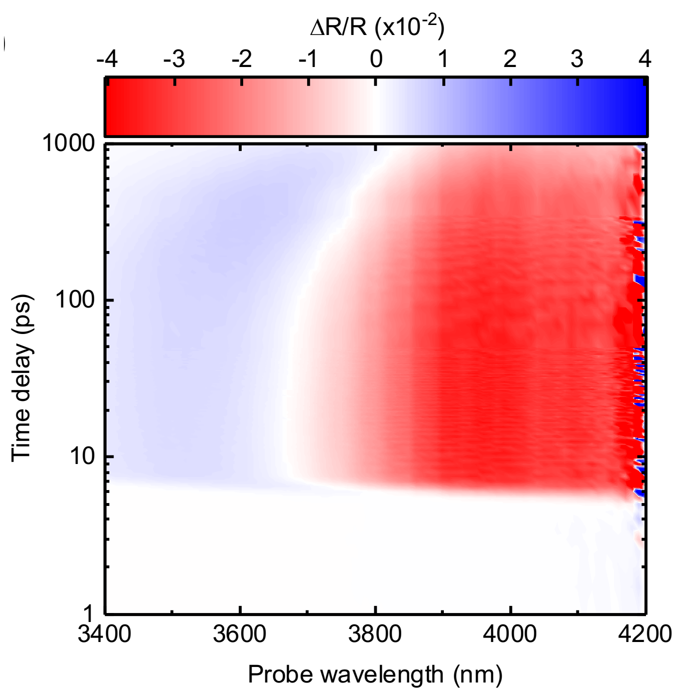
And it's not an optical artifact



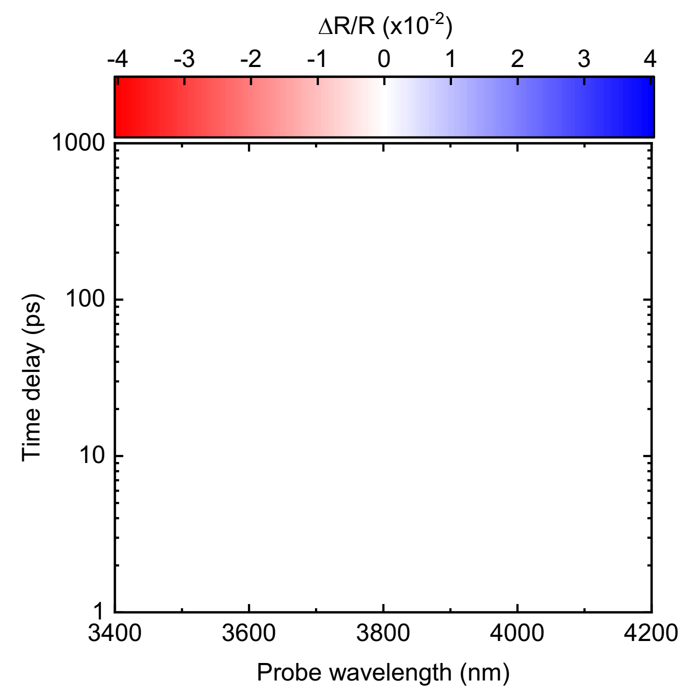
15 nm HfO_2 layer prevents any electron energy from moving from Au to CdO, resulting in no measurable response



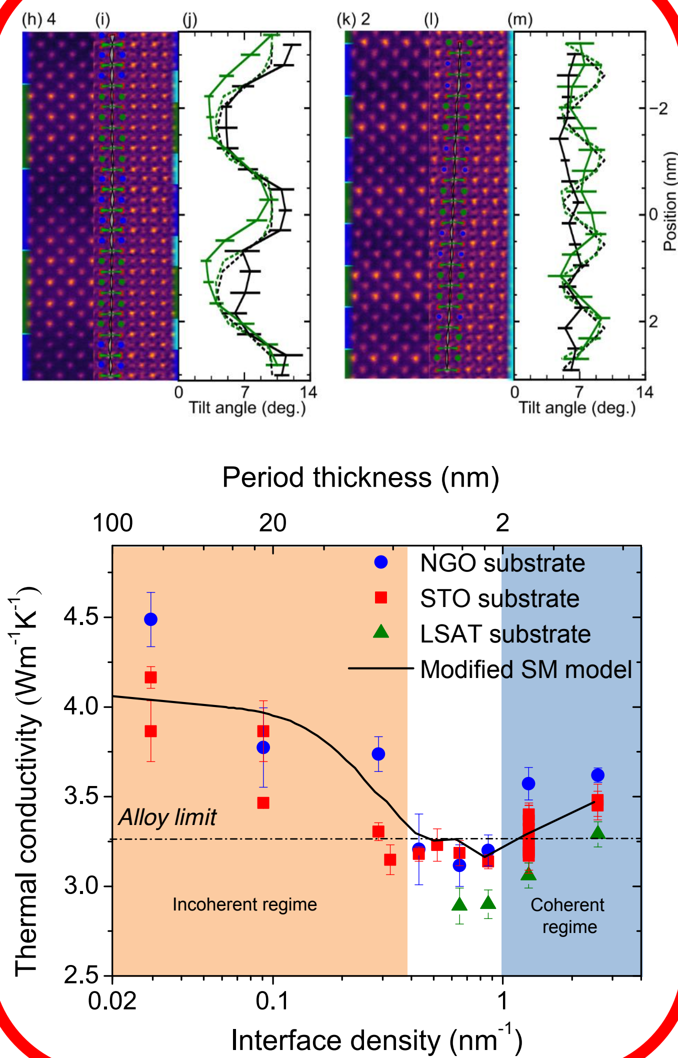
Au/CdO

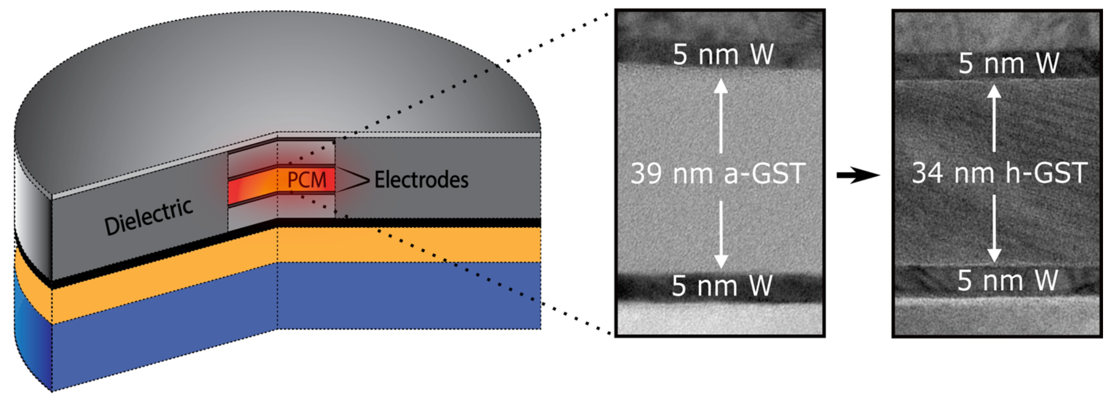


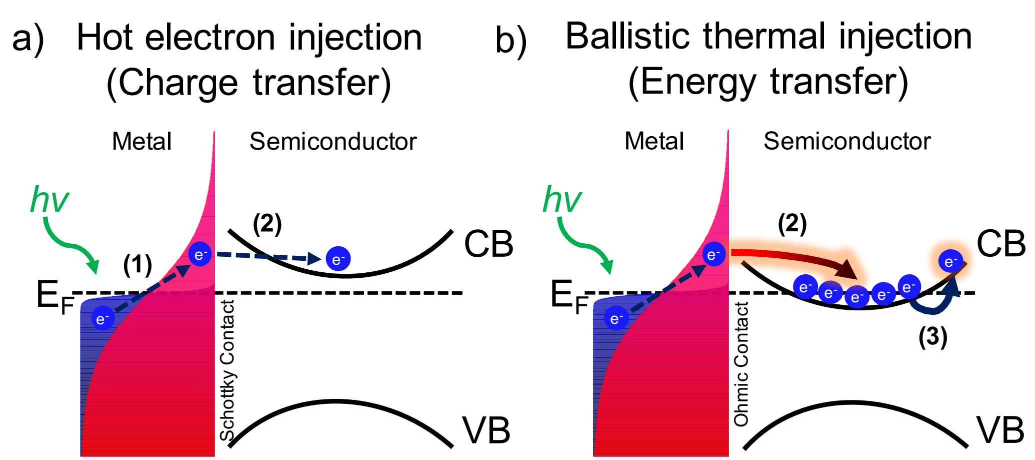
Au/HfO_2/CdO (same scale)



Summary: Interfaces can change the nature and behavior of electron and phonon transport, dictating how the interact with other carriers and impacting thermal transport

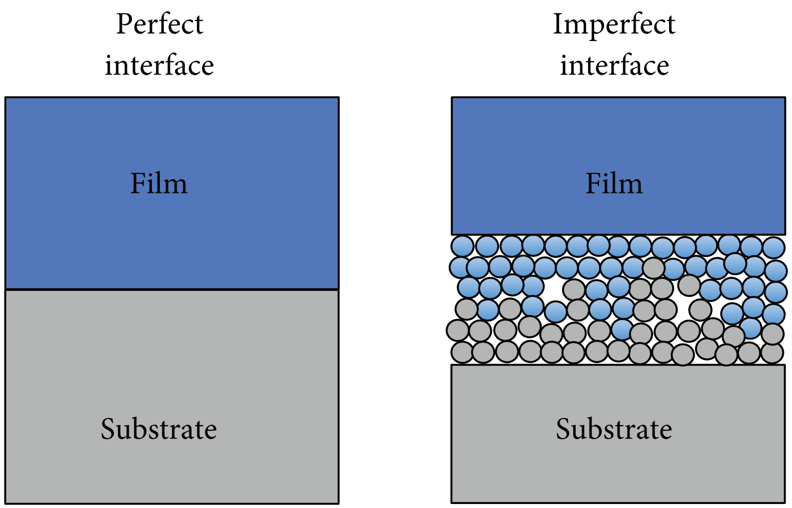




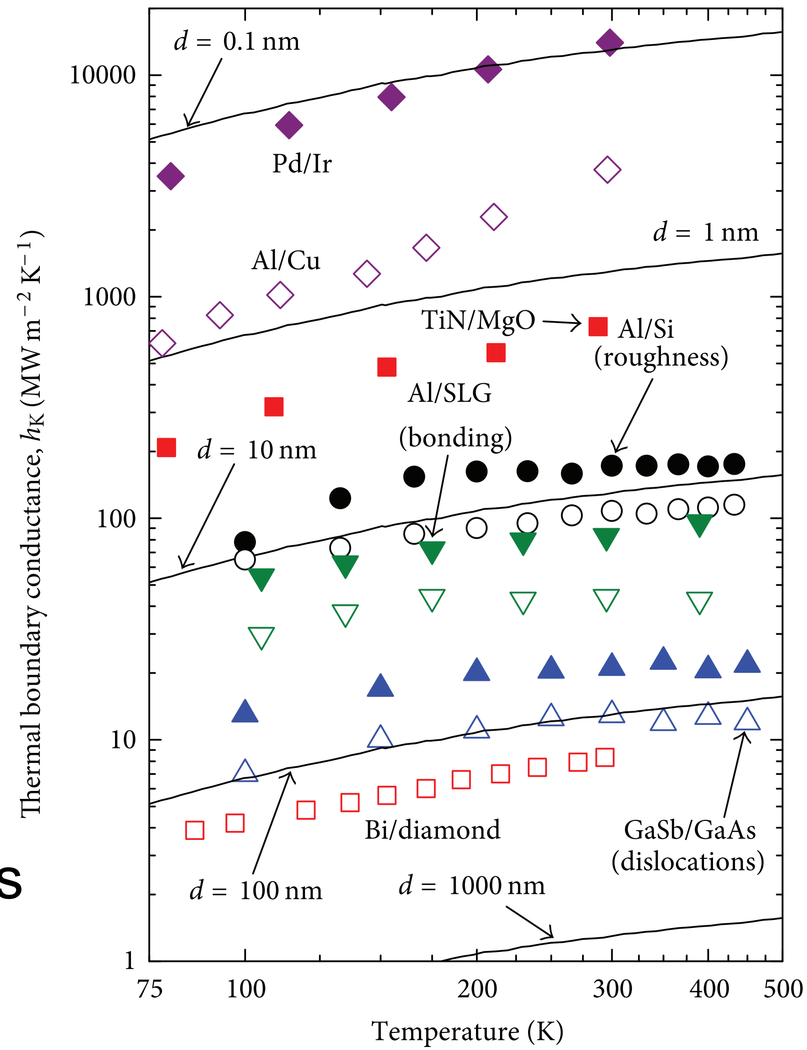


Thermal boundary conductance – quality & carriers matters

Metal/metal = electron dominated
Ultrahigh TBC (ultralow TBR)



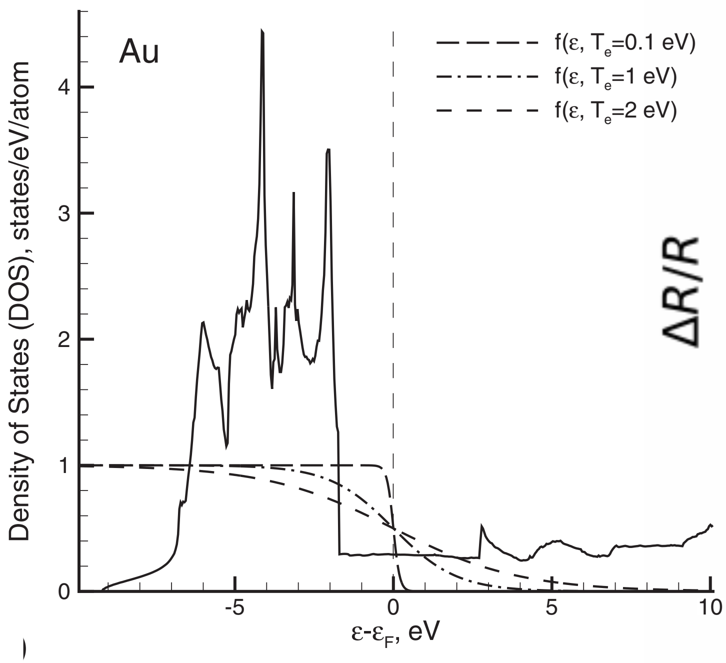
Metal/non-metal = Phonon dominated
High thermal conductivity material does not necessarily translate to high TBC (e.g., diamond)

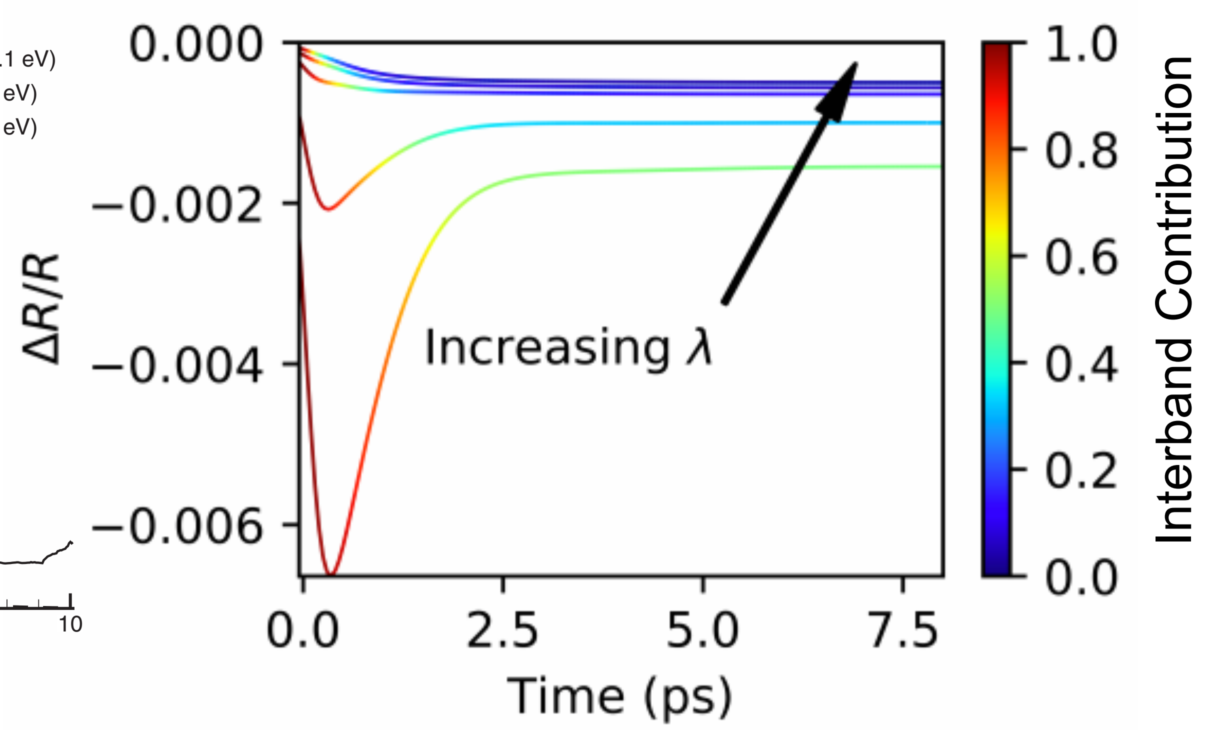


Hopkins *ISRN Mech. Eng.* **2013** 682586 (2013)

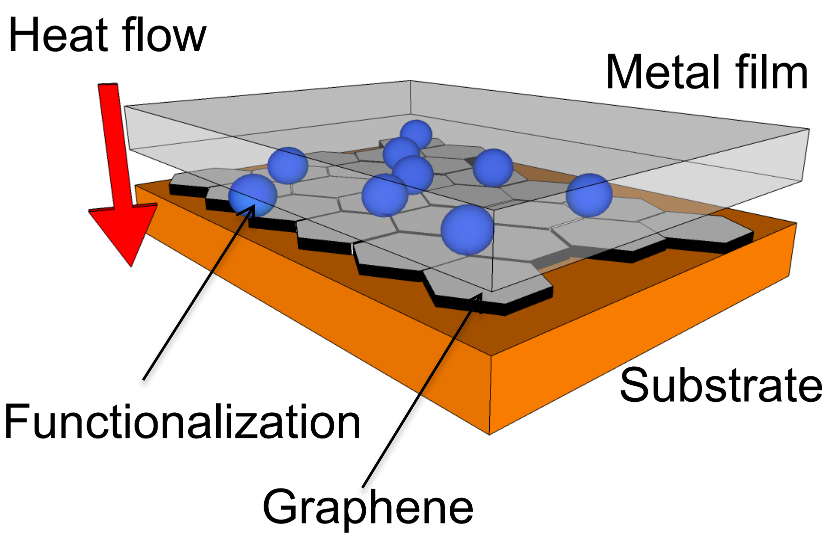
Tunable wavelength probes: turn to the IR

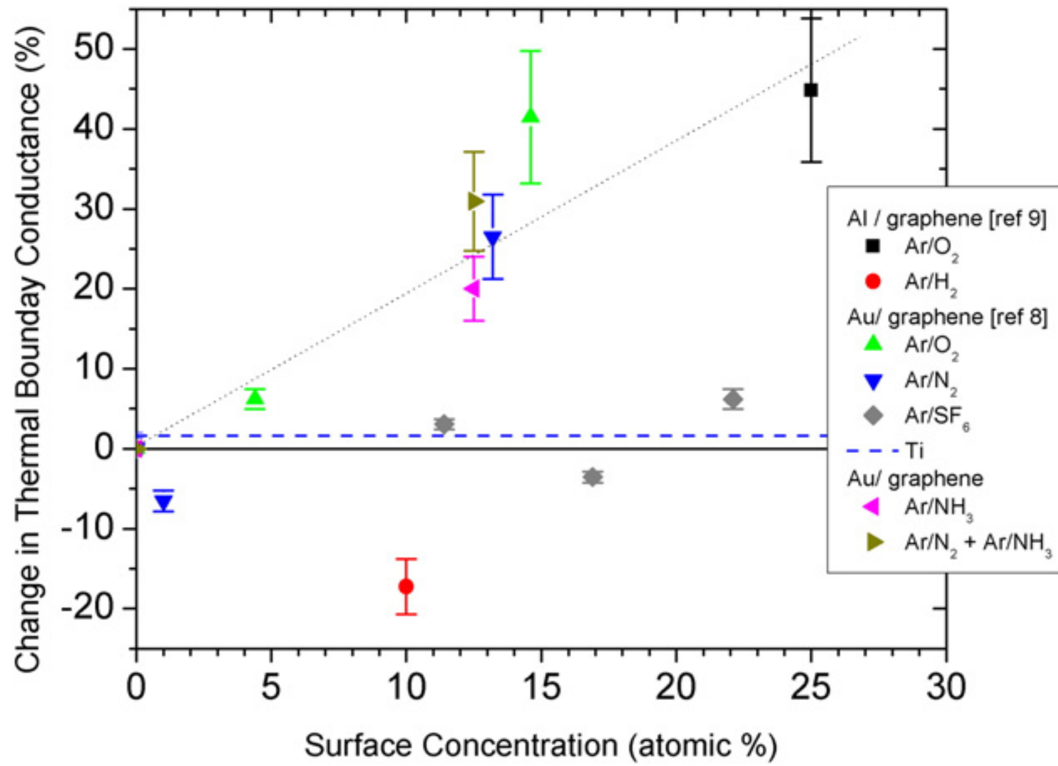
- The stage is set from the earlier works here at UIUC!
- Could our use of visible wavelengths be over complicating things by measuring "aggregate" scattering rates of electrons (including, but not limited to, electron-phonon scattering)?
- Low enough energy should just probe around Fermi energy





Chemical interactions at metal/graphene interfaces controls via plasma treatment can increase TBC

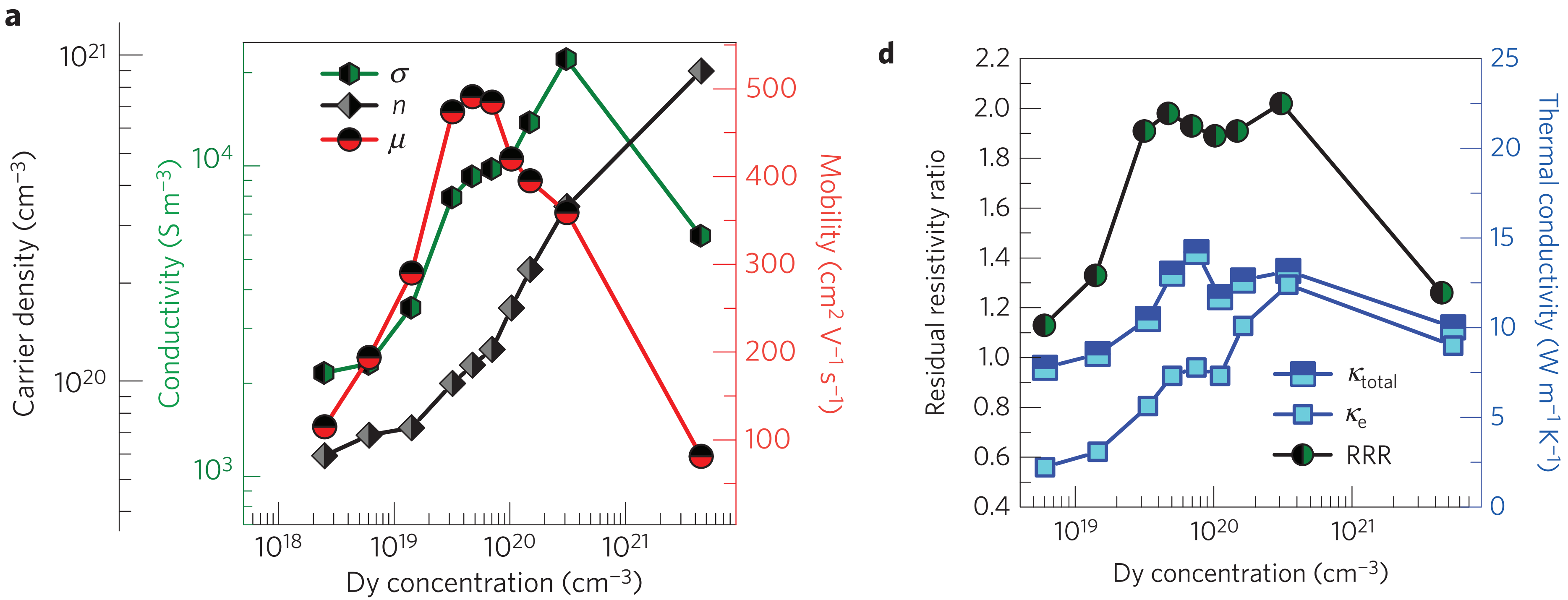




Collaboration with Scott Walton (NRL)

Nano Lett. **12**, 590 (2012)
Nano Lett. **15**, 4876 (2015)
Surf. Coat. & Tech. **314**, 148 (2017)

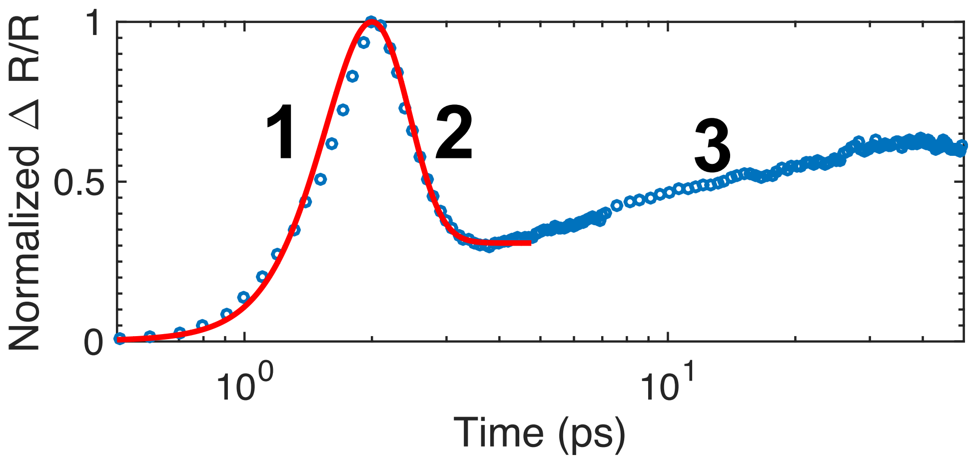
CdO – a gateway for mid-IR plasmonics

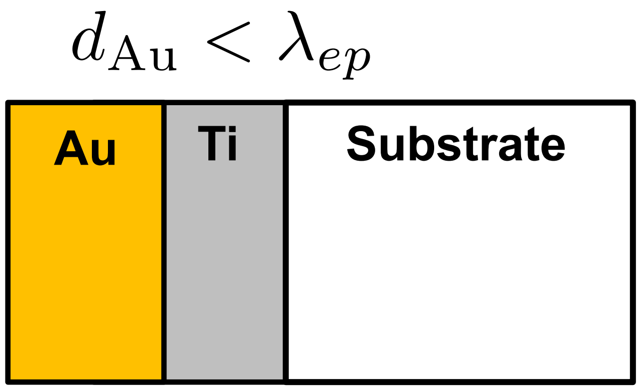


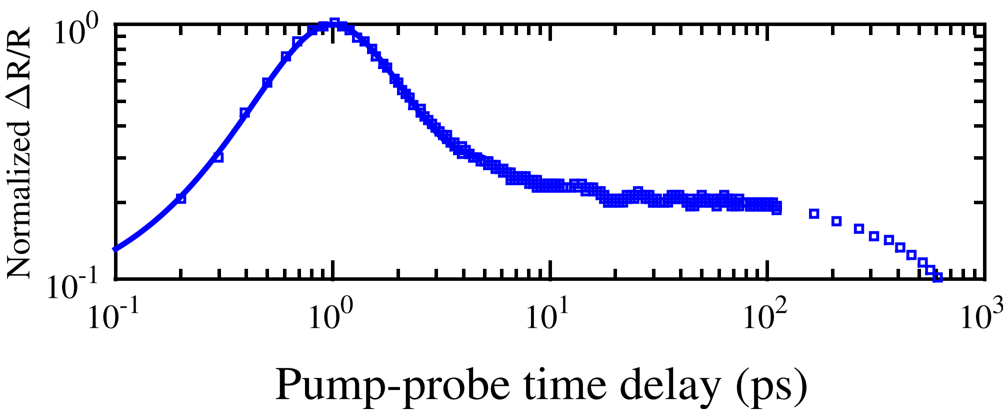
Nat. Mat. **14**, 414
Appl. Phys. Lett. **108**, 021901

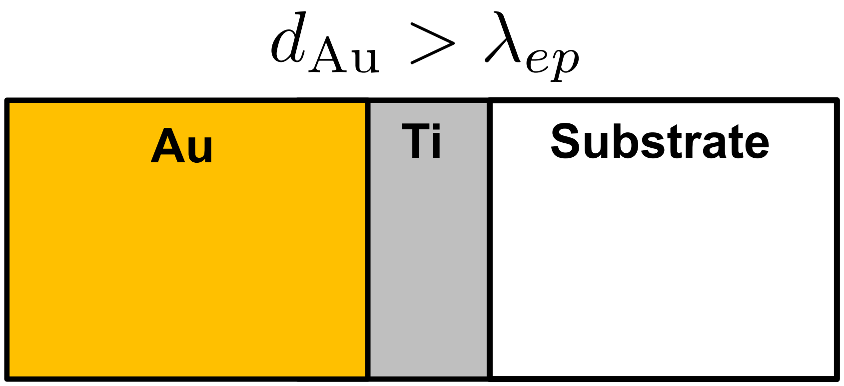
TDTR measurements of time scales of noneq. transport

Hypothesis: If Au thickness (d_{Au}) is thicker than electron-phonon mean free path (λ_{ep}), nonequilibrium at interface will be negligible and "back heating" (time regime 3) will not be observed



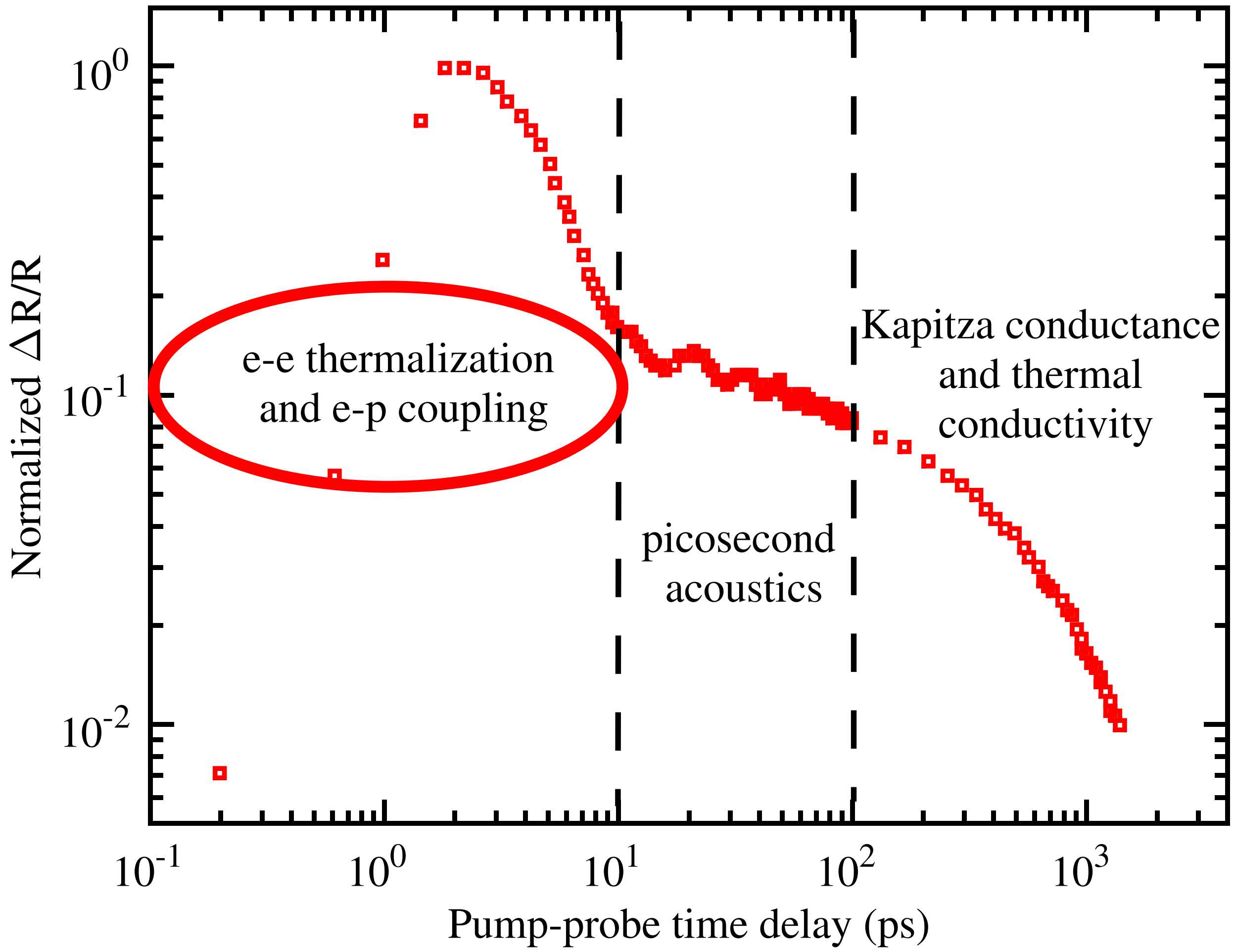






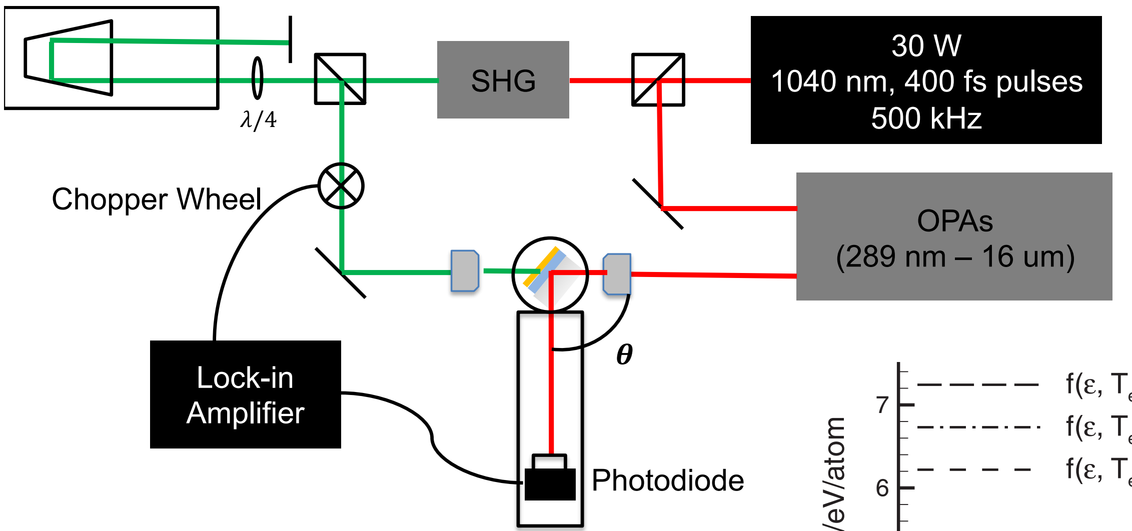
Gain insight with ultrafast electron relaxation

Recall TDTR and the "ultrafast" picosecond time scales



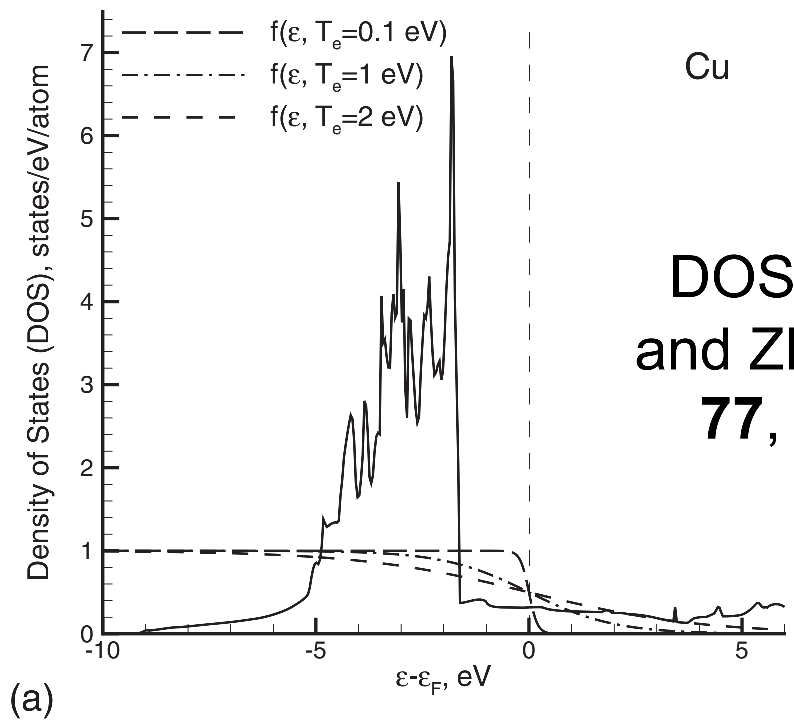
Data from: Giri *et al. J. Appl. Phys.* **117**, 105105 (2015)

Wavelength tunable pump-probe into the IR



Can now optically probe specific electronic transitions

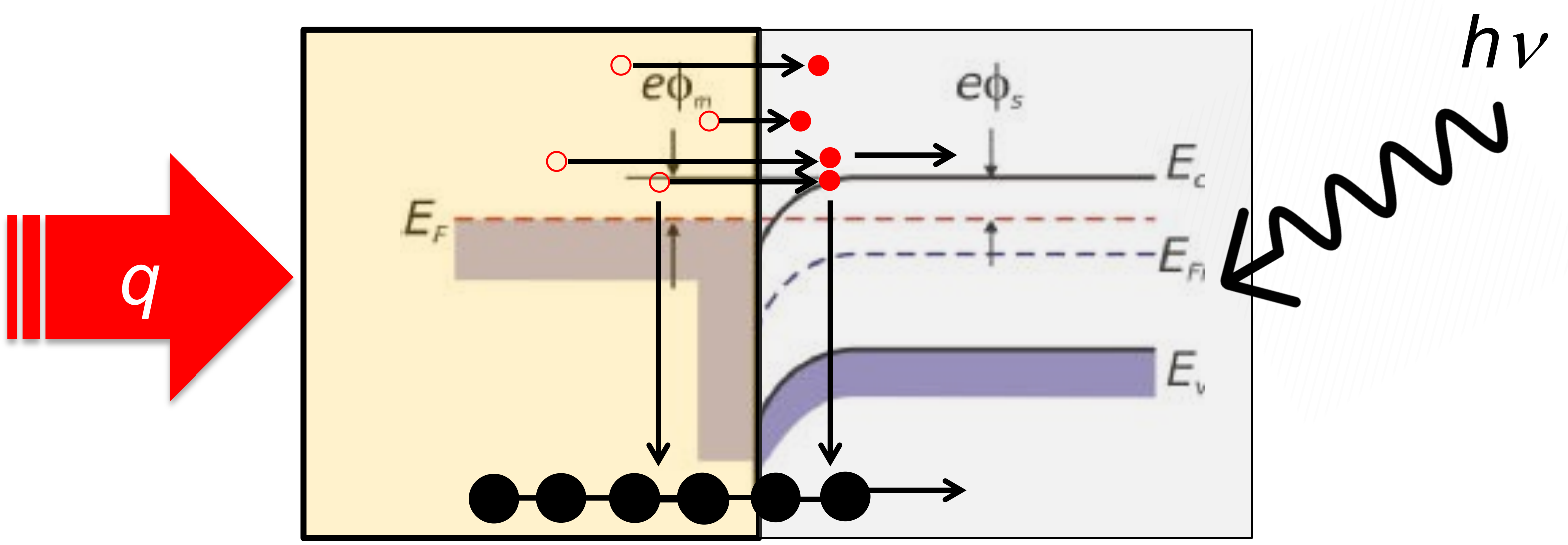
- Ultrafast pump-probe measurement (sub-picosecond resolution)
- Variable wavelength from 288 nm to 16 microns
- High-precision goniometer for angular measurements



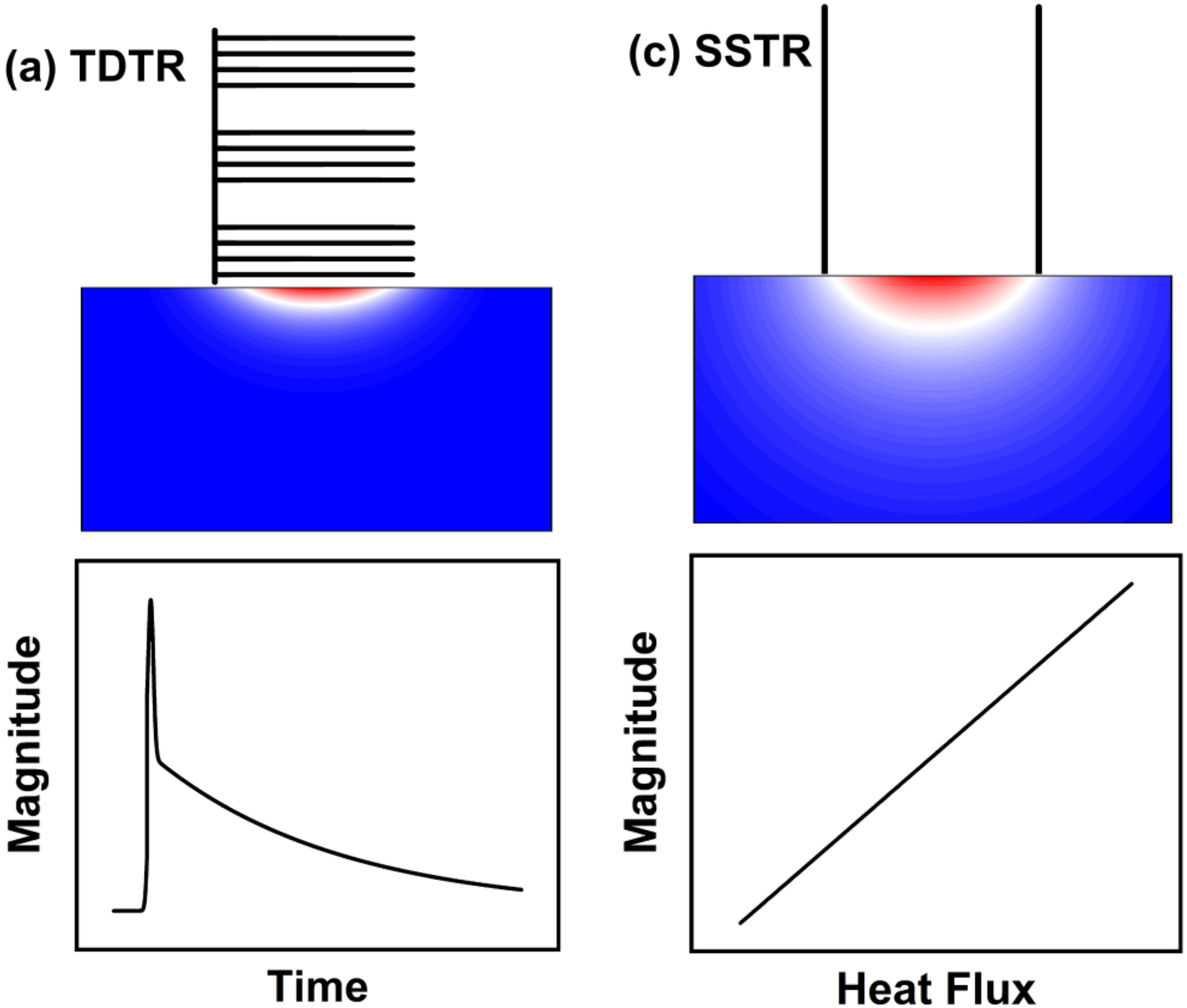
DOS from Lin and Zhiglei *PRB* **77**, 075133

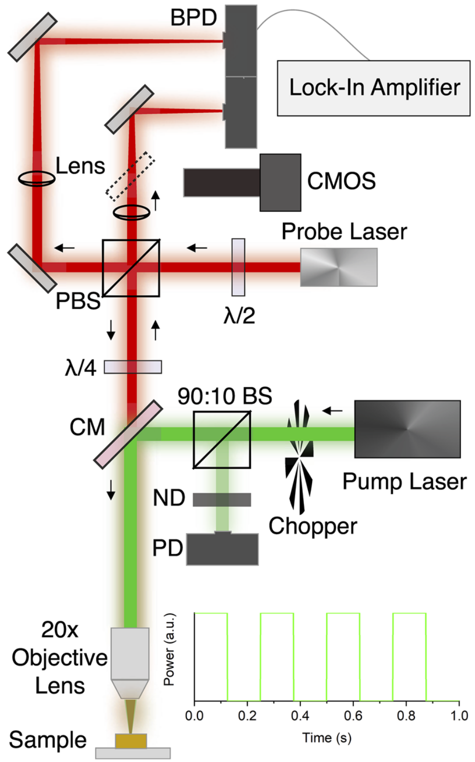
J. Appl. Phys. **129**, 193104 (2021)

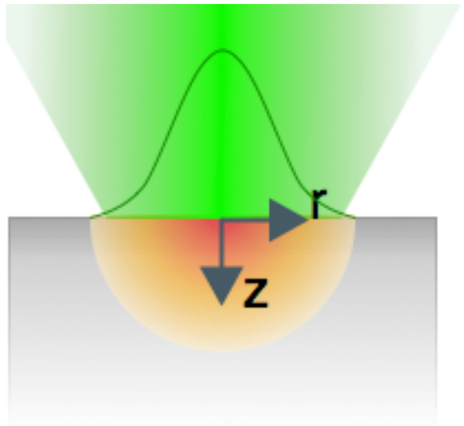
Electron energy transfer at metal/nonmetal interfaces



Steady state thermoreflectance: direct measure of κ



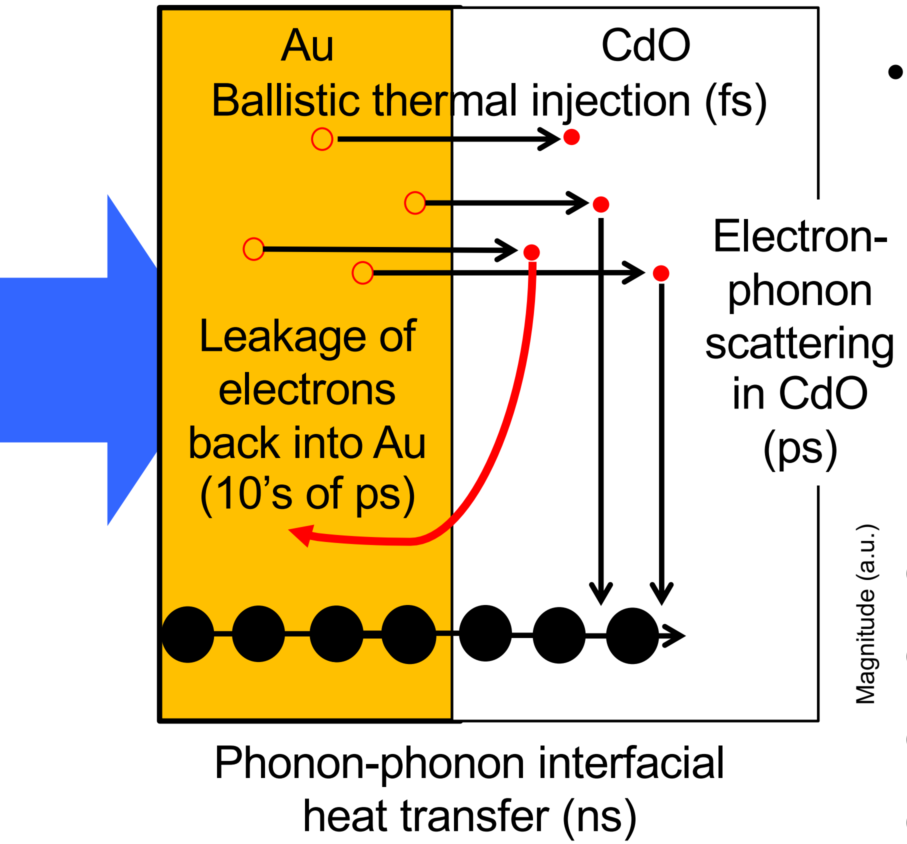


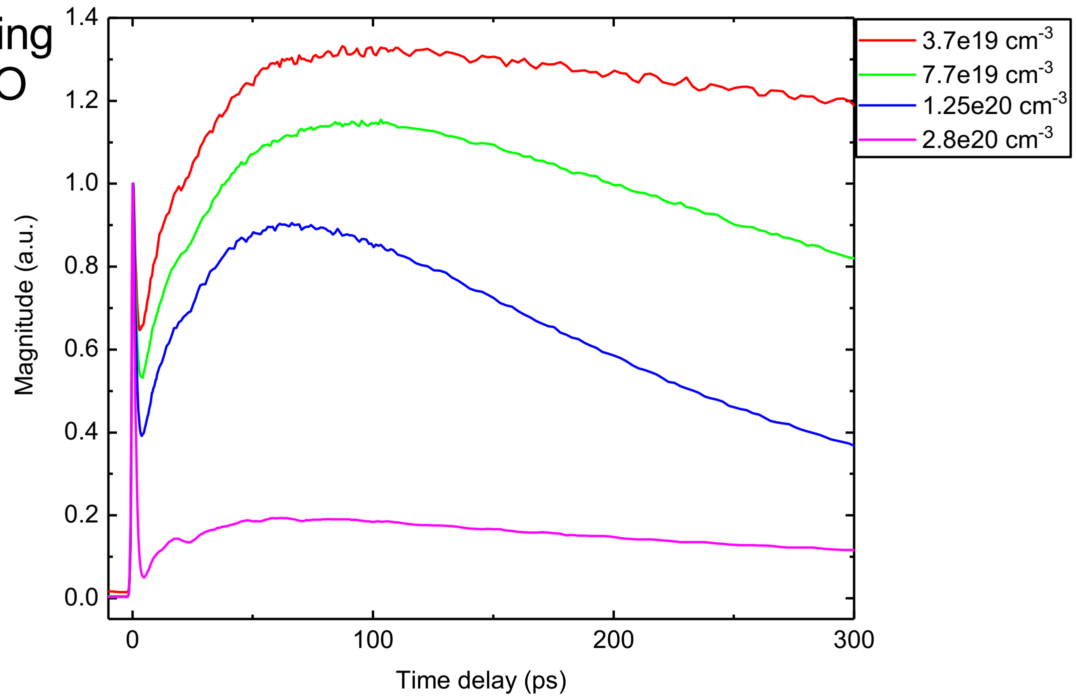


J. Appl. Phys. **126**, 150901 (2019).

Nonequilibrium processes at Au/CdO interfaces

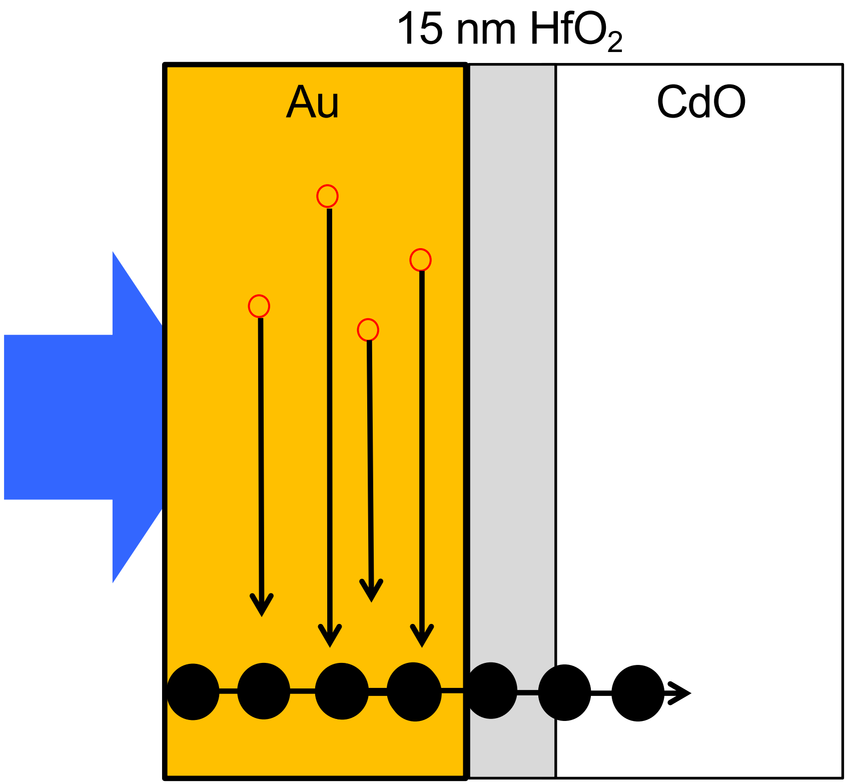
- Doping of CdO dictates amount of "electron leakage" back into Au
- Lower resistivity + higher e-ph coupling in CdO, less electronic back heating into gold contact





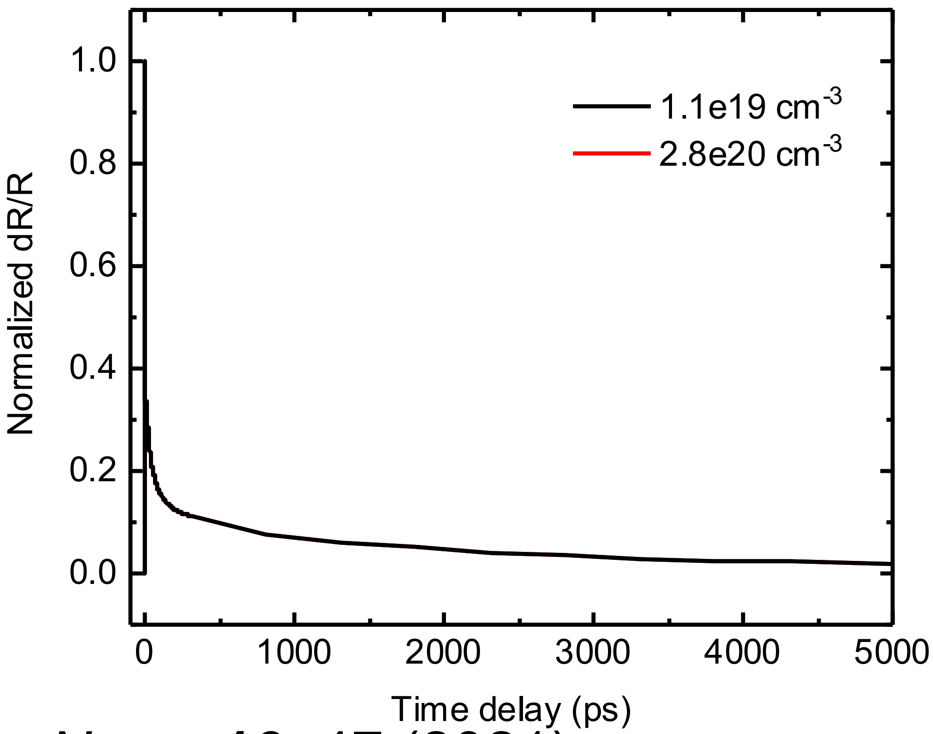
Tomko *et al.* *Nature Nano.* **16**, 47 (2021)

Nonequilibrium processes at Au/CdO interfaces



Phonon-phonon interfacial heat transfer (ns)

- Transparent buffer layer stops ballistic electrons, but allows light to transmit
- No back-heating observed for any dopant concentration!



Tomko *et al. Nature Nano.* **16**, 47 (2021)