Thermal transport processes in functional organic and organic/inorganic nanomaterials: The role of the chemical bond

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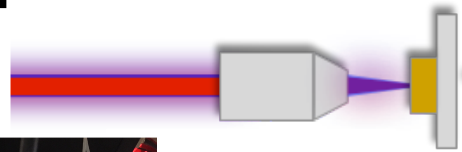
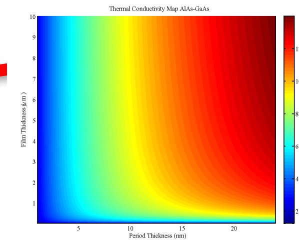
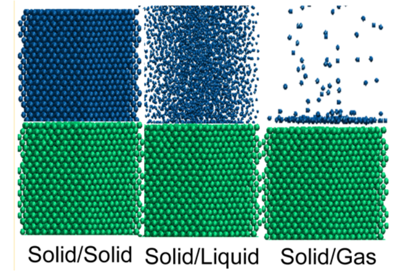
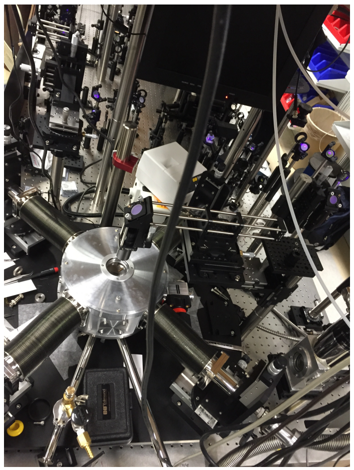
My group – ExSiTE Lab

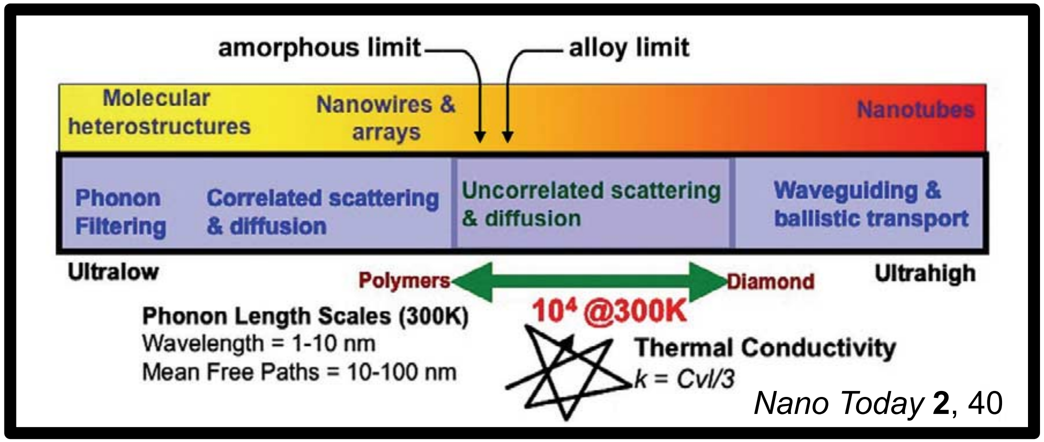
Experiments and Simulations in Thermal Engineering

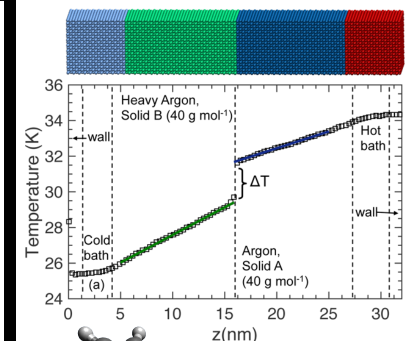


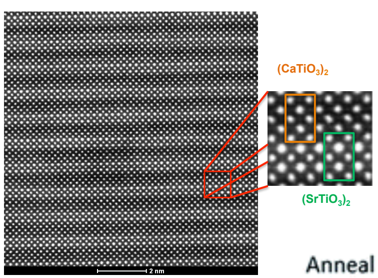


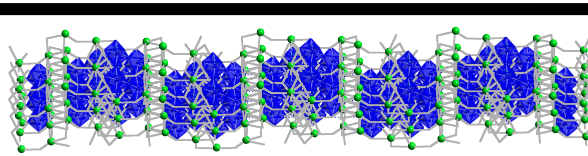


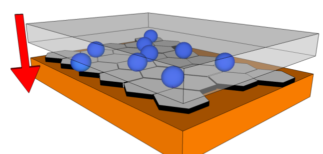


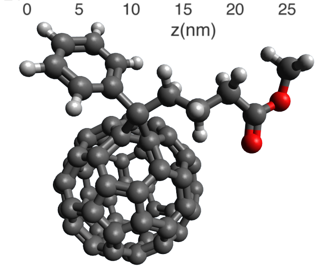


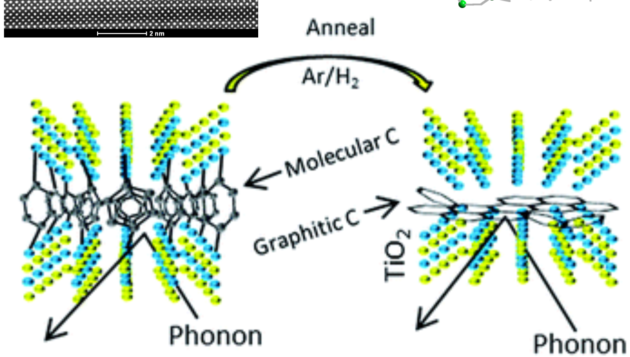


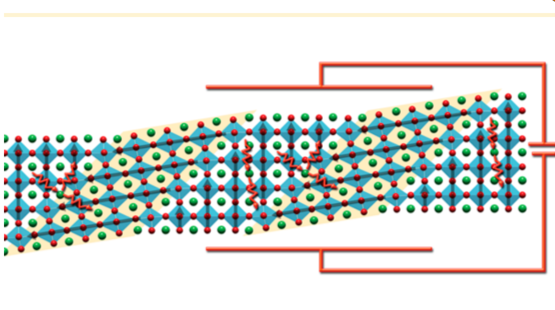


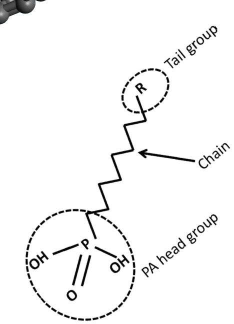






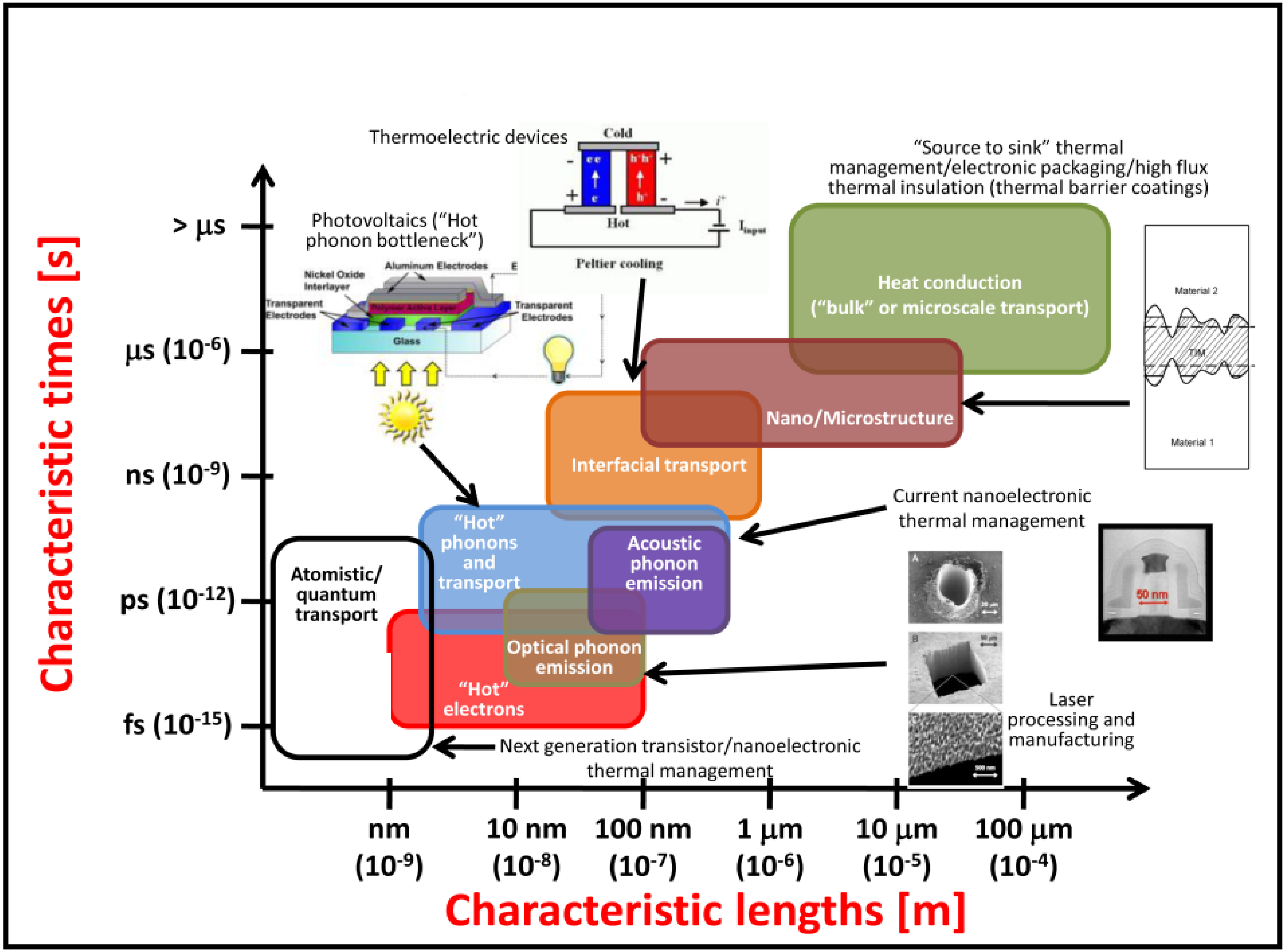




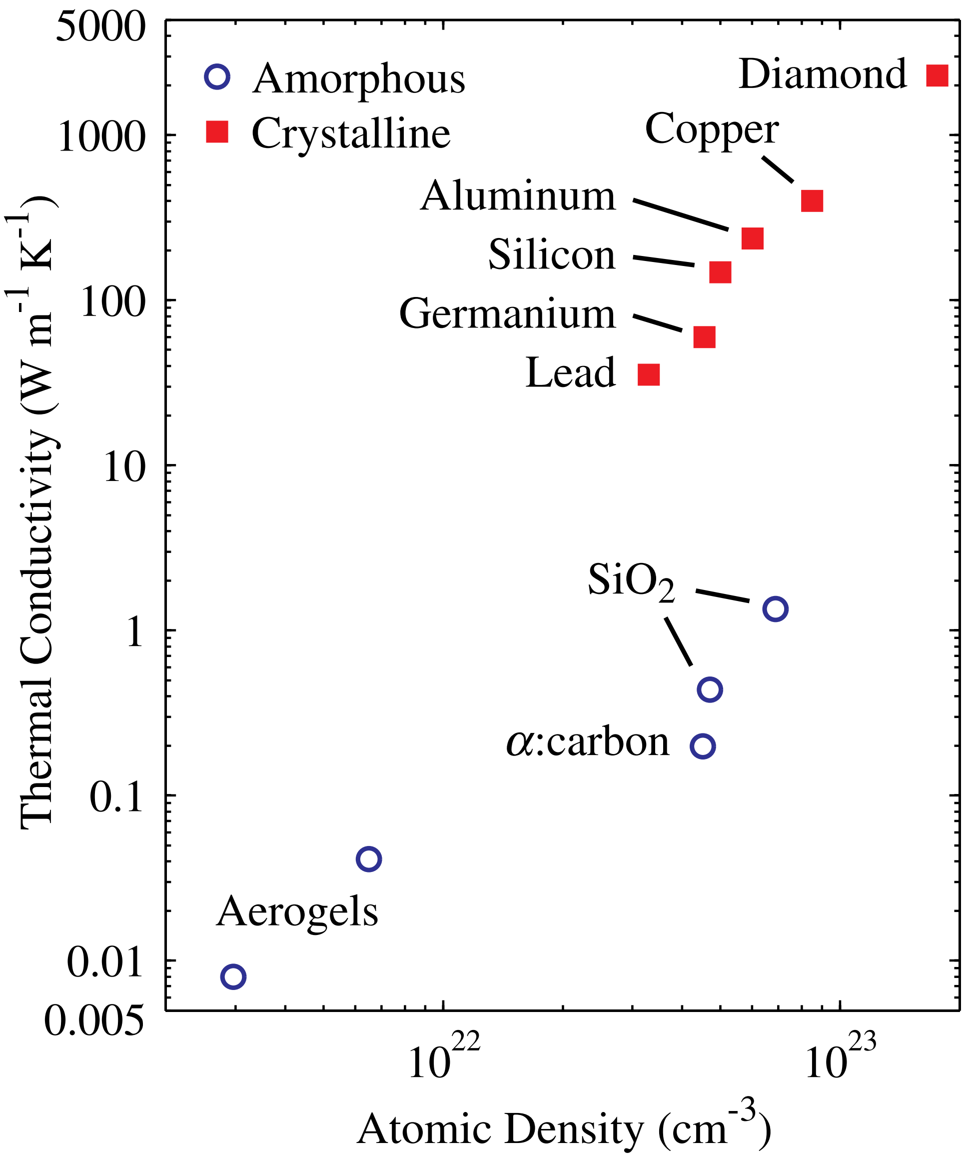


My group – ExSiTE Lab

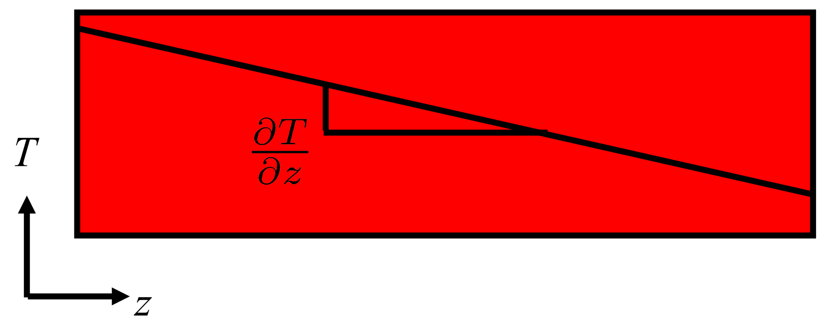
Engineering energy transport, conversion and storage in materials over multiple time and length scales



Thermal conductivity of materials – Traditional picture



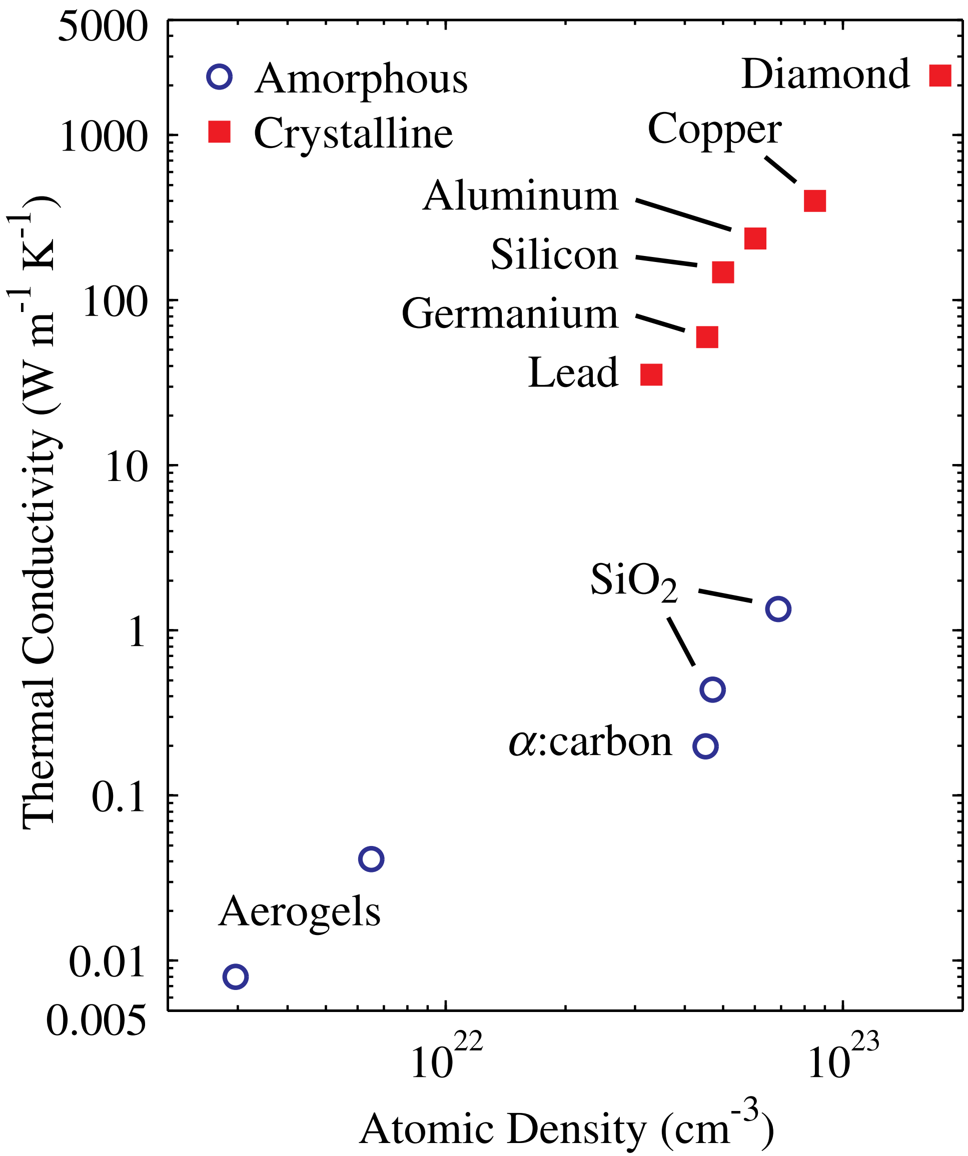
Bulk picture (Fourier Law)

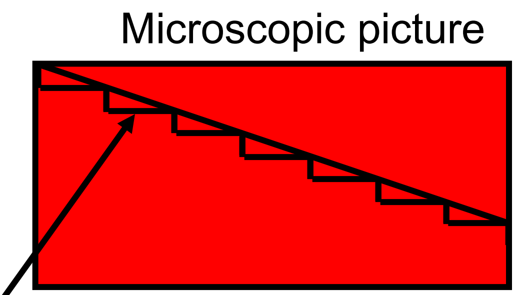


$$q_z = -\kappa \frac{\partial T}{\partial z}$$

PRL **110**, 015902 (2013)

Thermal conductivity of materials – Kinetic Theory picture





λ = Mean free path

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

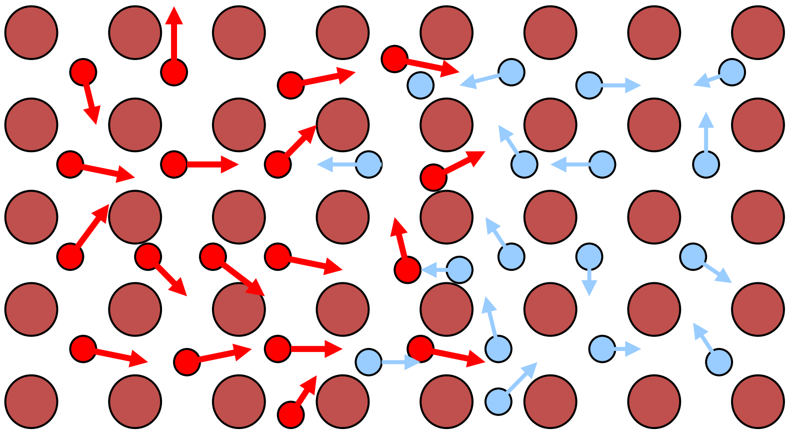
Energy

Velocity

PRL **110**, 015902 (2013)

Thermal conductivity of materials - nanoscopic

Diffusion of "hot" electrons →



Metals:

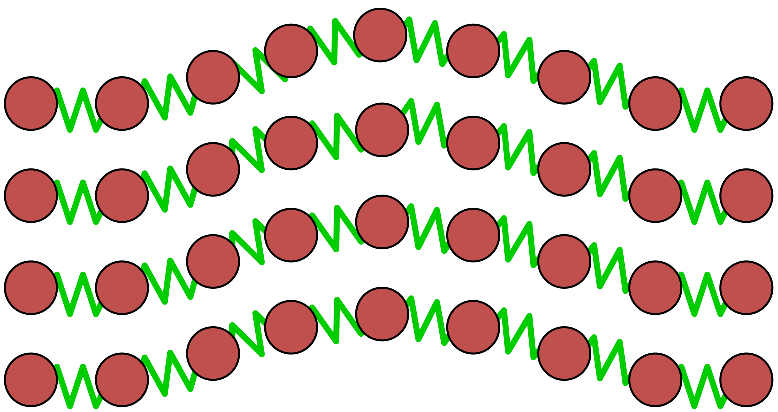
Free electrons are the dominant energy carriers in metals, ballistic velocity ~10^6 m/s

atom

"hot" free electron

"cold" free electron

Electron carrier density:
in metals ~10^{23} cm^{-3}
in semiconductors ~10^{18} cm^{-3}



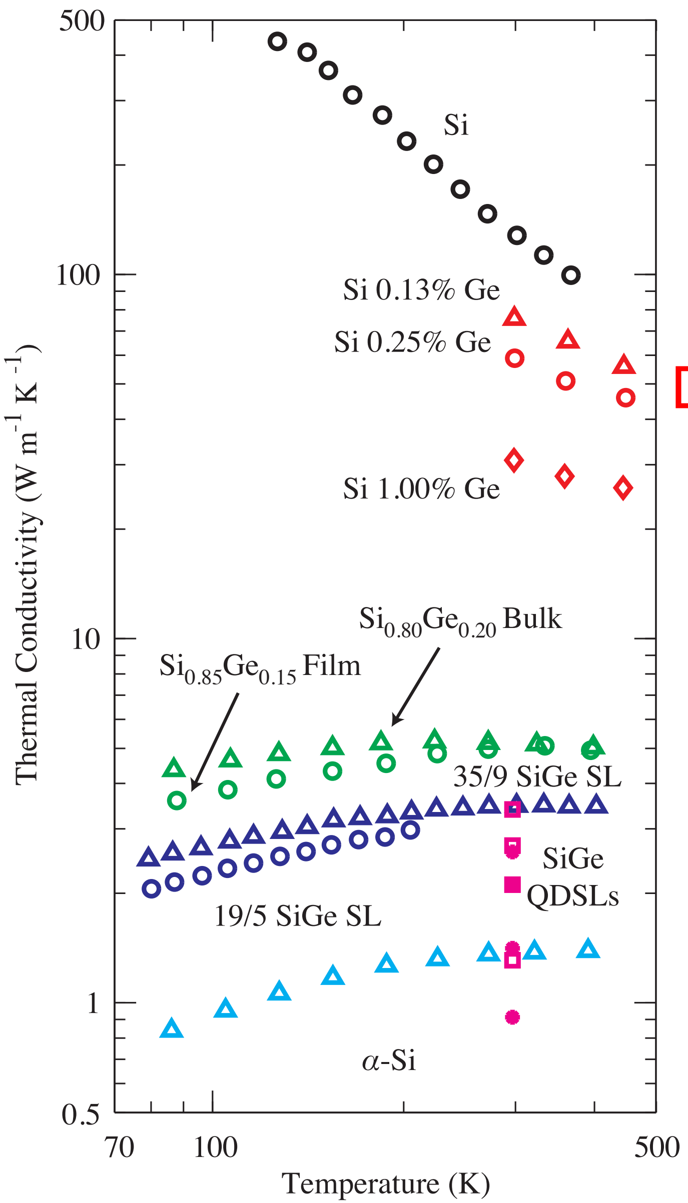
Semiconductors:

Phonons (lattice vibrations) are the dominant energy carriers in semiconductors, velocity ~10^3 m/s

Phonon propagation →

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

Thermal conductivity of materials - nanoscopic



Dilute alloy

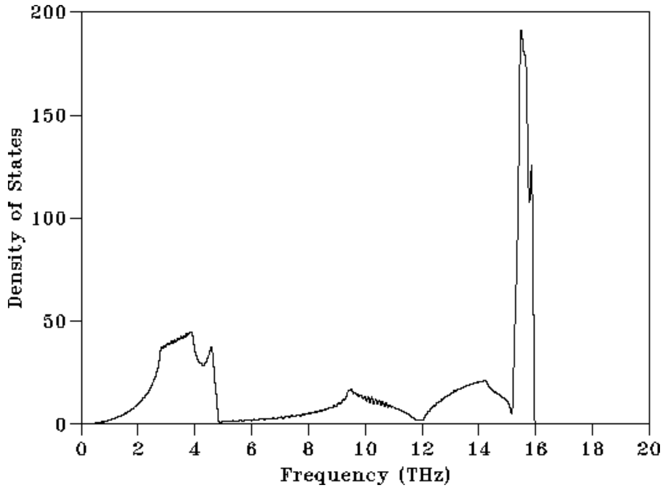
Alloy

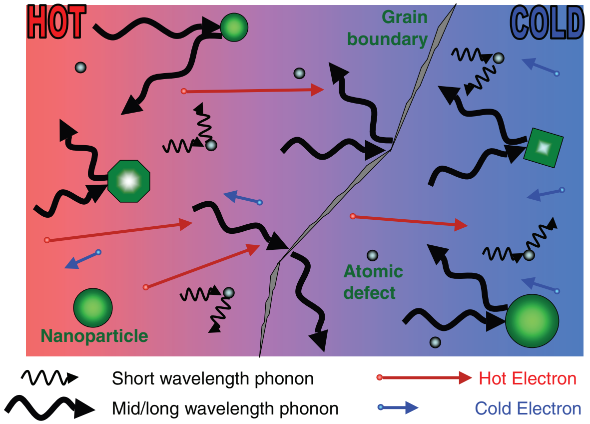
Interface

Disorder

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

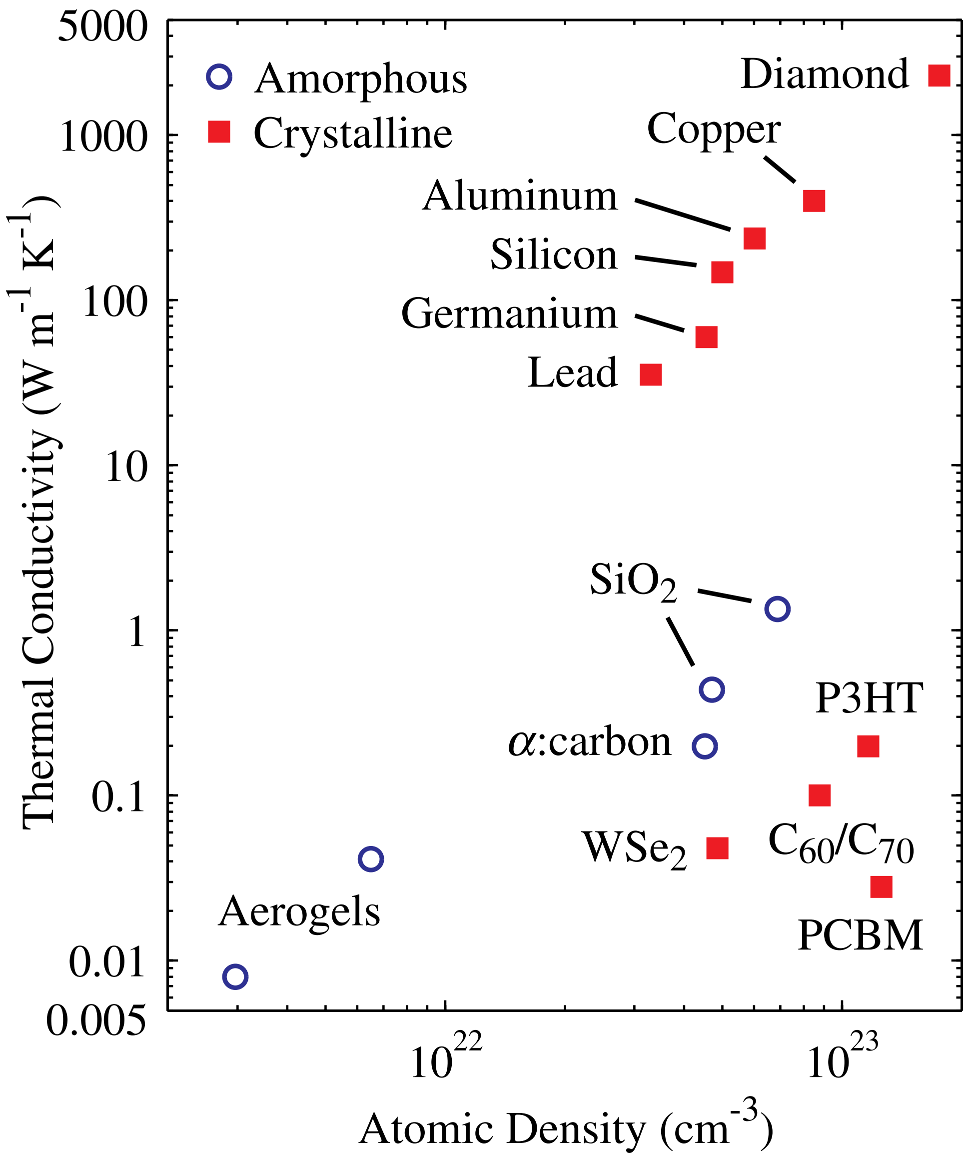
$$\tau = f\left(\tau_{\mathrm{intrinsic}}, \tau_{\mathrm{impurity}}, \tau_{\mathrm{boundary}}\right)$$

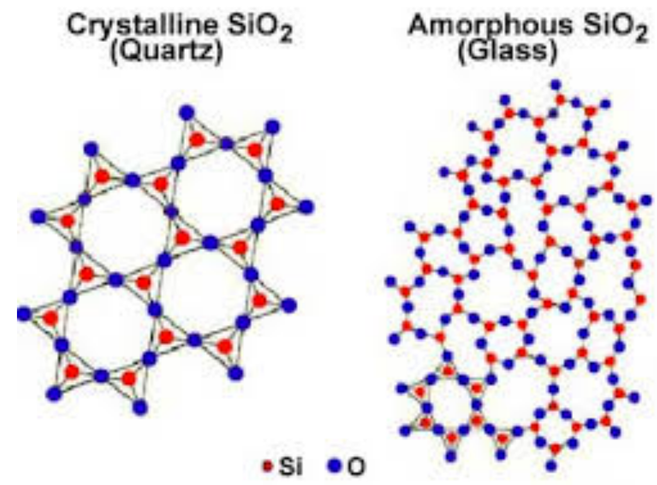




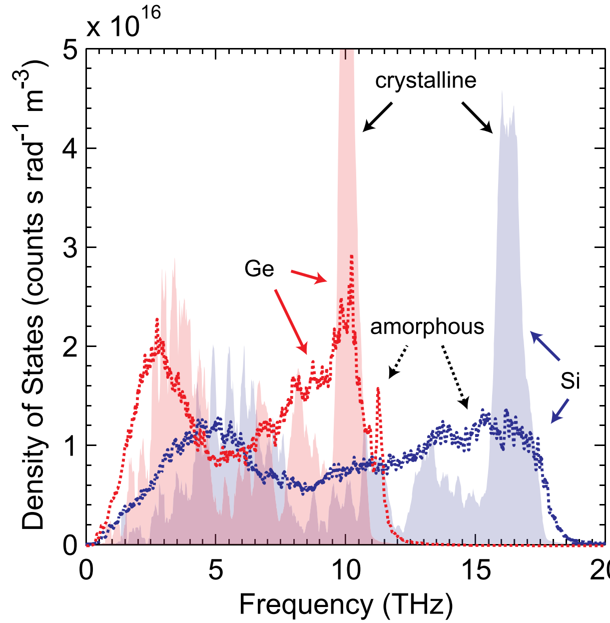
Advanced Materials **22**, 3970

Thermal conductivity of non-crystalline solids



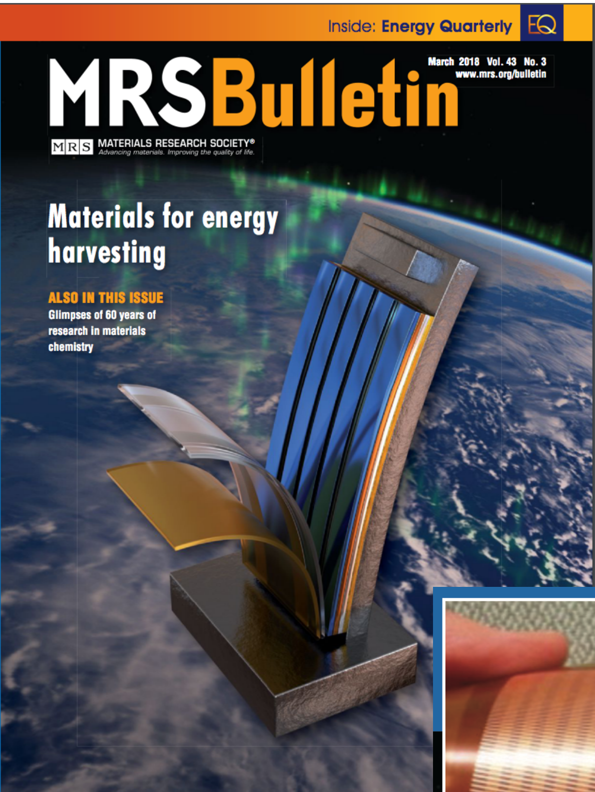


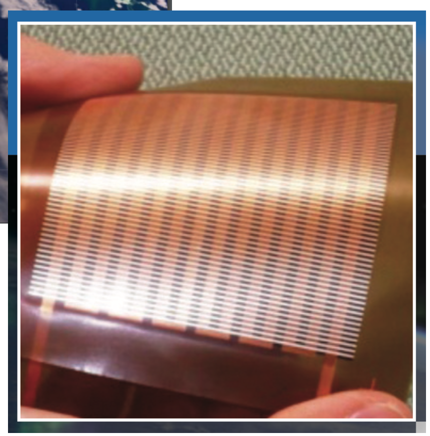
NDT Resource Center



J. Appl. Phys. **118**, 165303

A future for energy recovery: wearable thermoelectrics





March 2018 MRS Bulletin

Seebeck coefficient [V K^{-1}]

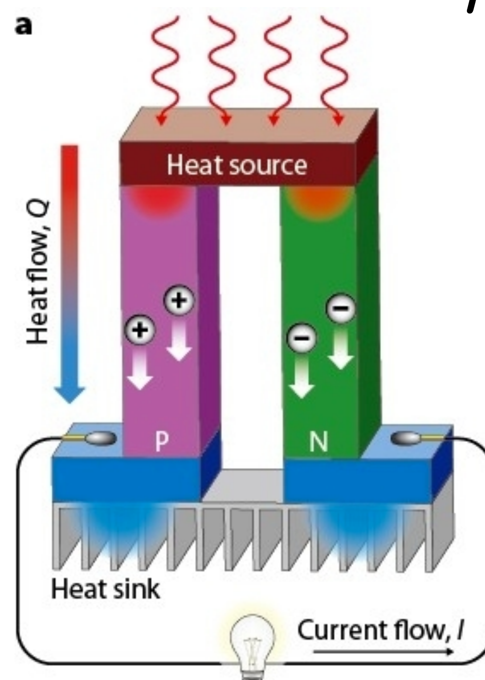
Electrical conductivity [S m^{-1}]

Temperature [K]

Figure of merit [unitless]

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

Thermal conductivity [W m^{-1} K^{-1}]



Wearable and flexible thermoelectrics for energy harvesting

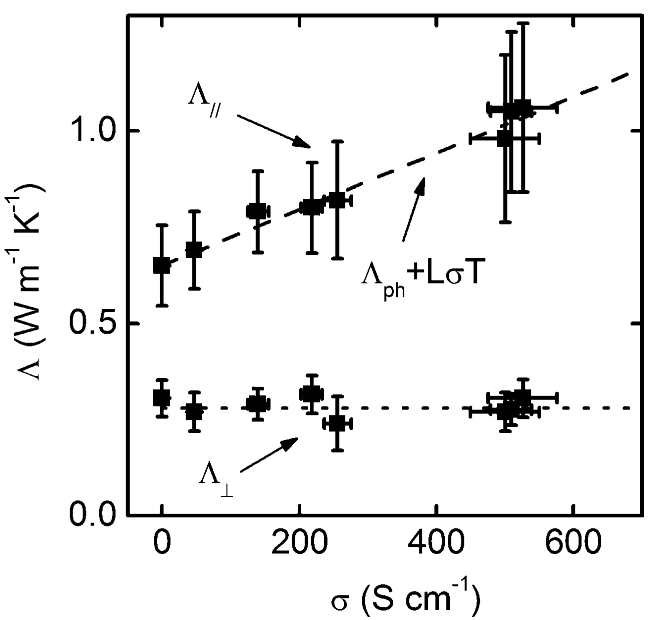
Ruoming Tian, Chunlei Wan, Naoyuki Hayashi, Toshiaki Aoai, and Kunihito Koumoto

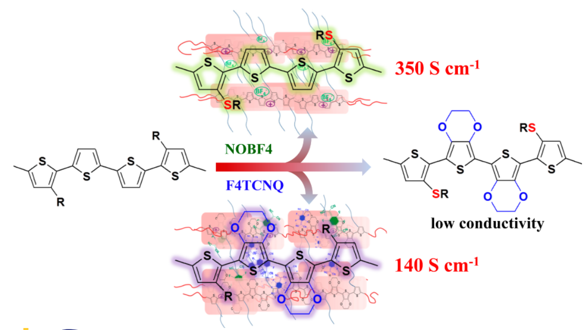
renewableenergy focus.com

Engineering thermal conductivity in polymeric TE materials

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

Macromolecules **48**, 585

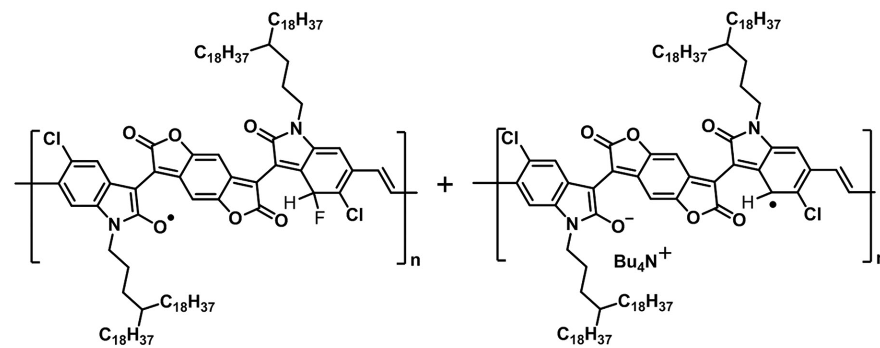




JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

Modification of the Poly(bisdodecylquaterthiophene) Structure for High and Predominantly Nonionic Conductivity with Matched Dopants

Hui Li,[†] Mallory E. DeCoster,[‡] Robert M. Ireland,[†] Jian Song,[†] Patrick E. Hopkins,[‡] and Howard E. Katz*[,†]



(ClBDPPV-F)• (ClBDPPV)-•

COMMUNICATION
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Thermoelectrics
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High Conductivity and Electron-Transfer Validation in an n-Type Fluoride-Anion-Doped Polymer for Thermoelectrics in Air

Xingang Zhao, Deepa Madan, Yan Cheng, Jiawang Zhou, Hui Li, Susanna M. Thon, Arthur E. Bragg, Mallory E. DeCoster, Patrick E. Hopkins, and Howard E. Katz**

Outline

- **TDTR: Measurement of thermal conductivity of thin films and thermal resistance across interfaces**
- Weakly bonded solids: new lower limits to thermal conductivity
- Functionalized interfaces at graphene contacts: tuning heat and electrical transport via the interfacial bond
- Heat transport across single molecule interfaces: when does a molecule become a defect?
- Molecular interfaces in organic/inorganic composites: diffusive scattering via the vibron-phonon interaction

Measuring heat flow in thin films: TDTR

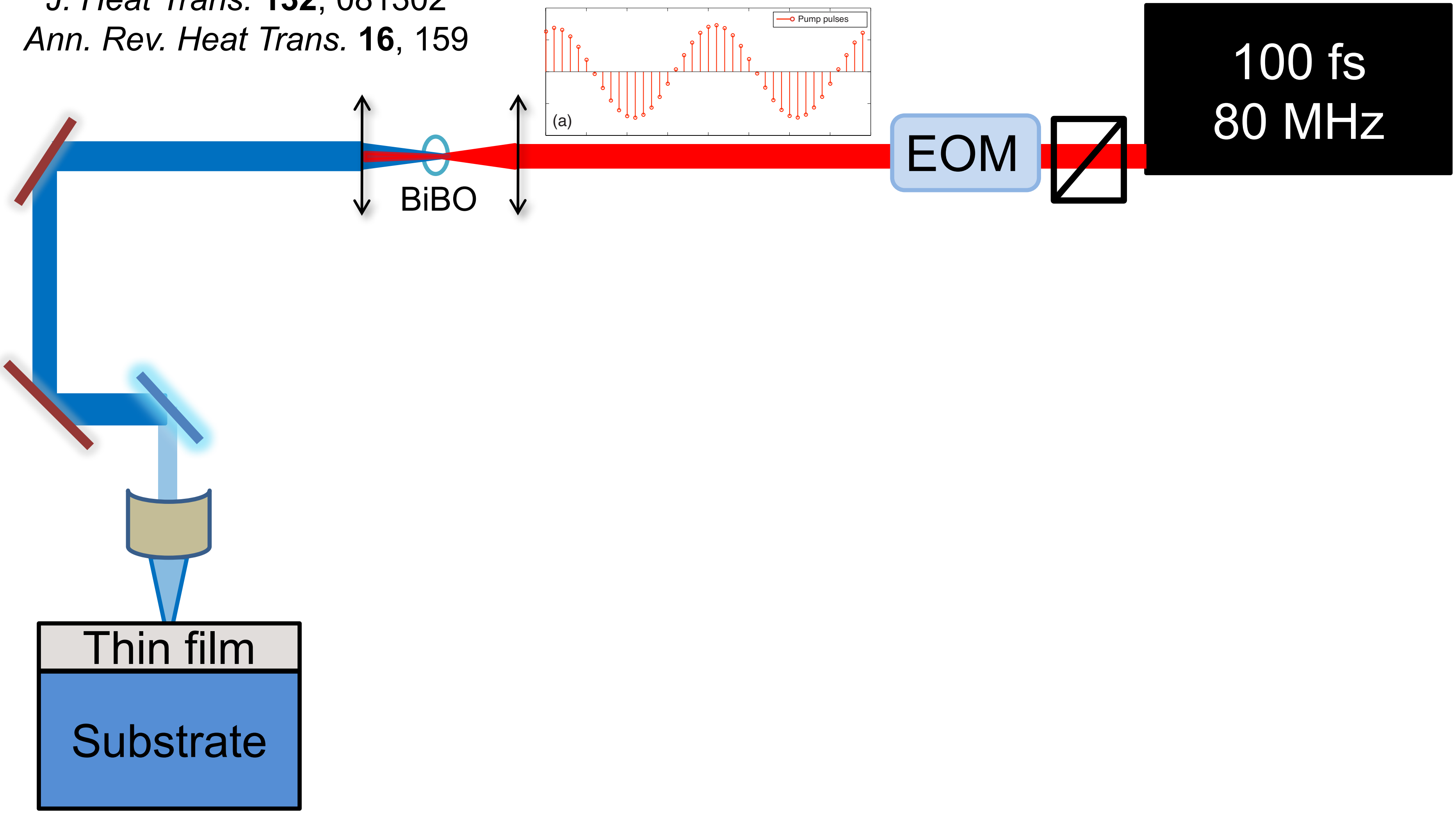
TDTR Reviews and Analyses

Rev. Sci. Instr. **75**, 5119

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

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

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



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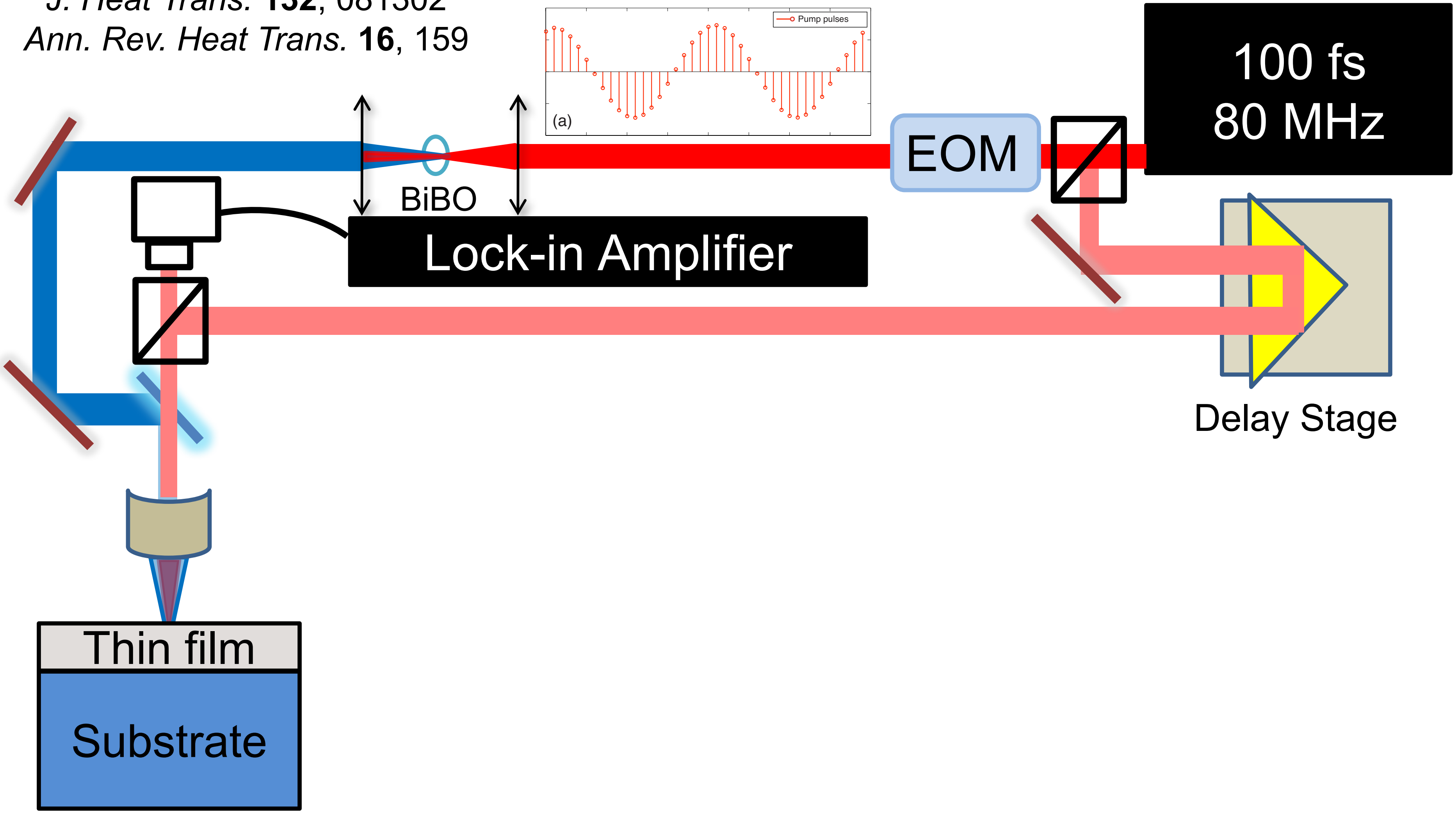

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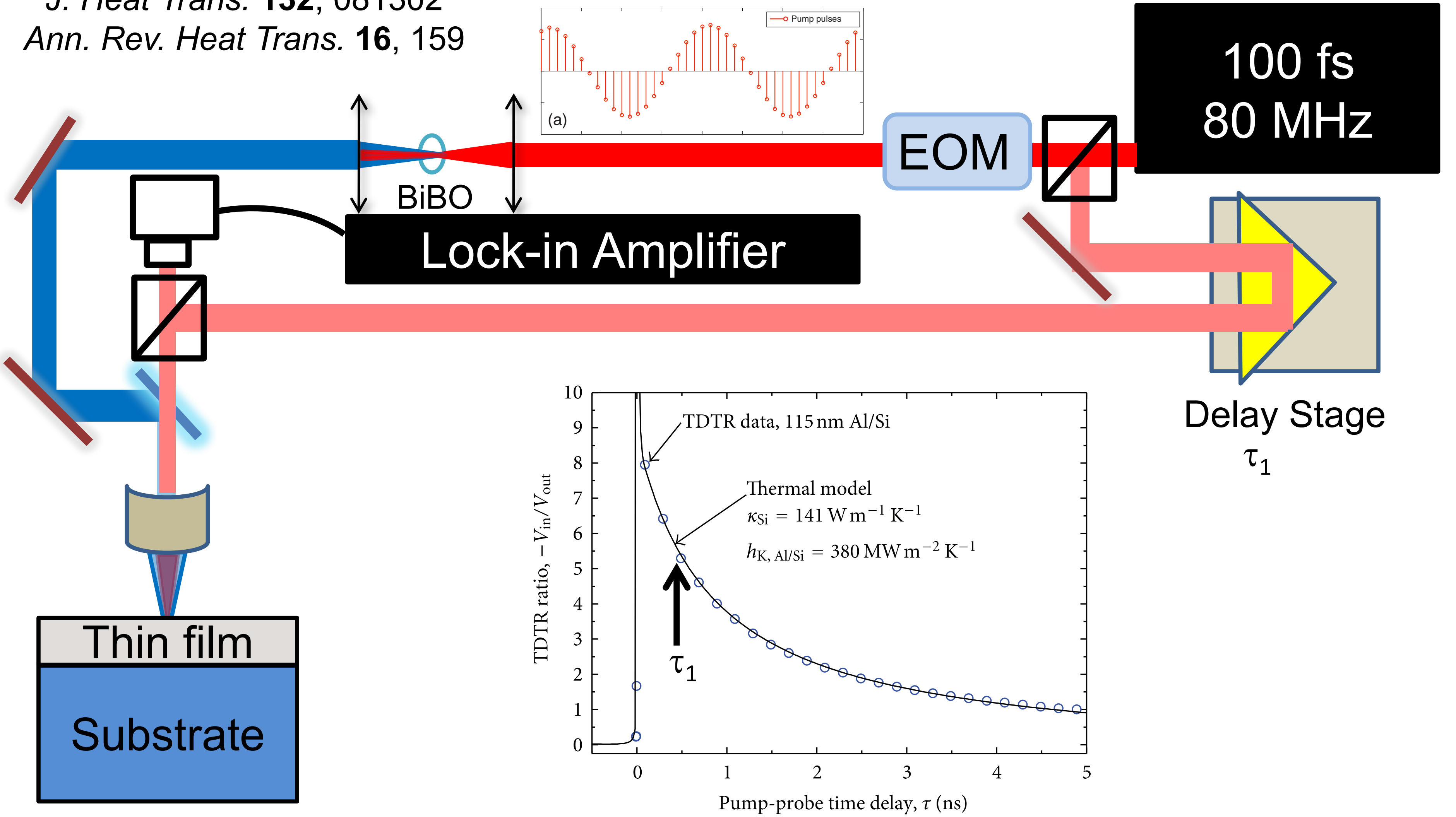

Measuring heat flow in thin films: TDTR

TDTR Reviews and Analyses

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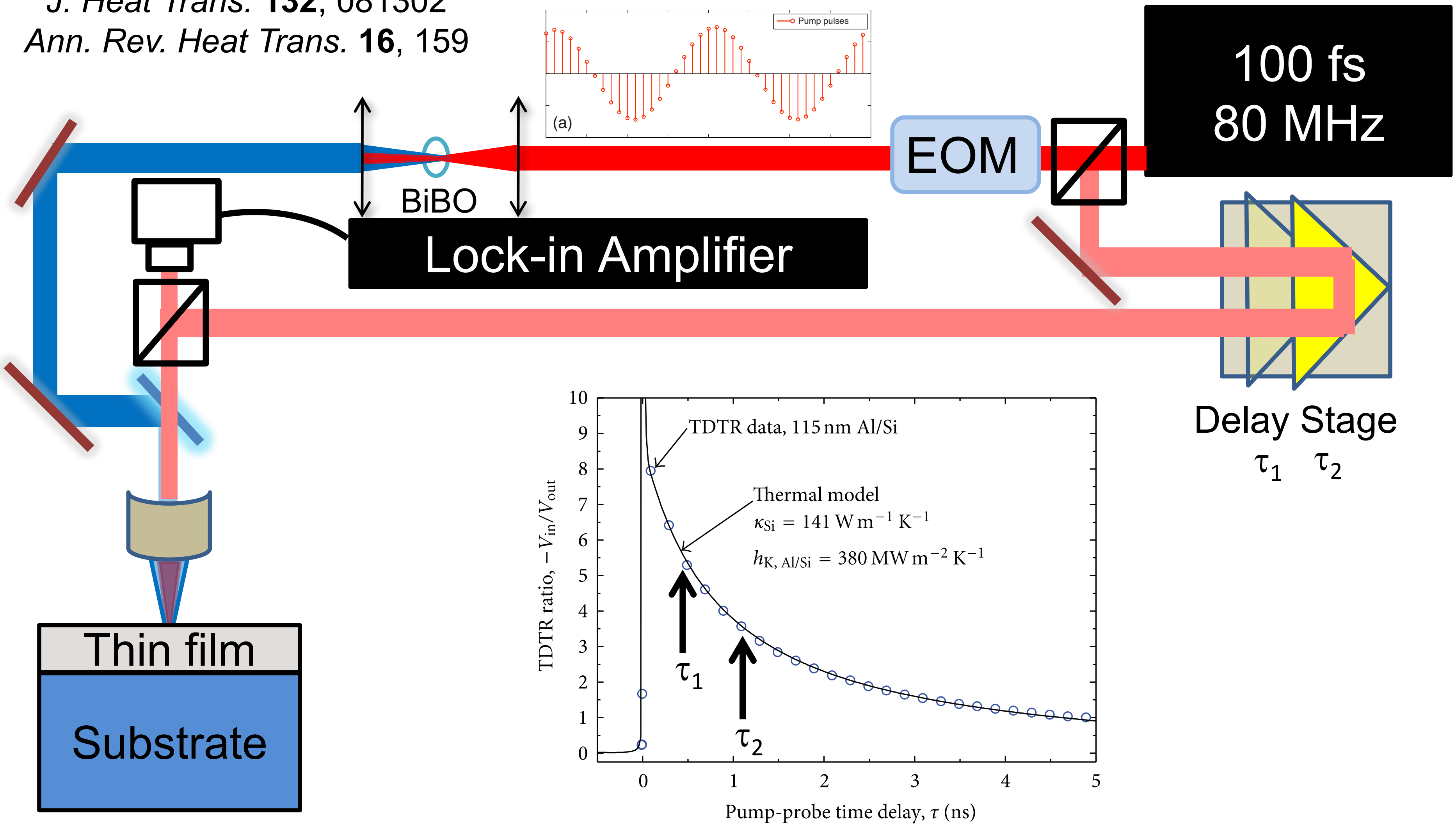
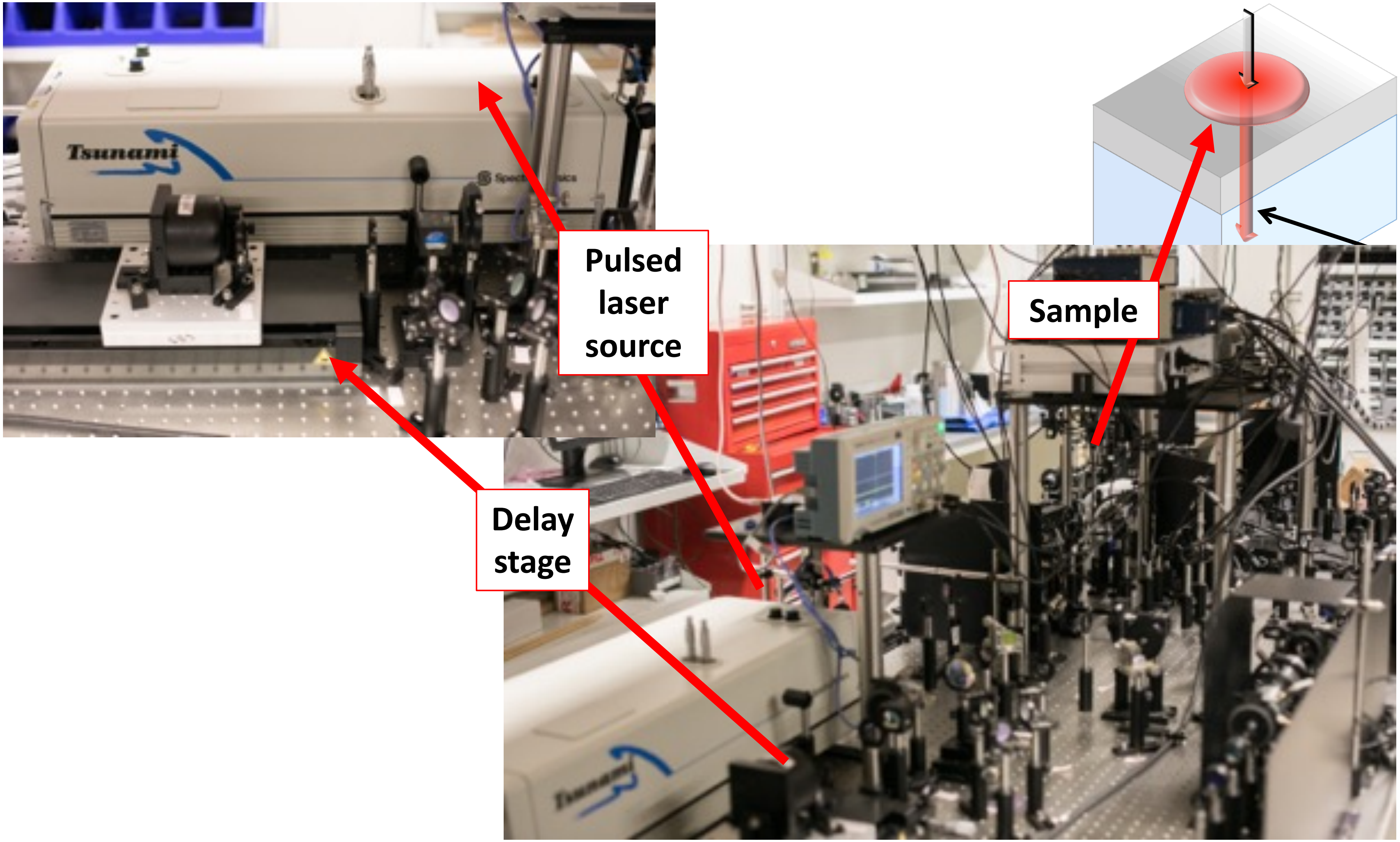
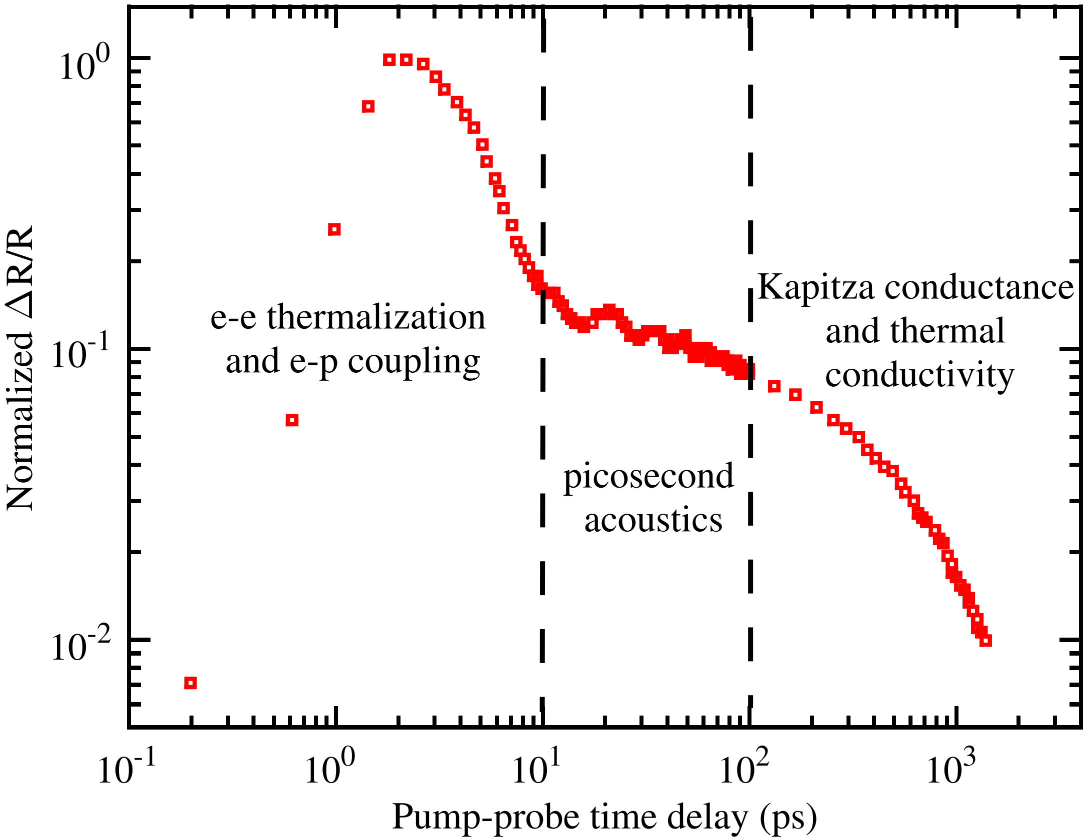


Measuring heat flow in thin films: TDTR



How can we measure nanoscale heat transport processes?

Need time scale resolution < picoseconds



Pulse absorption (~100 fs)

↓

Fermi relaxation and ballistic transport (few hundred fs)

↓

Electron-phonon coupling (a few ps)

↓

Strain propagation in film (10's of ps)

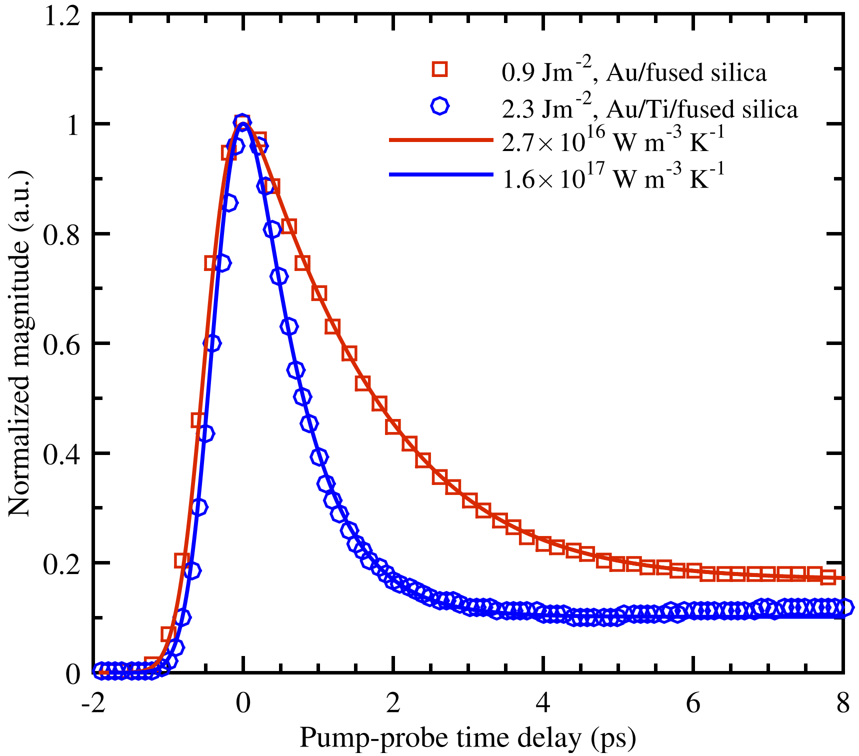
↓

Thermal diffusion (hundreds of ps to ns)

What can we measure with TDTR?

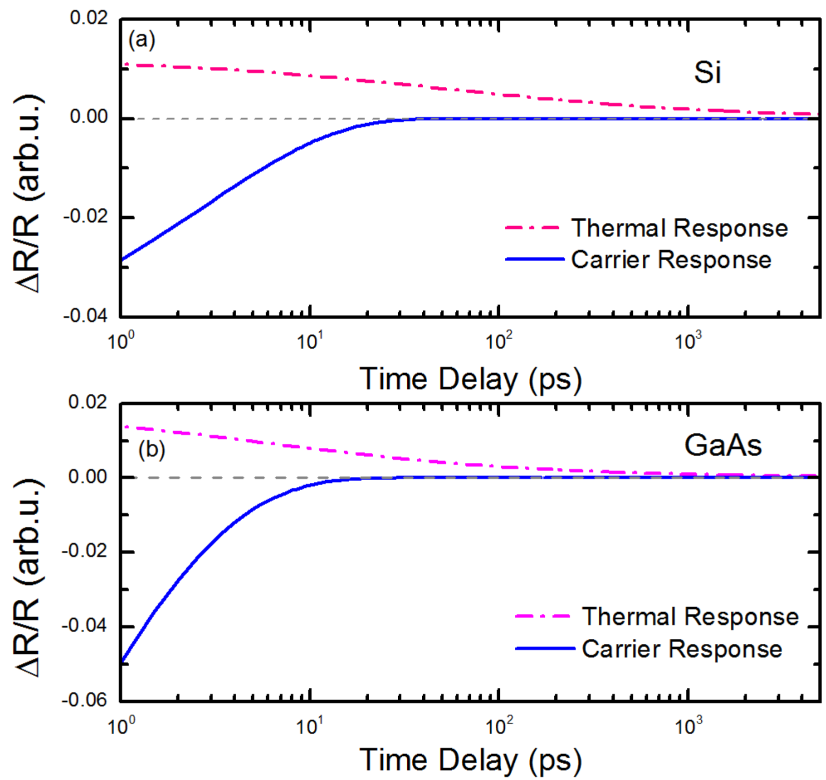
Hot electron relaxation and recombination

Electron-phonon coupling in metals



JAP **117**, 105105

Excited state recombination in semiconductors

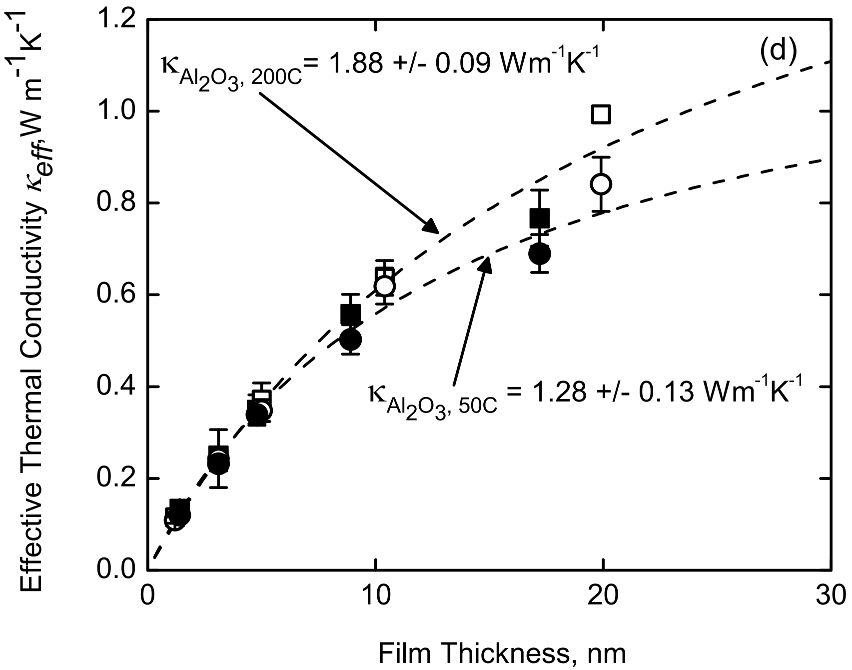


Rev. Sci. Instrum. **87**, 094902

What can we measure with TDTR?

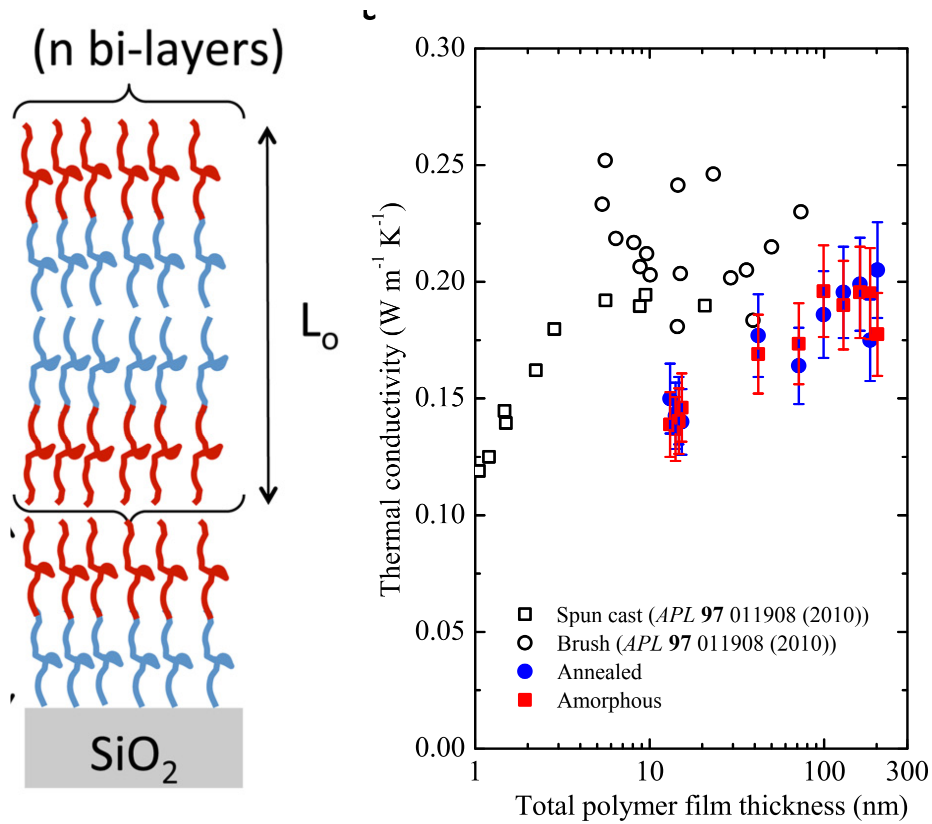
Thermal conductivity of extremely thin films/interfaces

ALD-grown thin films



Thin Solid Films **650**, 71

Block co-polymer thin films

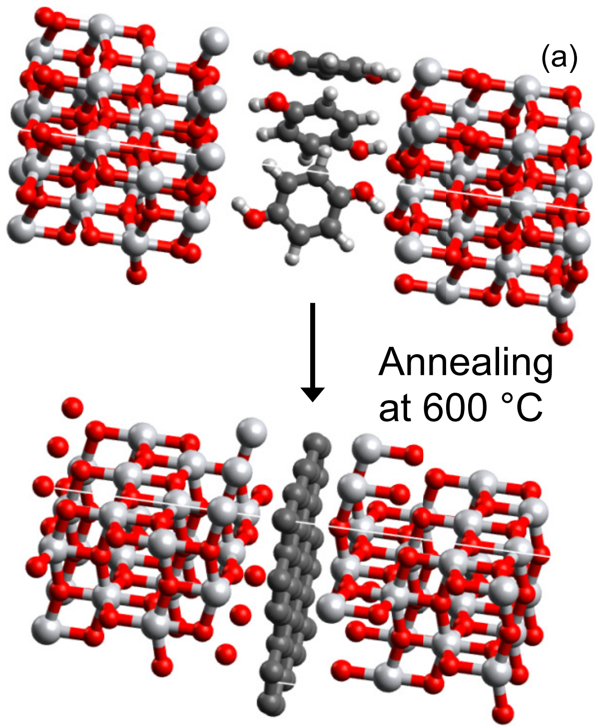


J. Heat Trans. **138** 024505

What can we measure with TDTR?

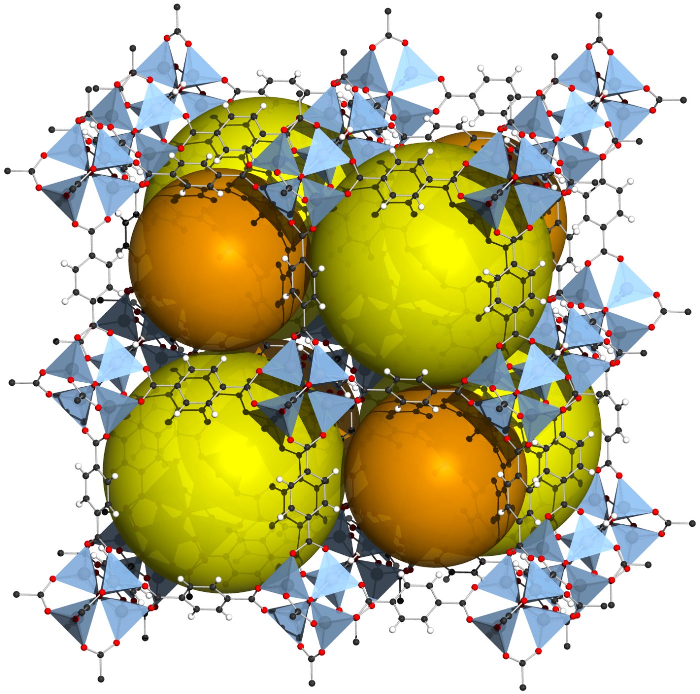
Heat capacity of thin films and some bulk systems

Organic/inorganic hybrid "superlattices"



Phys. Rev. B **93**, 024201

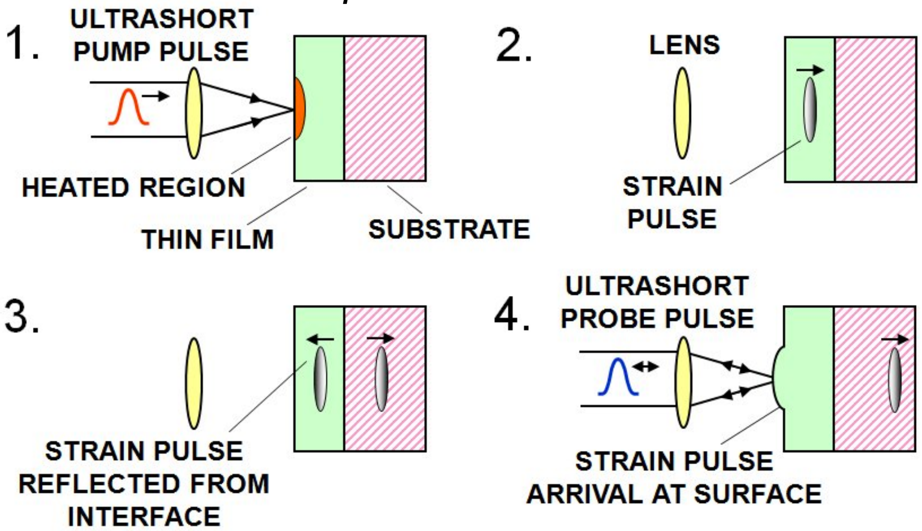
Metal-organic frameworks "MOFs"



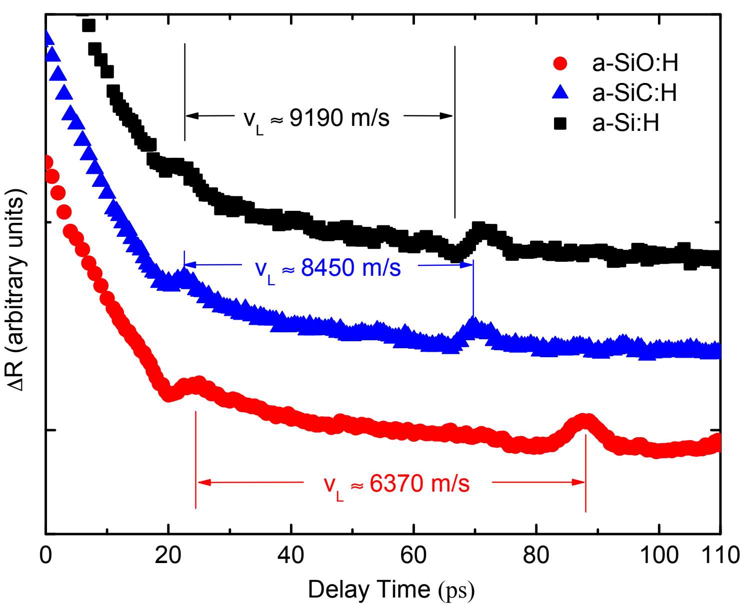
Adv. Mater. **27**, 3453
MRS Bulletin **41**, 877

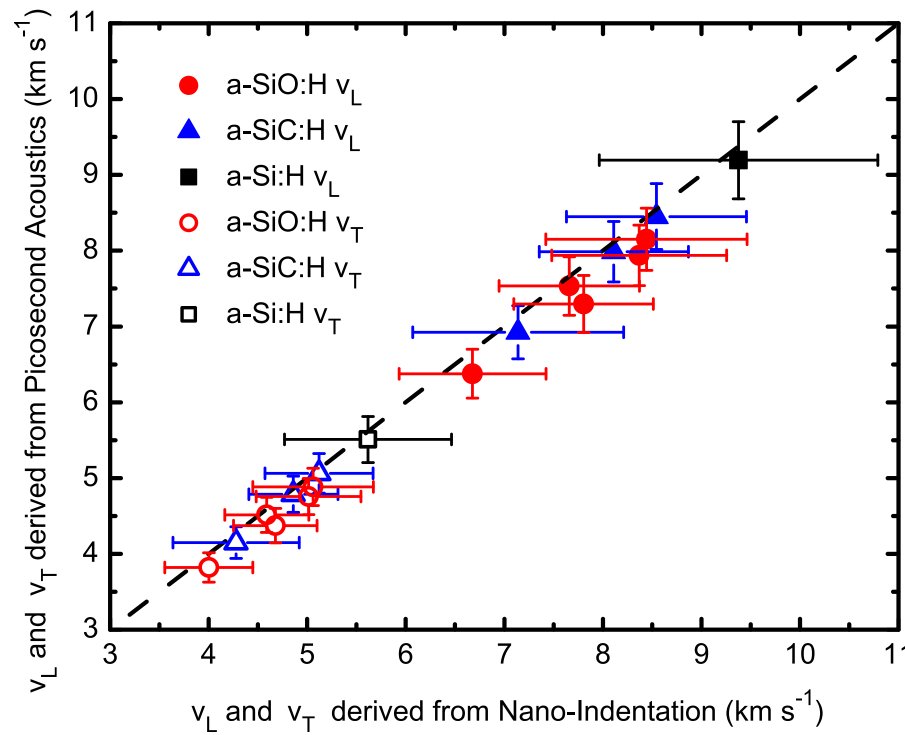
What can we measure with TDTR?

Wikipedia



Measurement of strain wave/acoustic wave propagation in thin films

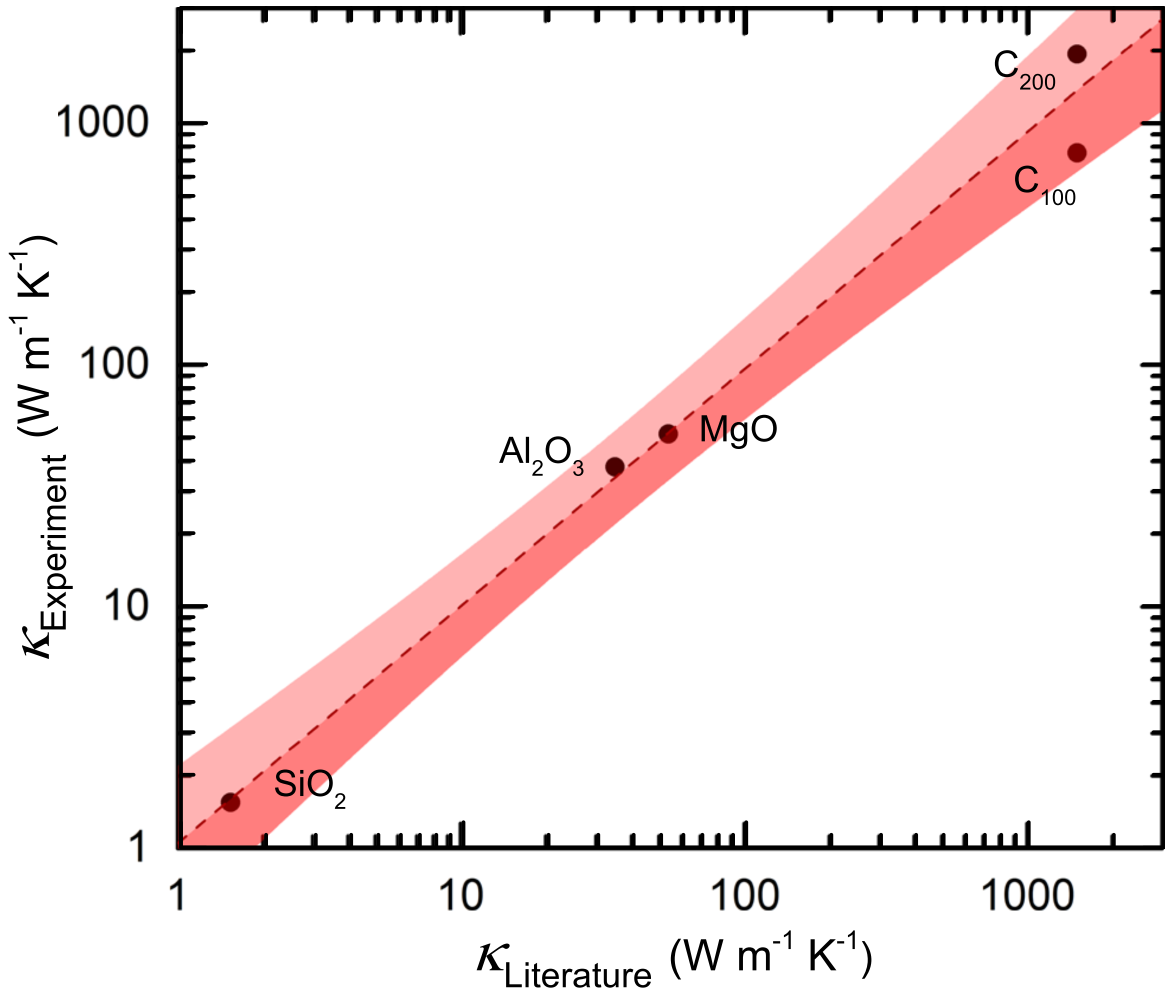




APL **109**, 191905

What can we measure with TDTR?

Bulk materials



Rev. Sci. Instrum. **87**, 094902

Appl. Phys. Lett. **111**, 151902

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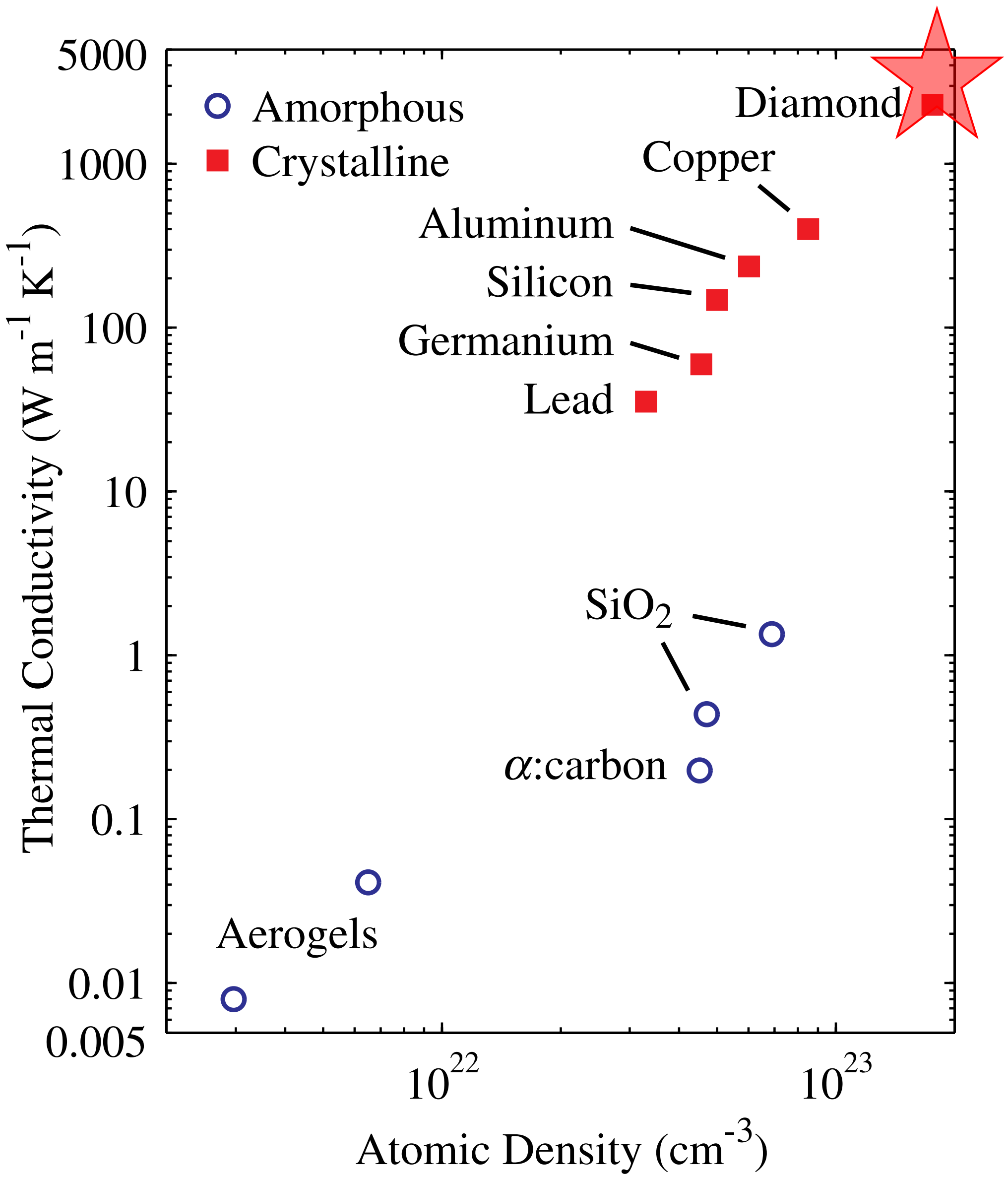
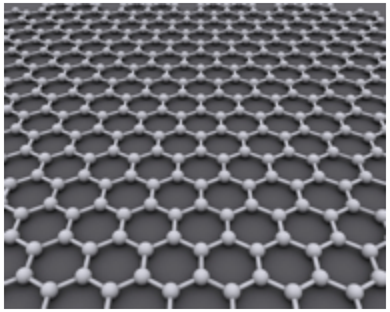
Thermal conductivity of materials – Role of the bond



Ultrahigh thermal conductivities (diamond, graphene, BAs, etc)



Light masses, stiff bonds

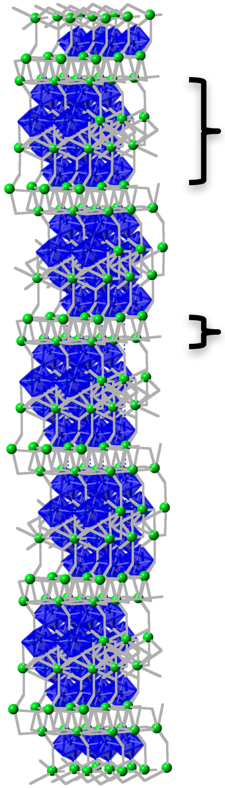
How do we go the other way?
Heavy masses, weak bonds

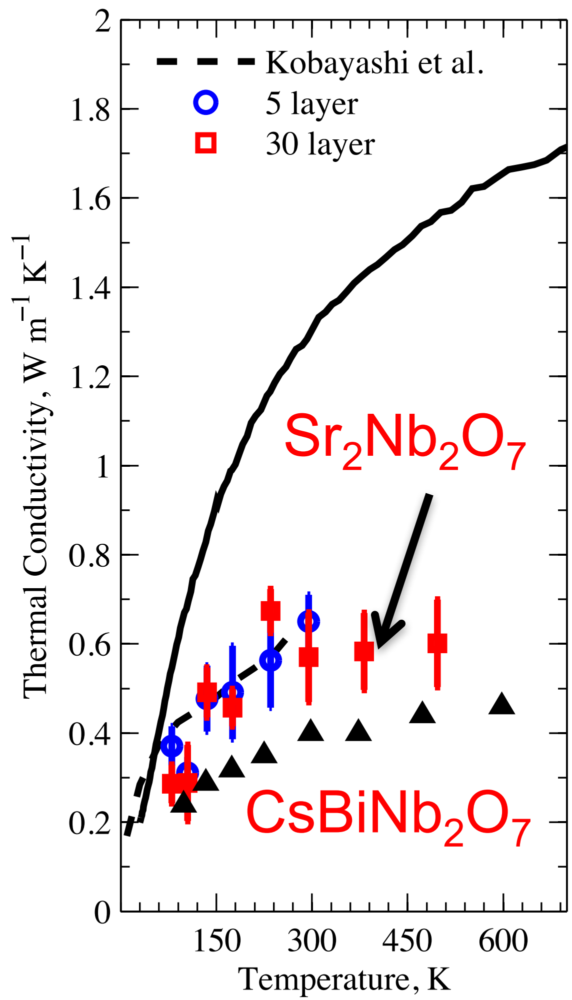
PRL **110**, 015902 (2013)

Thermal conductivity of materials – Role of the bond

Layered structures can exhibit ultralow thermal conductivity

Ex. $Sr_2Nb_2O_7$

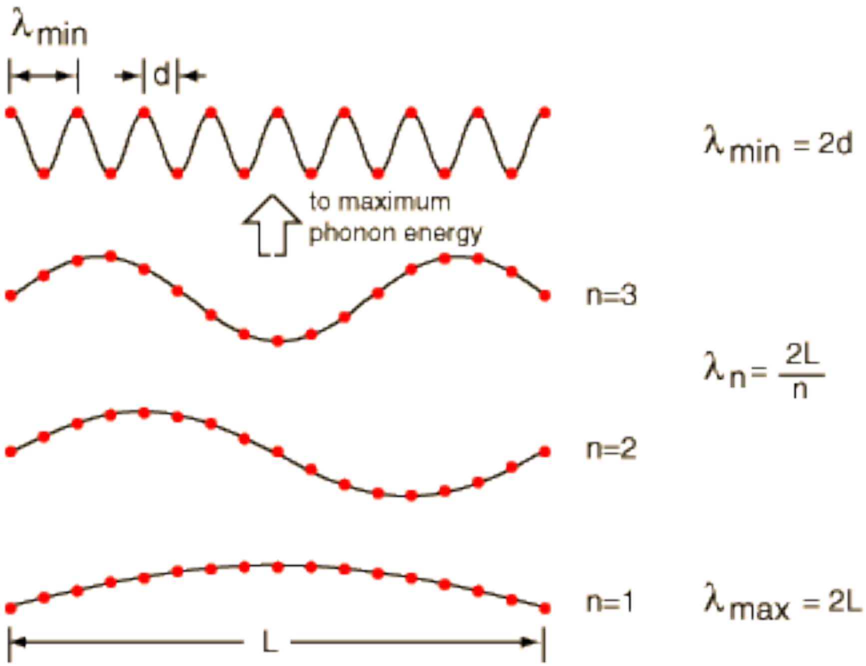




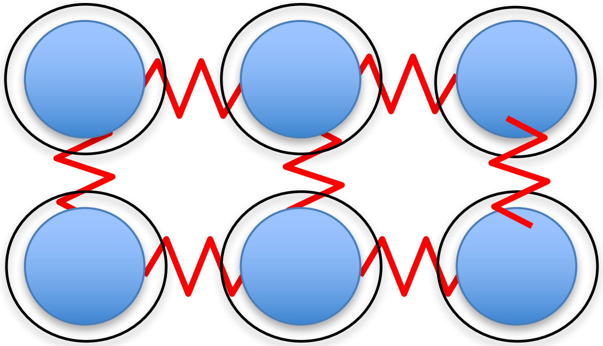
JACerS **98**, 624

The Einstein oscillator

The phonon picture (coupled oscillators): several different wavelength in a lattice (many energies)



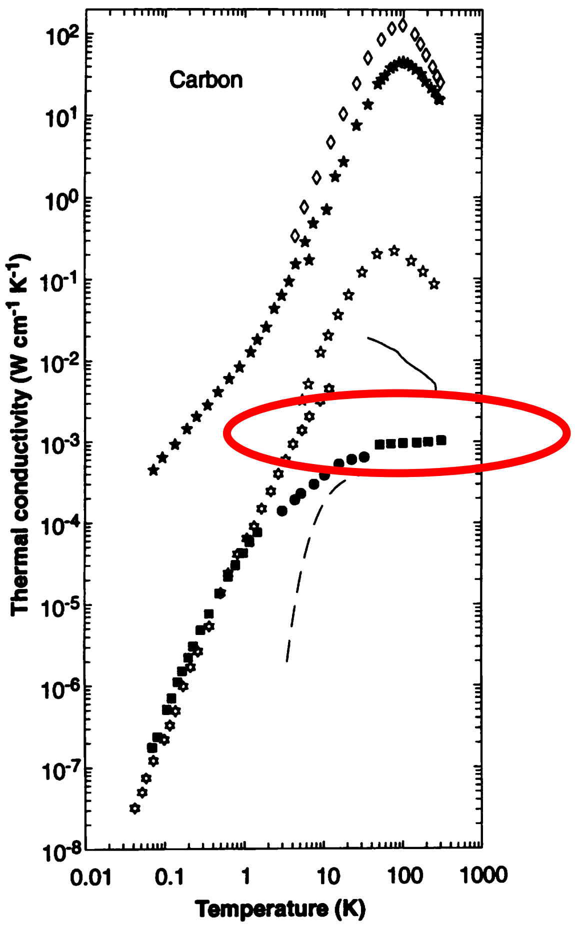
Single frequency of vibration of atom and energy “hops” from one site to another



“Springs” are very very weak

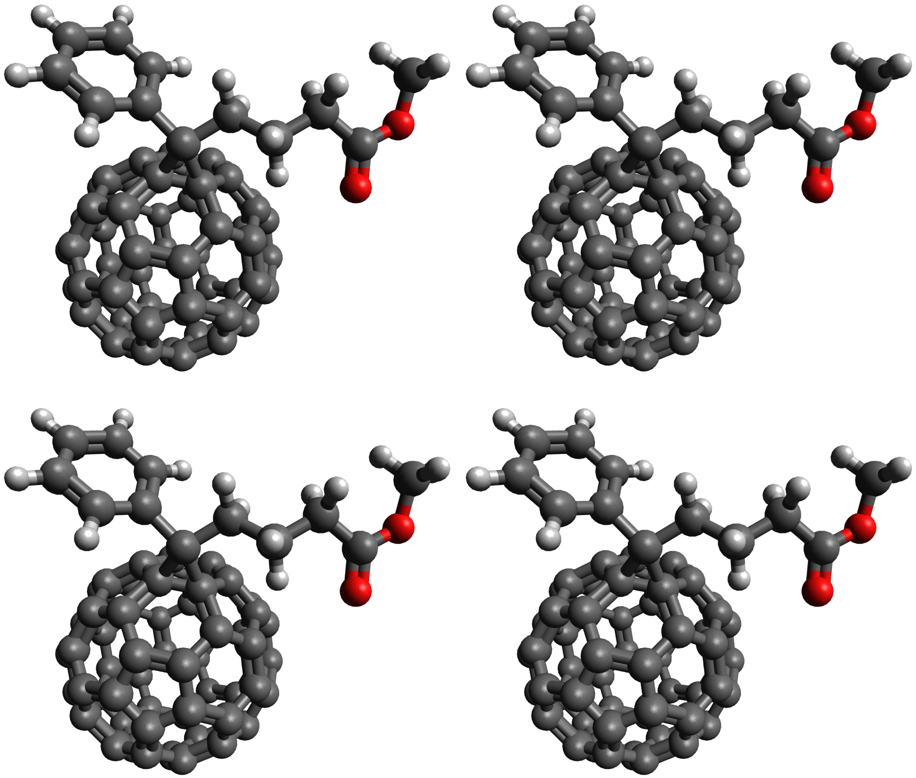
The Einstein oscillator – weakly interacting buckyballs

Fullerene films: Low thermal conductivities



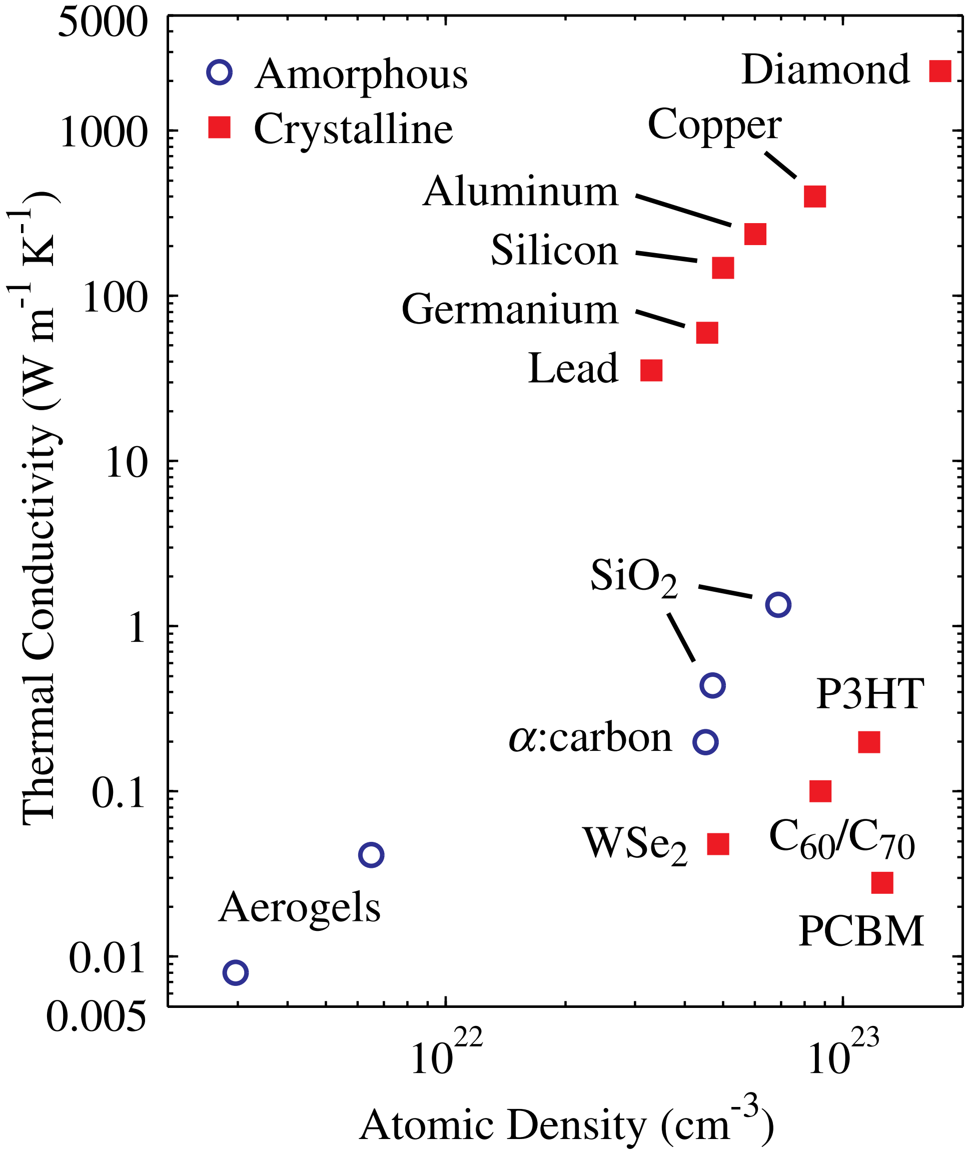
Science **259**, 1145

Add "disorder" with molecules: [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM)

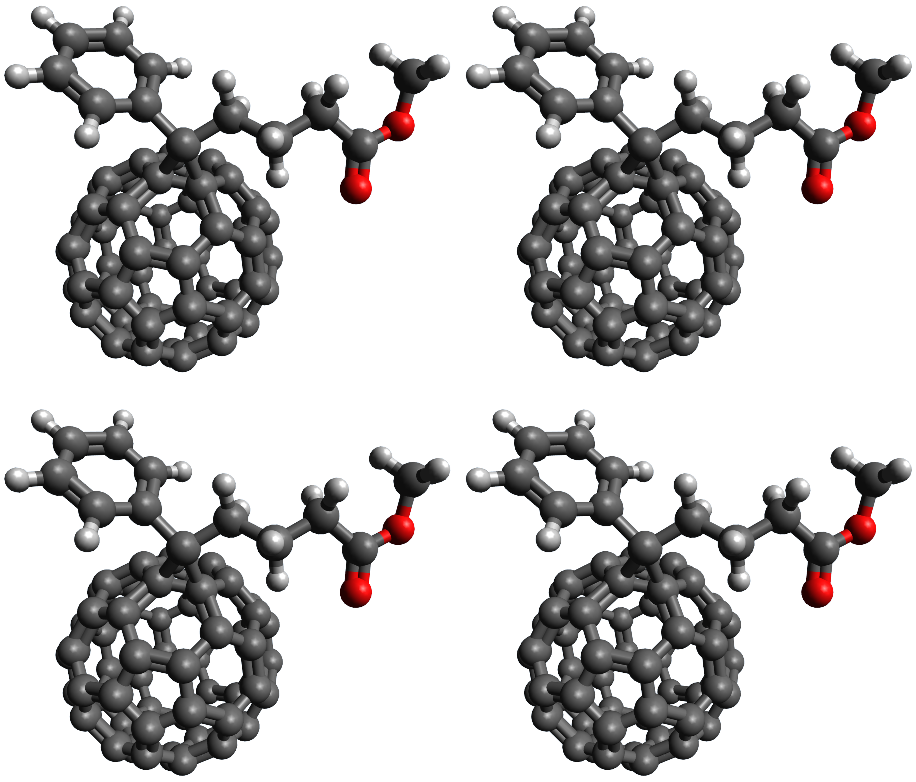


New lower extreme of thermal conductivity of materials

But why???

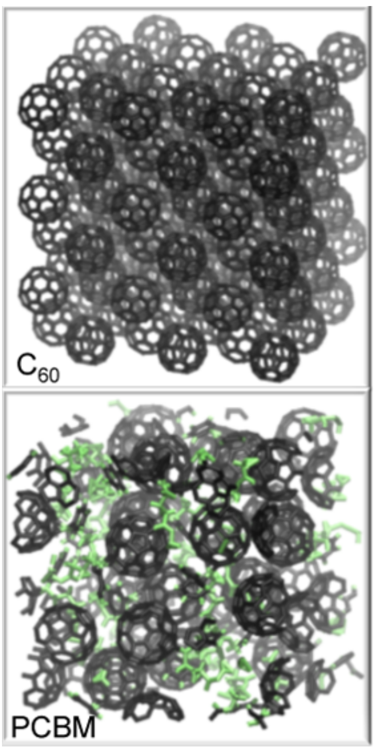


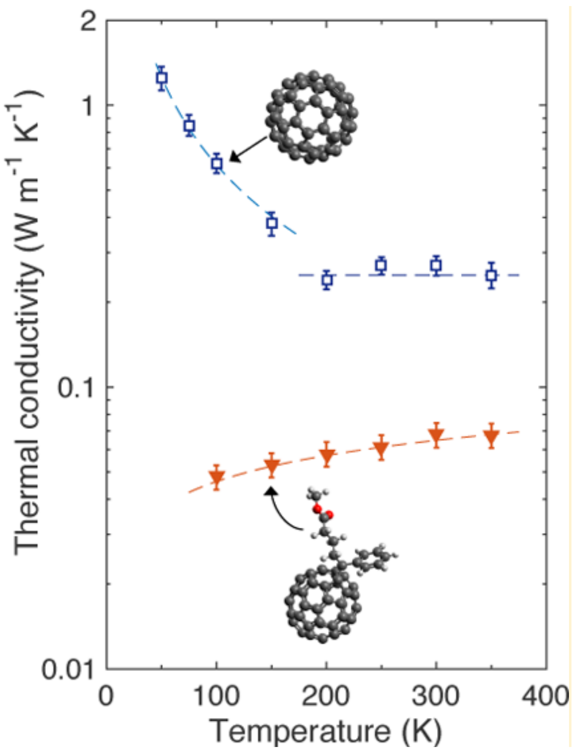
$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

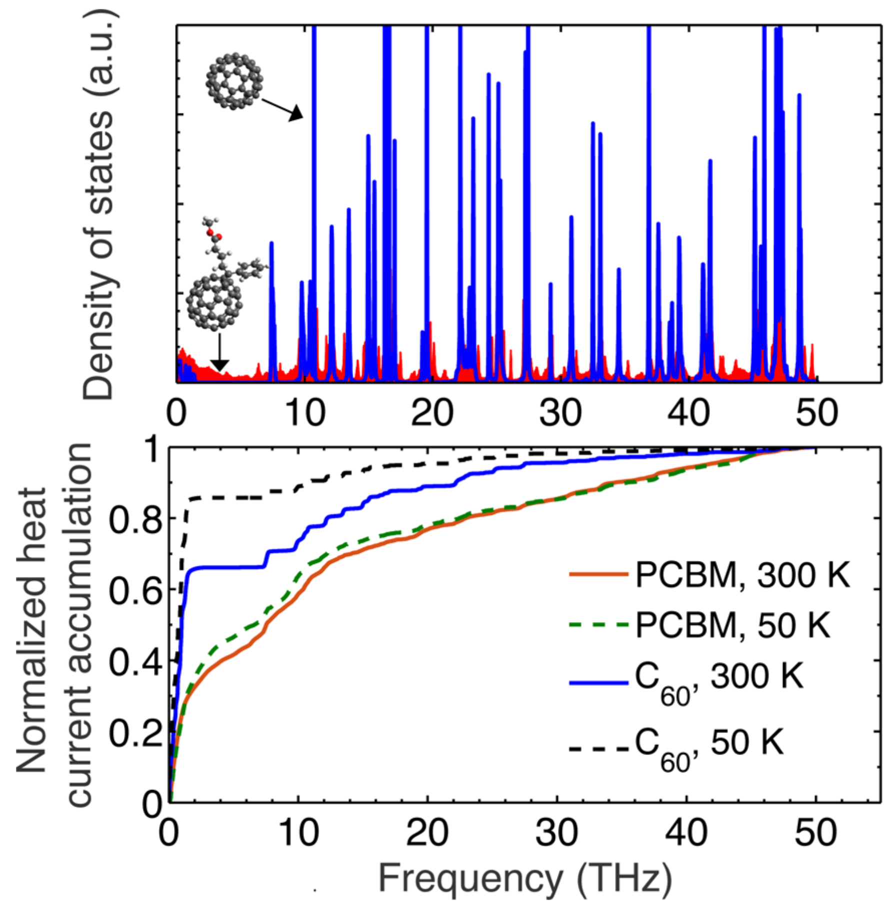


PRL **110**, 015902 (2013)

Turn to molecular dynamics simulations



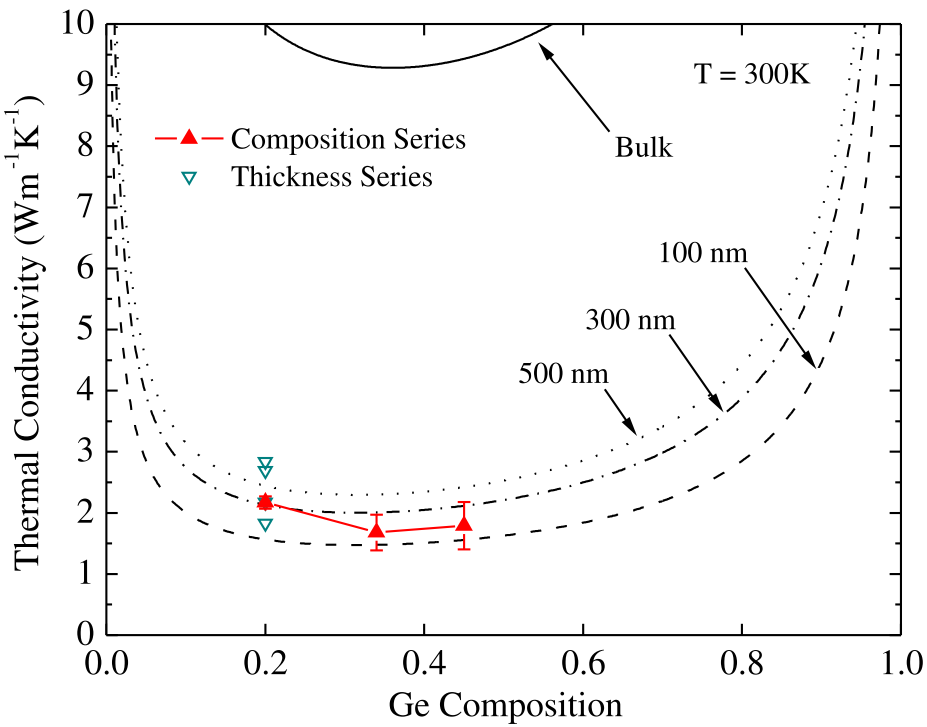




J. Phys. Chem. Lett. **8**, 2153 (2017)
Phys. Rev. B **96**, 220303 (2017)

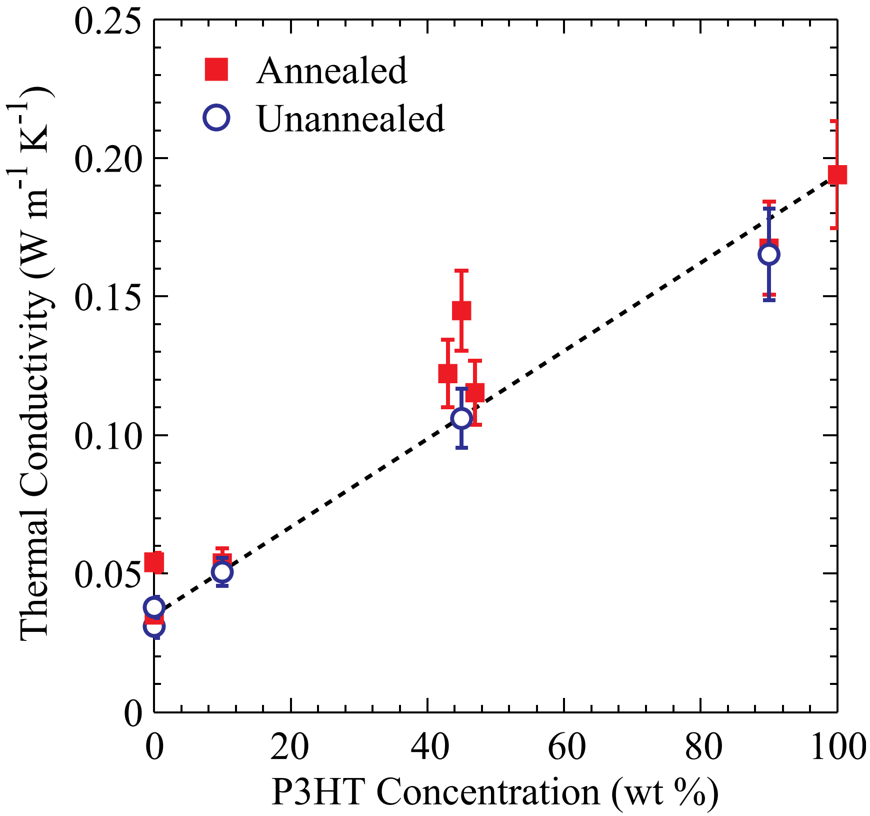
Tuning the thermal conductivity of molecular films

Covalent bonds
Crystals/“phonons”
Si_xGe_{1-x} alloy



Phys. Rev. Lett. **109**, 195901

Weak bonds
Vibrons
PCBM-P3HT blend



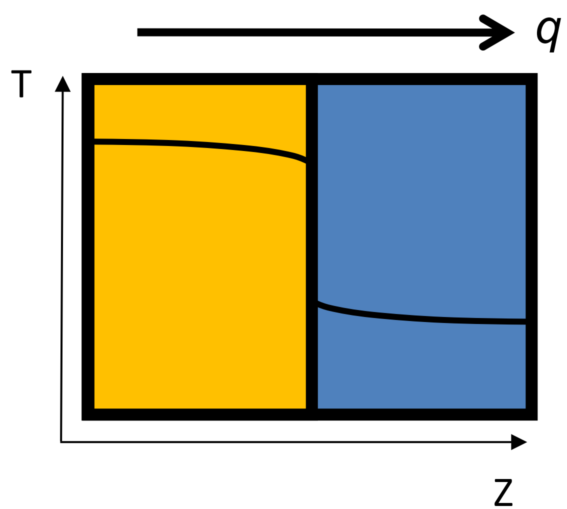
Appl. Phys. Lett. **102**, 251912

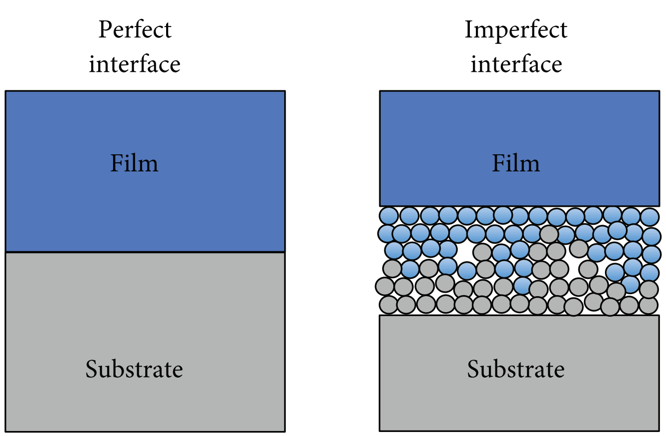
Outline

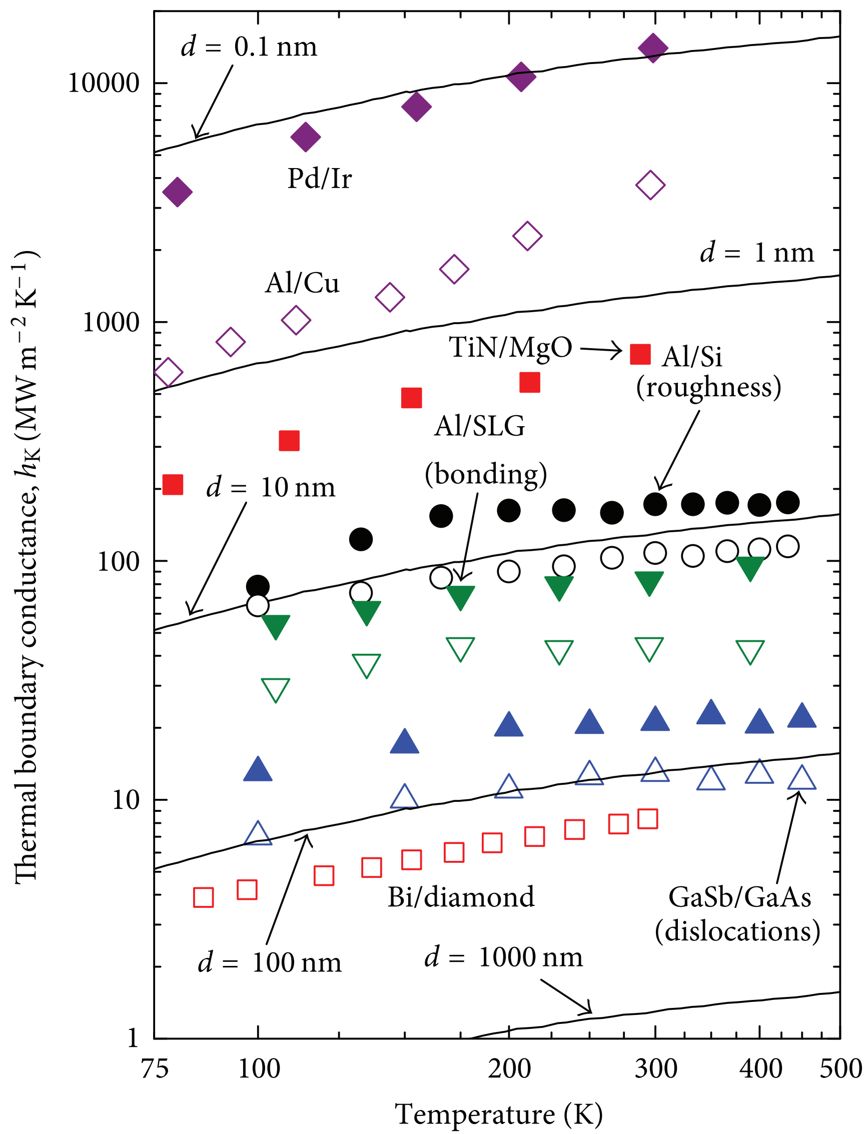
- TDTR: Measurement of thermal conductivity of thin films and thermal resistance across interfaces
- Weakly bonded solids: new lower limits to thermal conductivity
- **Functionalized interfaces at graphene contacts: tuning heat and electrical transport via the interfacial bond**
- Heat transport across single molecule interfaces: when does a molecule become a defect?
- Molecular interfaces in organic/inorganic composites: diffusive scattering via the vibron-phonon interaction

Thermal boundary conductance – nanoscale resistances

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

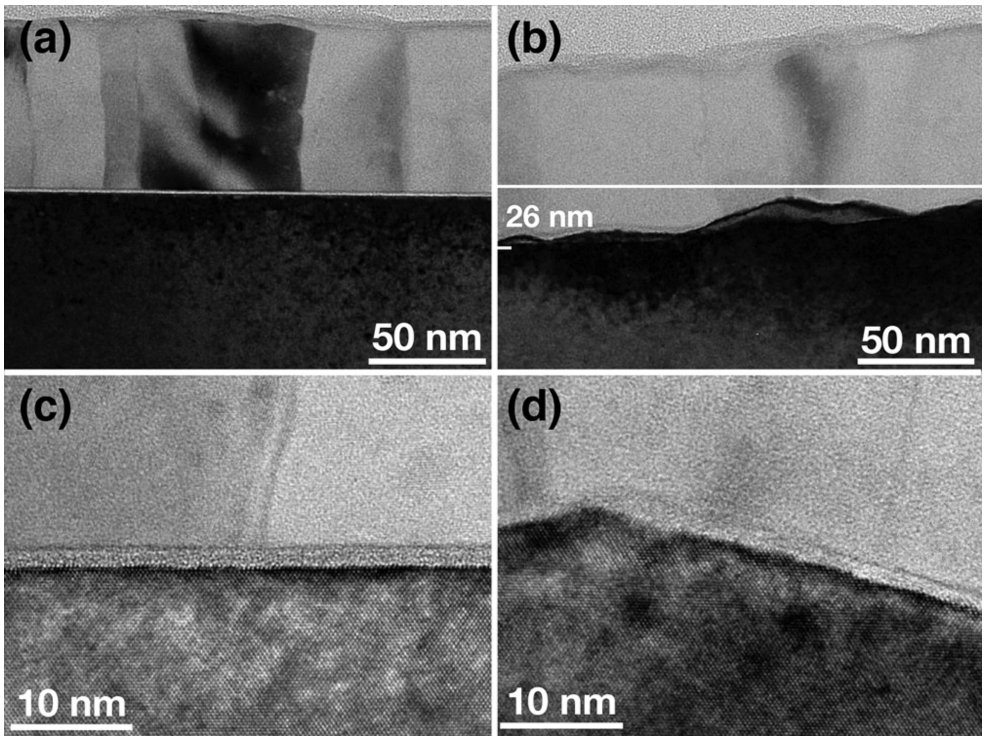


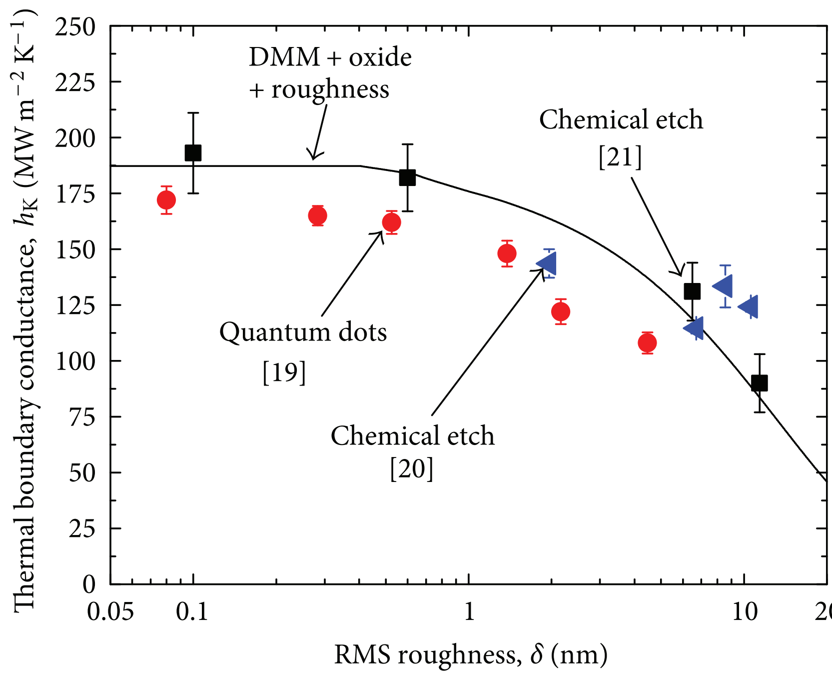




ISRN Mech. Eng. **2013**, 682586

Thermal boundary conductance – nanoscale resistances

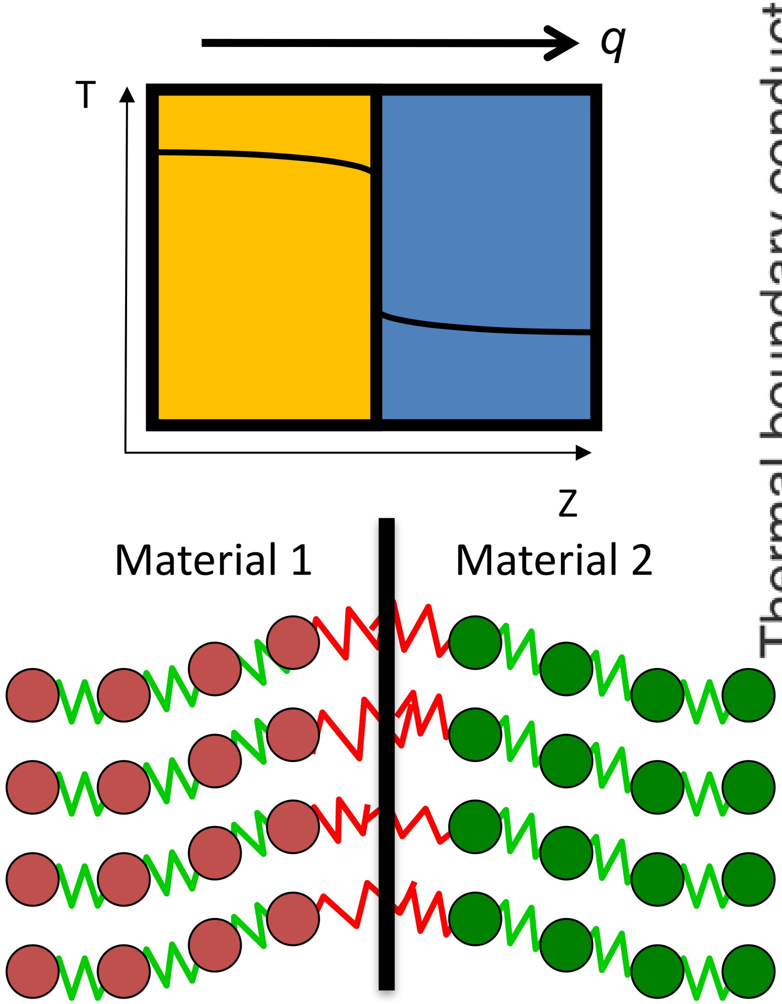


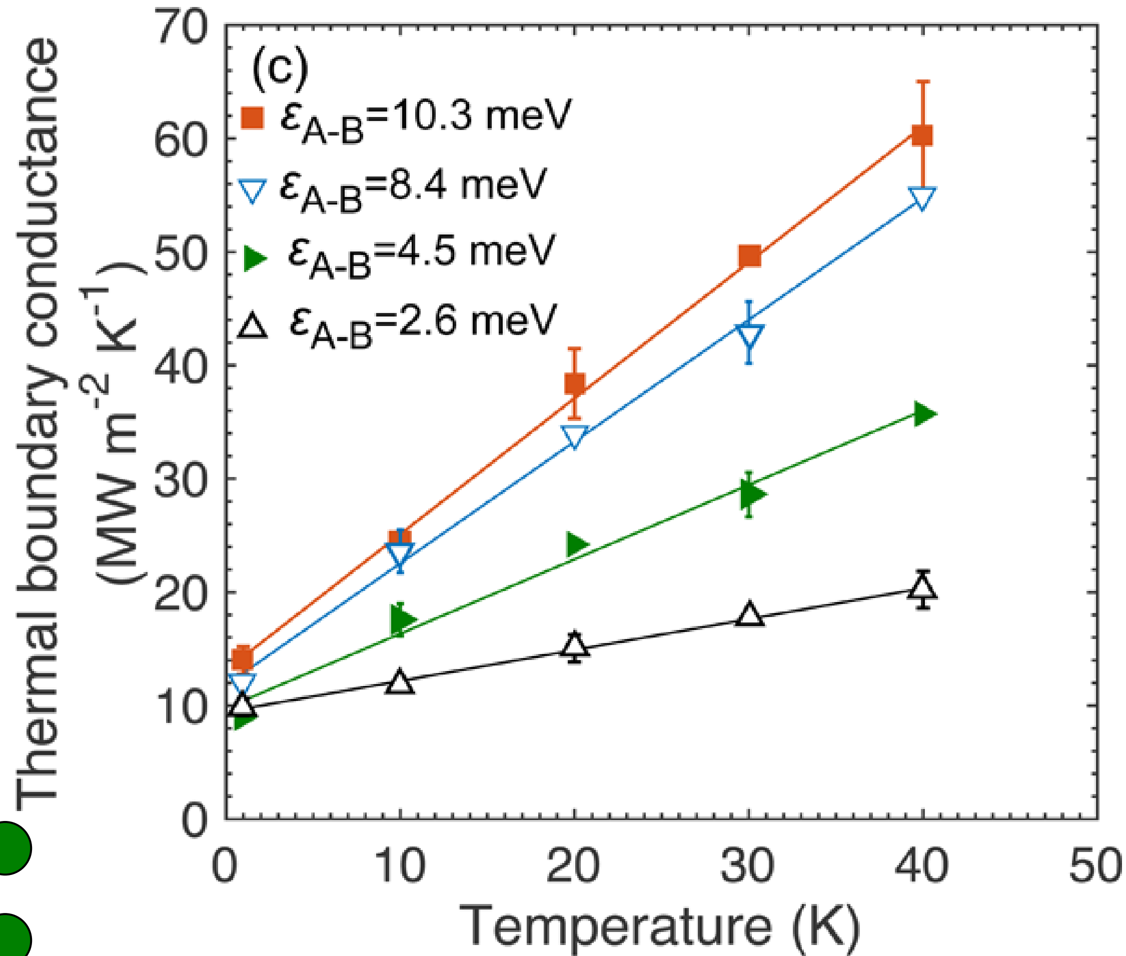


ISRN Mech. Eng. **2013**, 682586

Increase in bonding increases solid/solid TBC

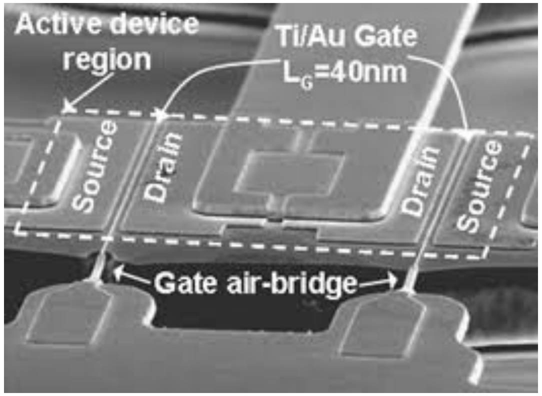
$$q = h_{\mathrm{K}} \Delta T = \frac{1}{R_{\mathrm{K}}} \Delta T$$



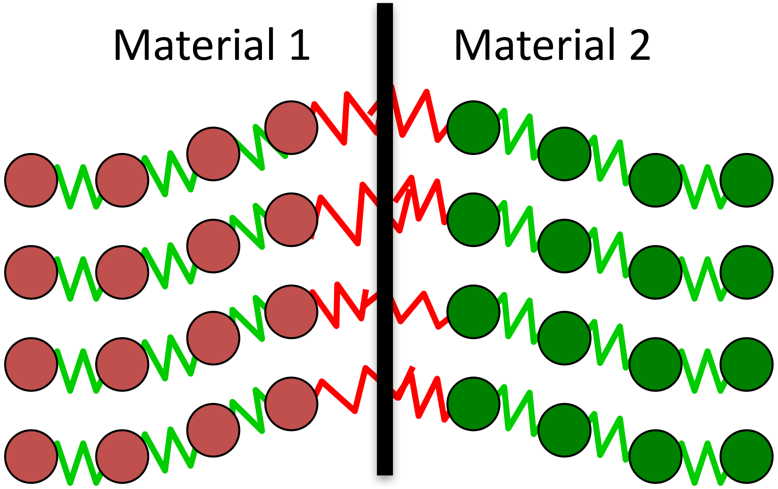


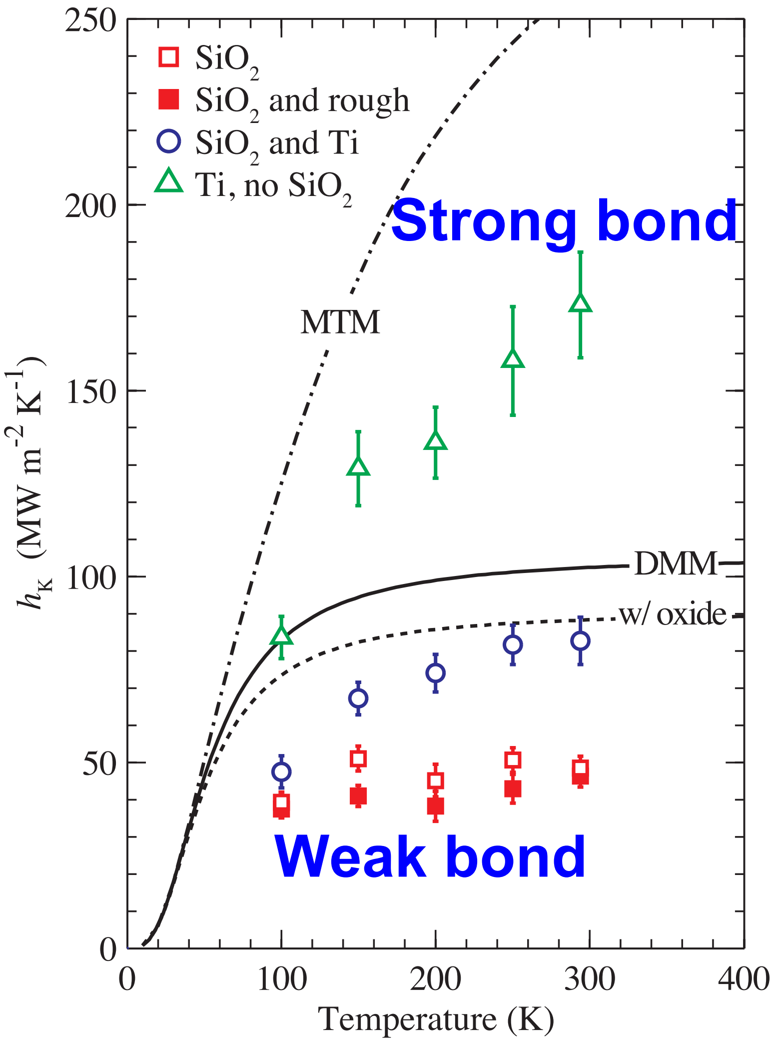
J. Phys. Chem. C **120**, 24847

Thermal boundary conductance – bonding effects



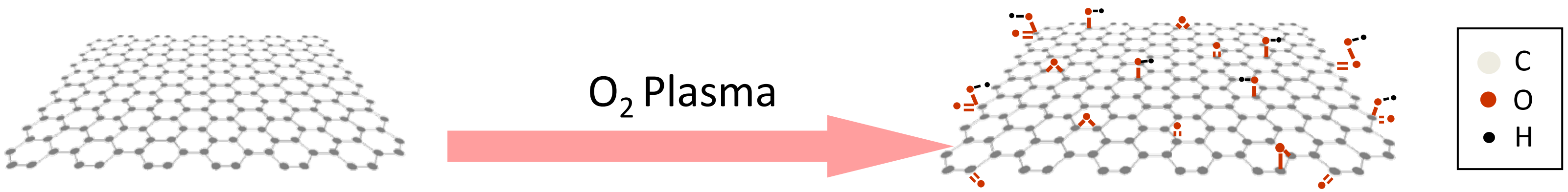
However, bonding plays a HUGE ROLE at the Au/Si interface

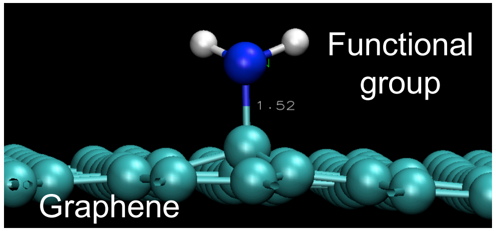




Appl. Phys. Lett. **102**, 081902 (2013)

Atmospheric plasma functionalization of graphene surfaces



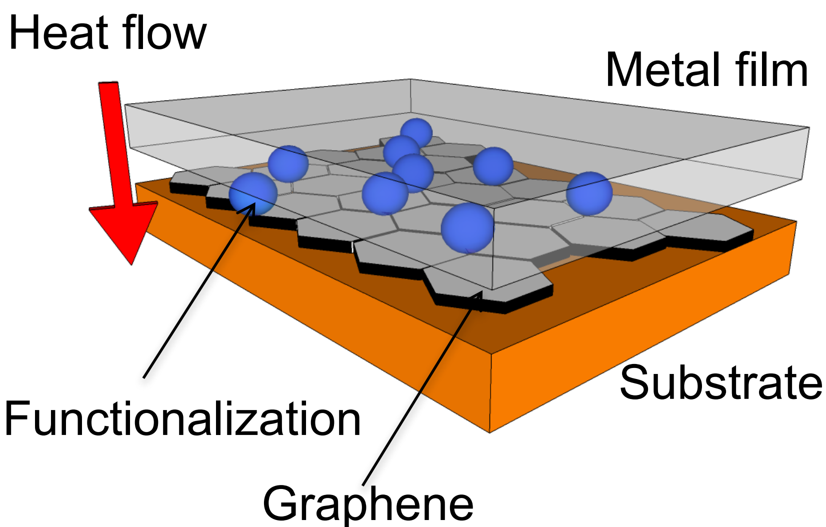


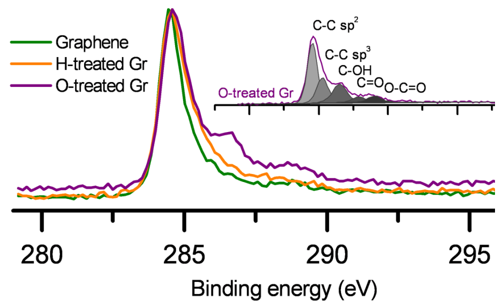
Functional groups covalently bound to graphene
Reversible after anneal

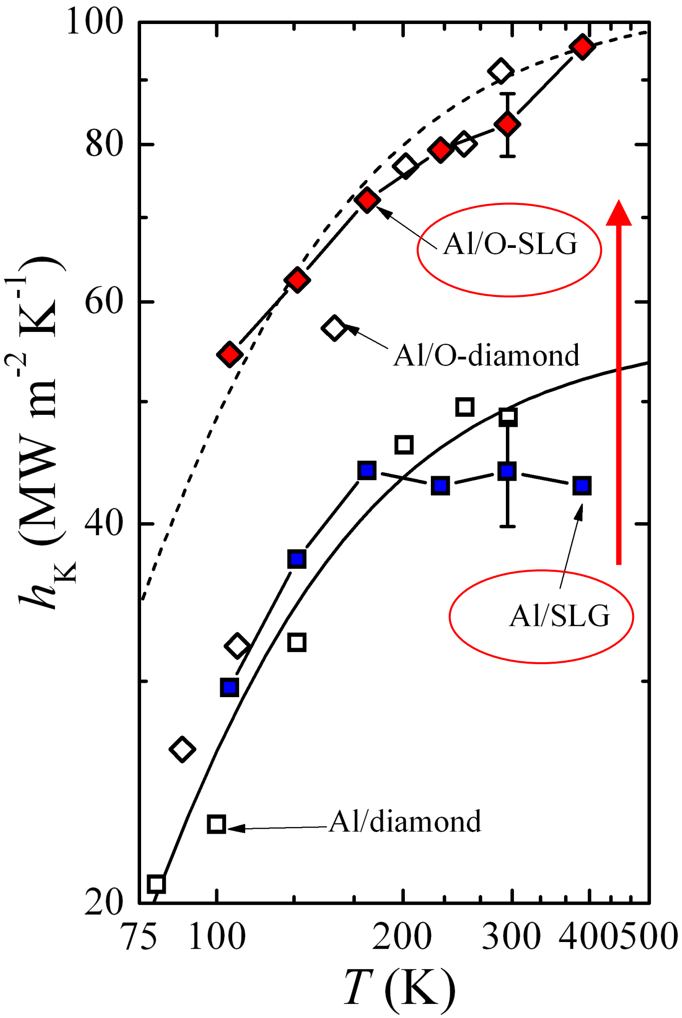
Appl. Phys. Lett. **96**, 231501

Collaboration: Scott Walton (NRL)

Atmospheric plasma functionalization of graphene surfaces





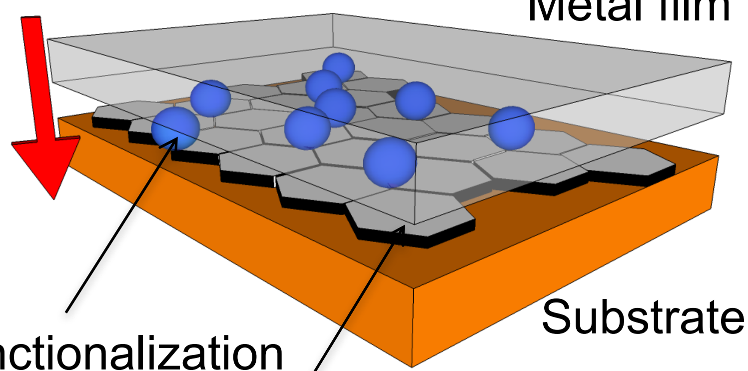


Nano Lett. **12**, 590 (2012)

- **Al/graphene interaction increased with oxygen bond (Al-O bond)**
- **But what implications does this have for SLG devices?**

Collaboration: Scott Walton (NRL)

Au/graphene electronic contacts

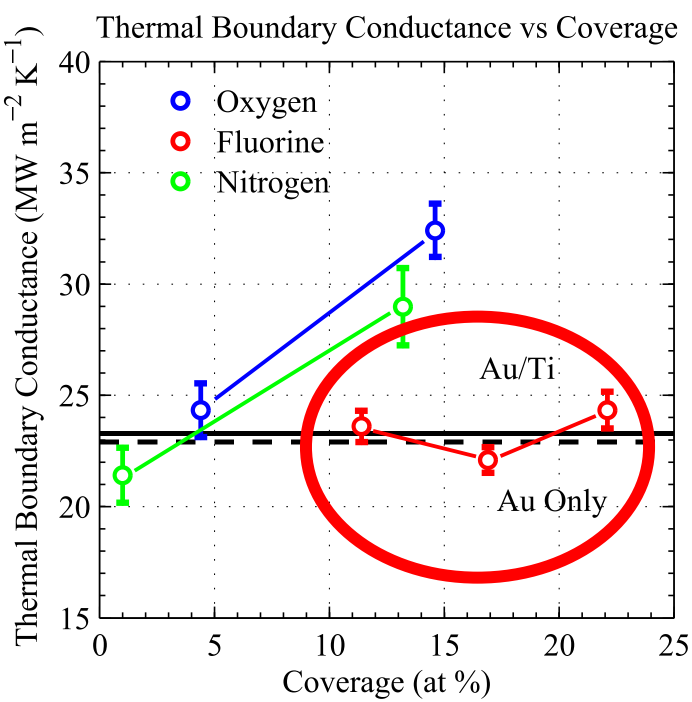


<u>Thermal boundary conductance results</u>

Similar trends for oxygen as Al

Ti adhesion layer does nothing

Fluorine does nothing

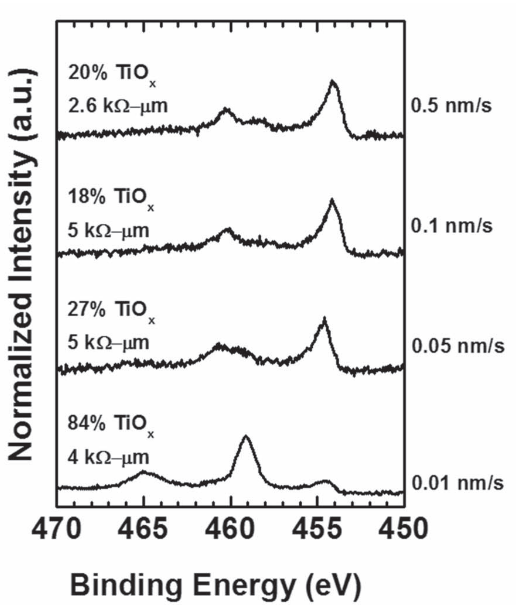


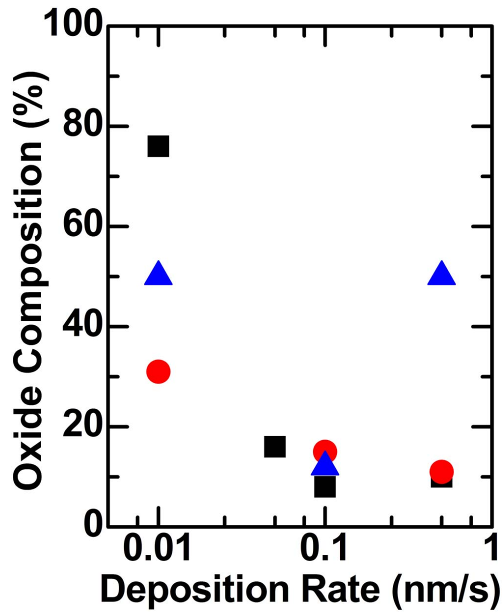
C-F bond inert does not want to interact!

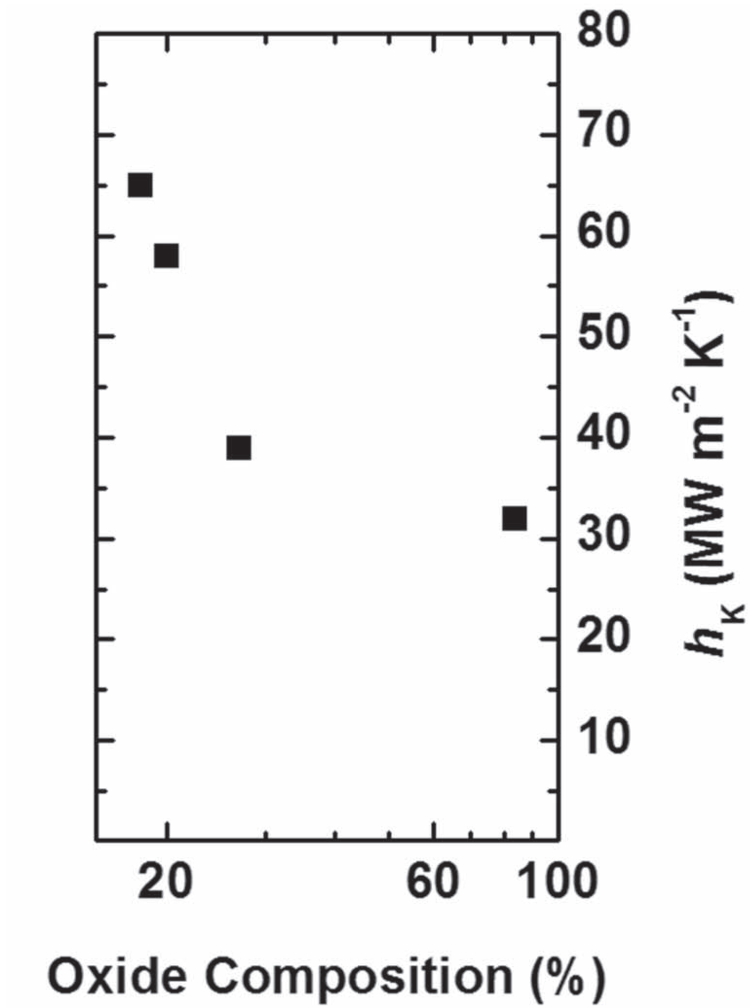
Nano Lett. **15**, 4876 (2015)

Collaboration: Scott Walton (NRL)

Chemistry effects on the TBC across Au/Ti/graphene





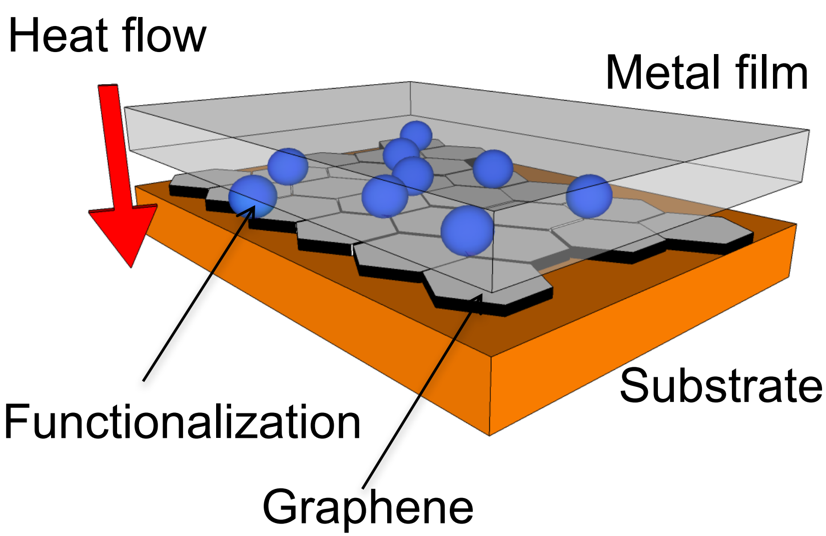


Nanotechnology **29**, 145201

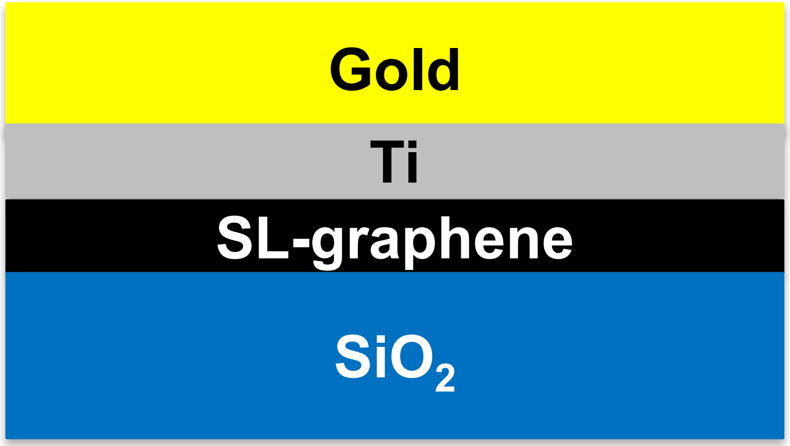
Collaboration: Stephen McDonnell (UVA)

Chemistry effects on the TBC across Au/Ti/graphene

Bonding engineering at interface



Defect engineering at interface



When does a molecular bond become a defect?

Outline

- TDTR: Measurement of thermal conductivity of thin films and thermal resistance across interfaces
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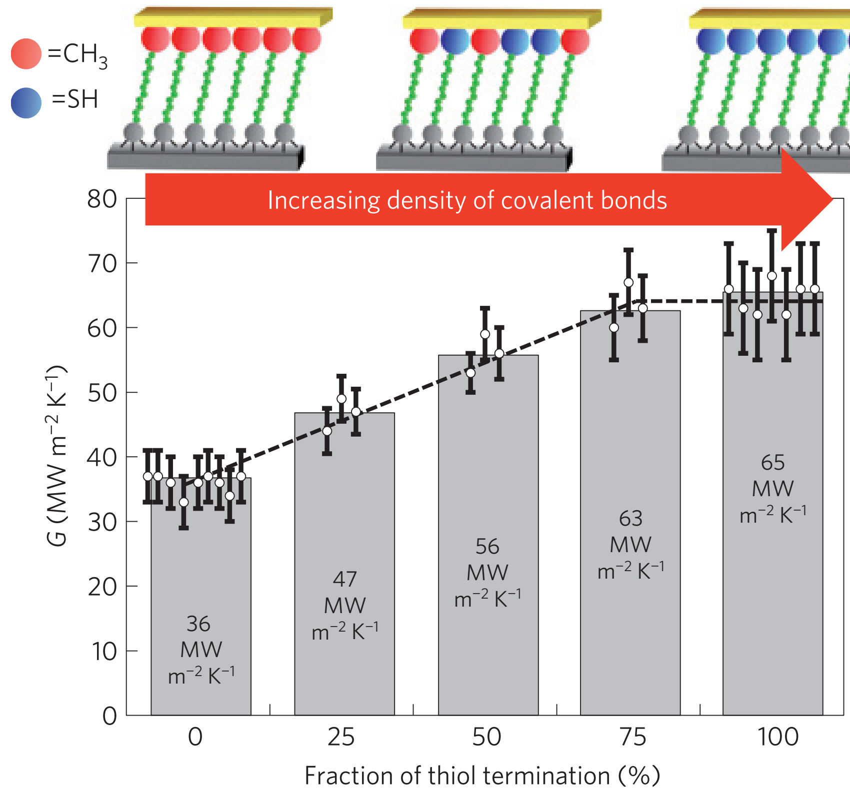
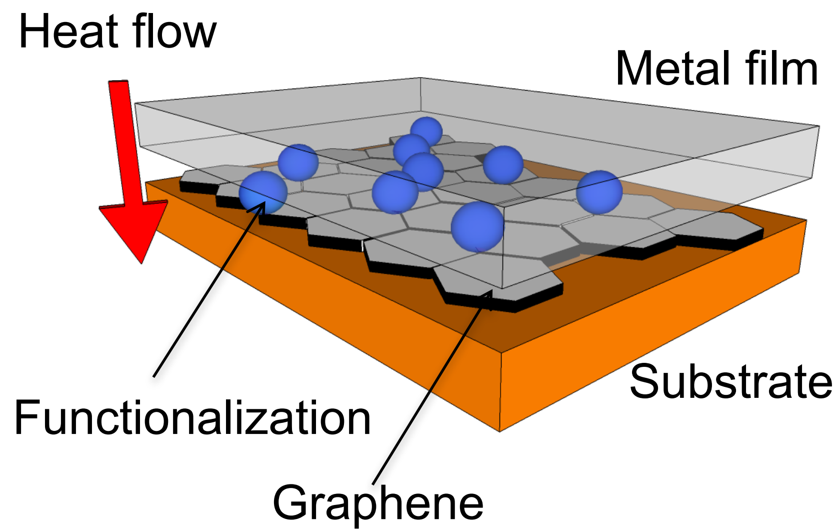
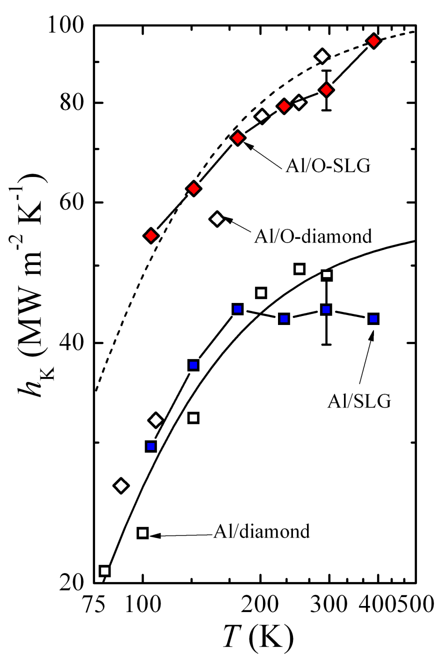
- **Heat transport across single molecule interfaces: when does a molecule become a defect?**
- Molecular interfaces in organic/inorganic composites: diffusive scattering via the vibron-phonon interaction

Contact chemistry to manipulate TBC



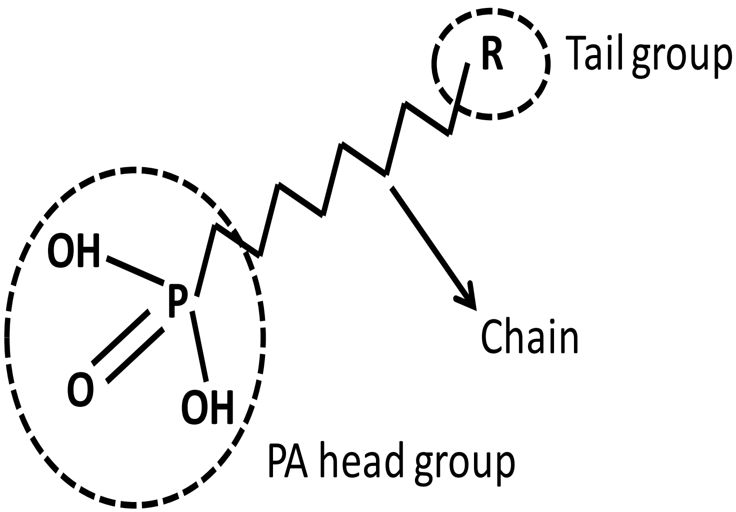
Nat. Mat. **11**, 502 (2012)

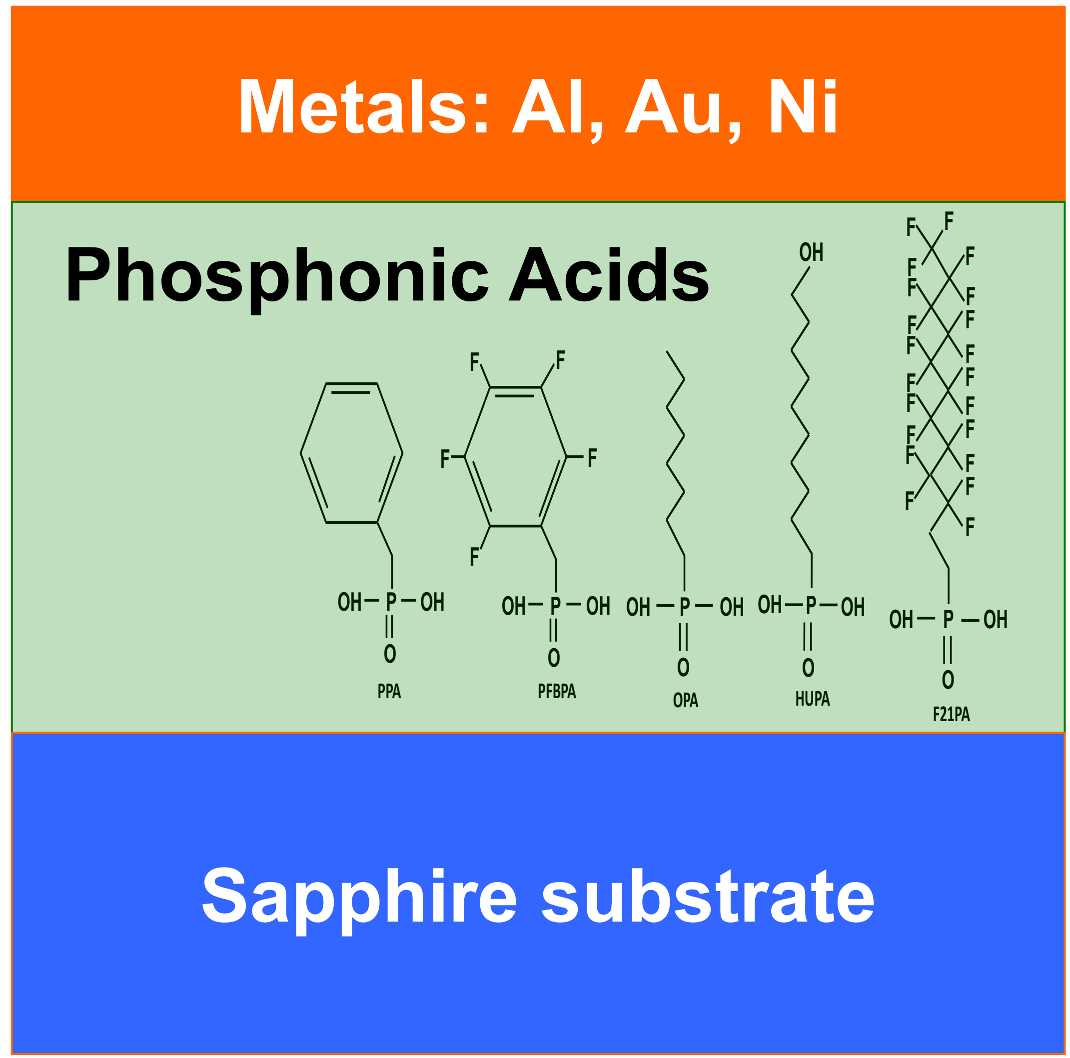




Nano Lett. **12** 590 (2012)

Phosphonic acid interfaces: Size and mass control

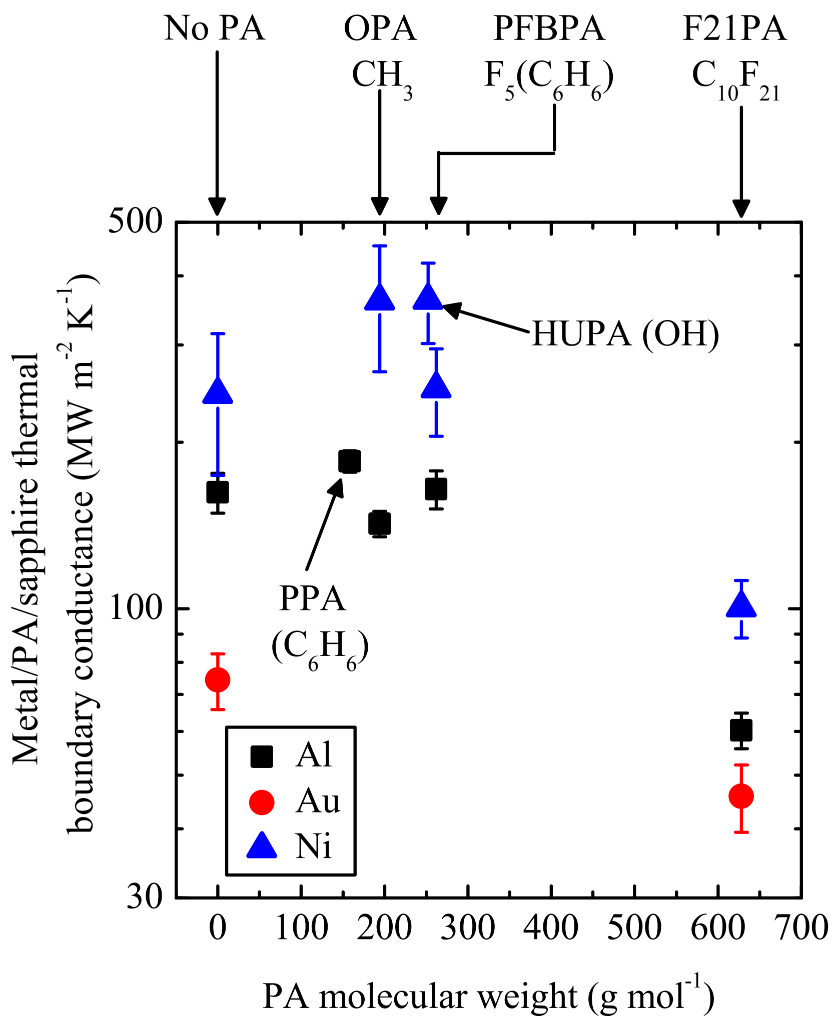




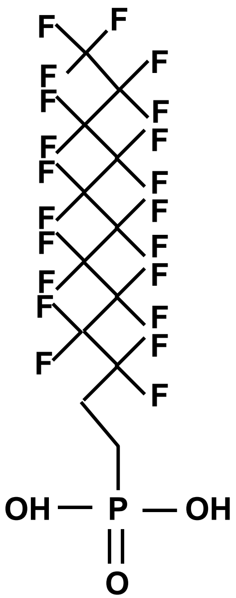
J. Phys. Chem C **119**, 20931

Synthesis at Ga. Tech: Prof. Sam Graham

Phosphonic acid interfaces: Size and mass control



- No correlation with length
- Most noticeable change in TBC with large MW F21PA
- Probably not length effect (HUPA~ 1.7 nm, F21PA ~ 2 nm)



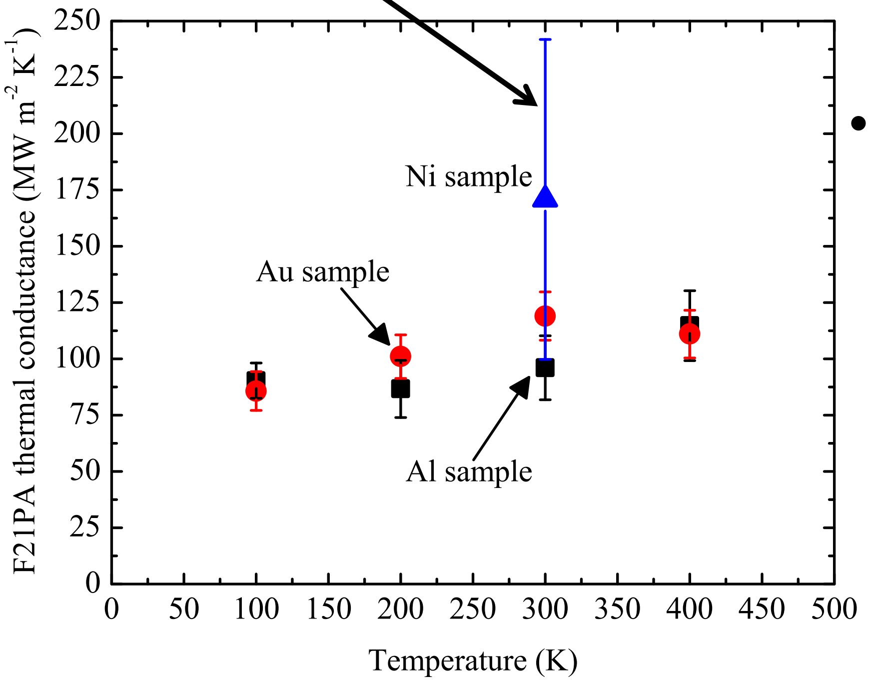
F21PA

Is the change in TBC the metal/PA interface or the F21PA itself?

J. Phys. Chem C **119**, 20931

Heat transport in single F21PA molecules

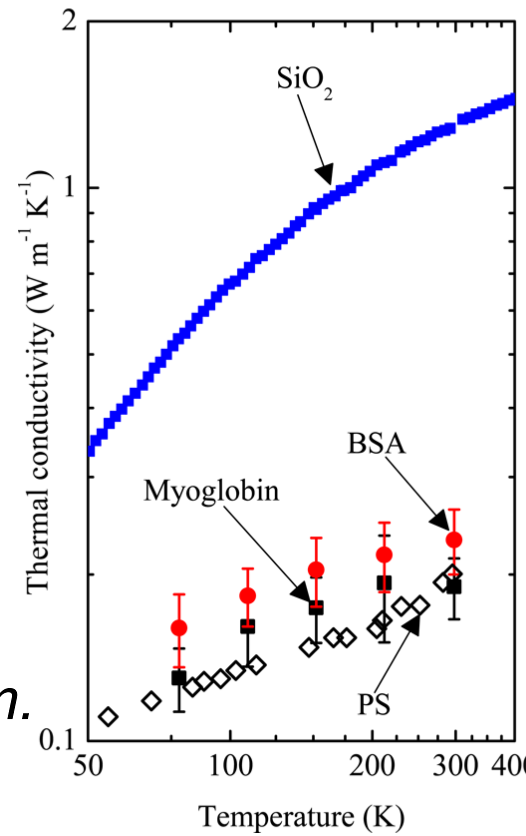
Uncertainty in Ni thickness, but in process of post-TDTR analysis to reduce uncertainty



J. Phys. Chem C **119**, 20931

- No prior evidence of diffusive heat flow in a molecule (ballistic observed by Wang *et al*. *Science* **317**, 787 (2007)
- ~2 nm molecule, so effective thermal conductivity of F21PA~0.2 W/m/K at RT

J. Phys. Chem. Lett. **5**, 1077



Outline

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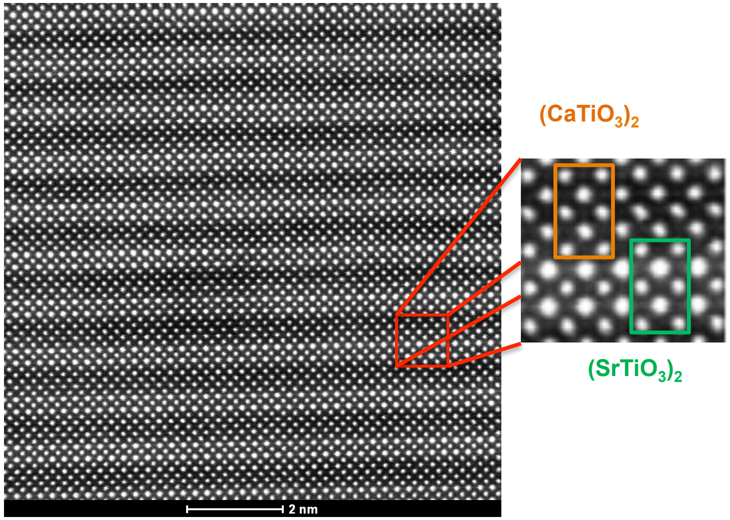
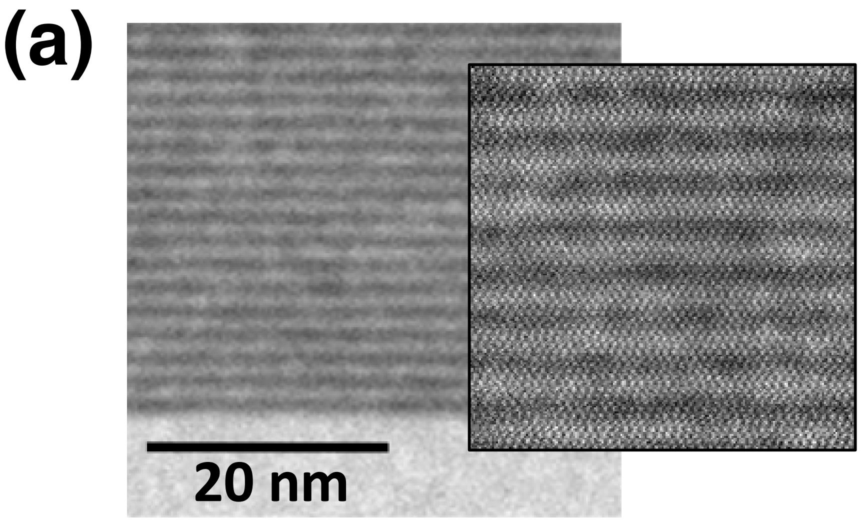
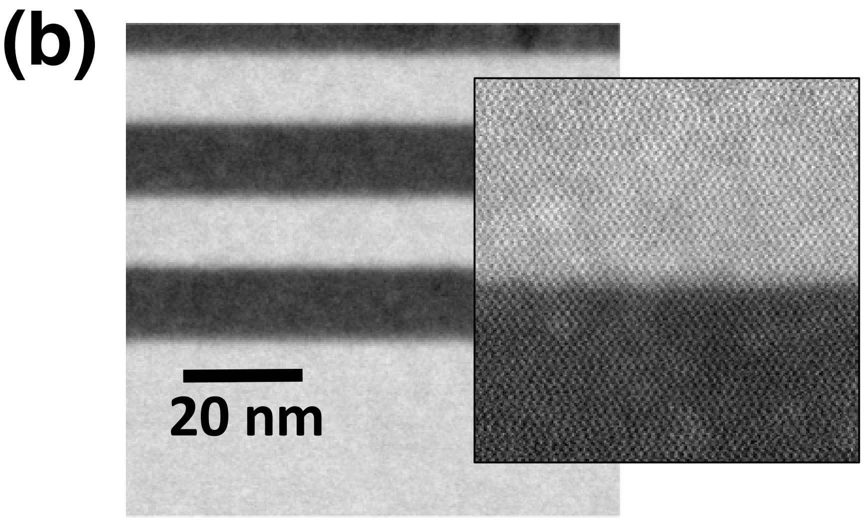
- **Molecular interfaces in organic/inorganic composites: diffusive scattering via the vibron-phonon interaction**

Heat transport mechanisms in superlattices

$CaTiO_3/SrTiO_3$

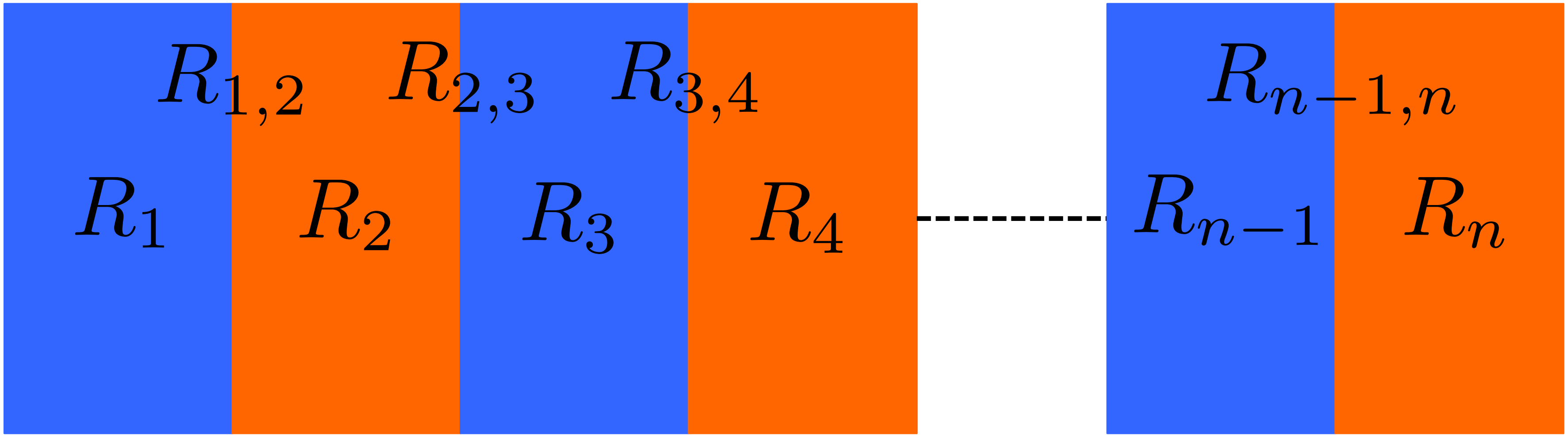






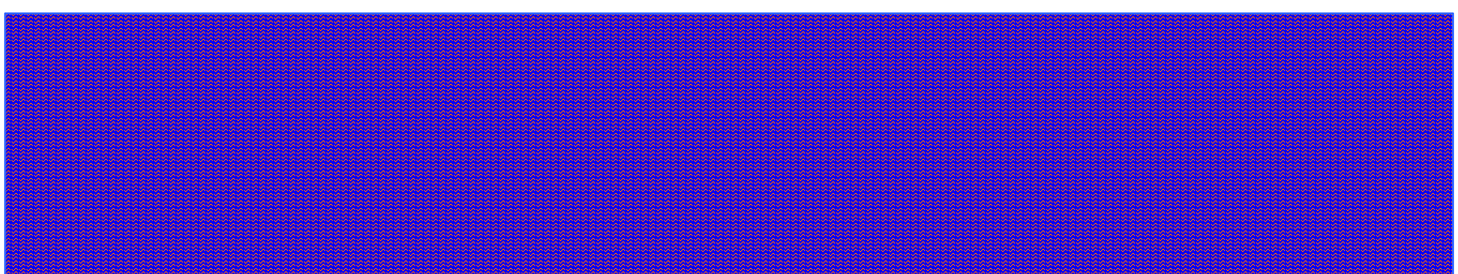
d_{SL} = 2 nm **GaAs/AlAs** d_{SL} = 24 nm

Incoherent/particle picture of phonon transport in SLs



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

What if layers are "linked"? – coherent transport

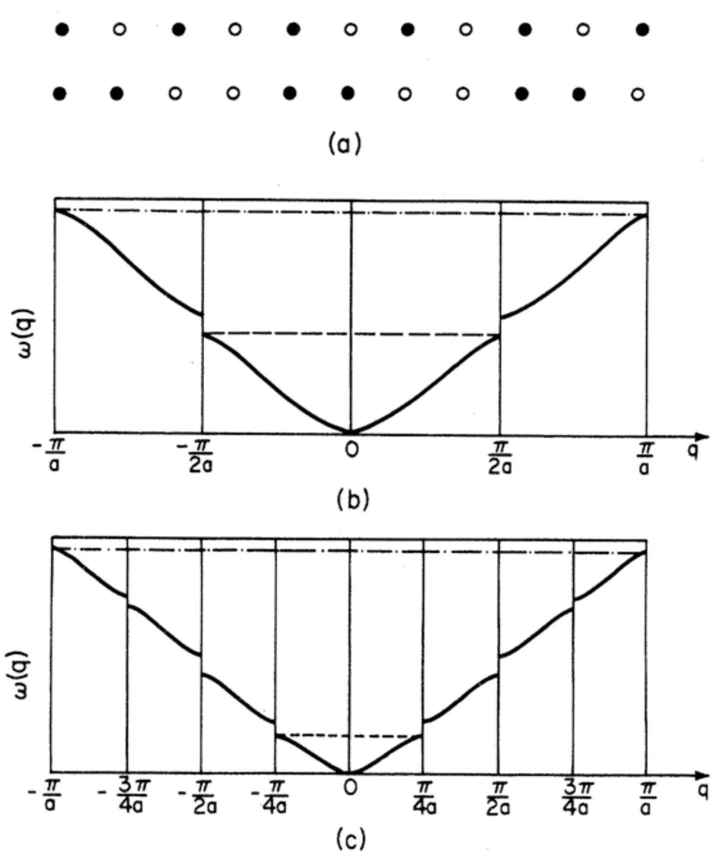


Coherent transport in superlattices

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)

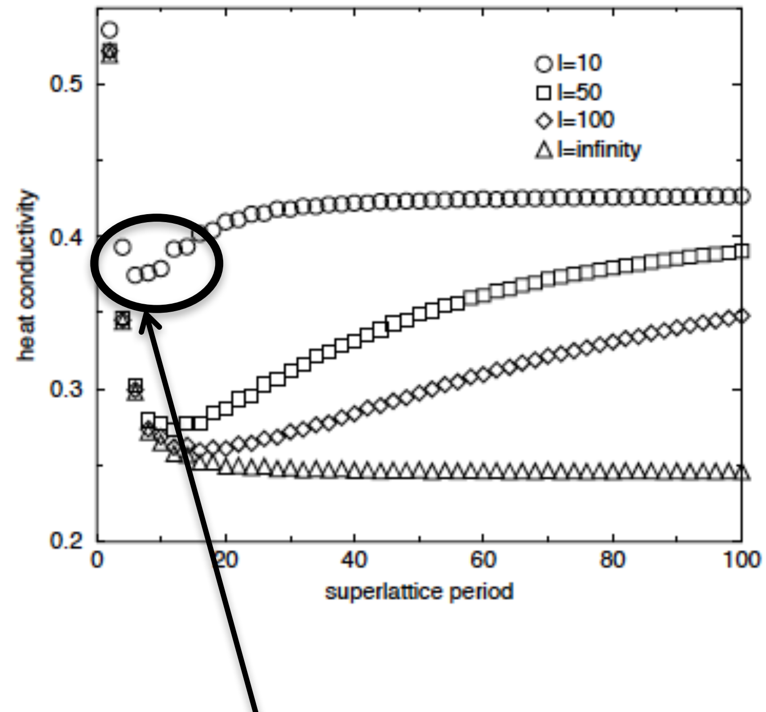


Interfacial periodicity can lead to "mini-band" formation

VOLUME 84, NUMBER 5 PHYSICAL REVIEW LETTERS 31 JANUARY 2000

Minimum Thermal Conductivity of Superlattices

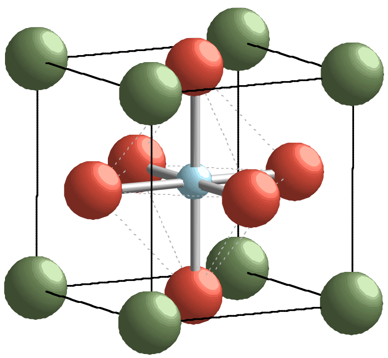
M. V. Simkin and G. D. Mahan
Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1200 and Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831
(Received 23 July 1999)



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

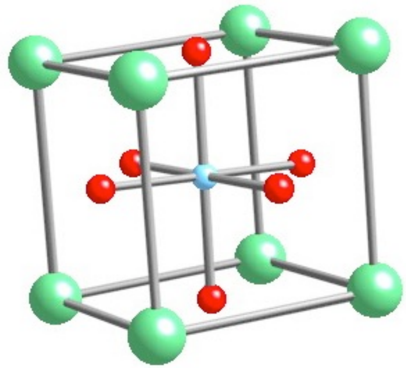
Coherent transport in superlattices

$SrTiO_3$

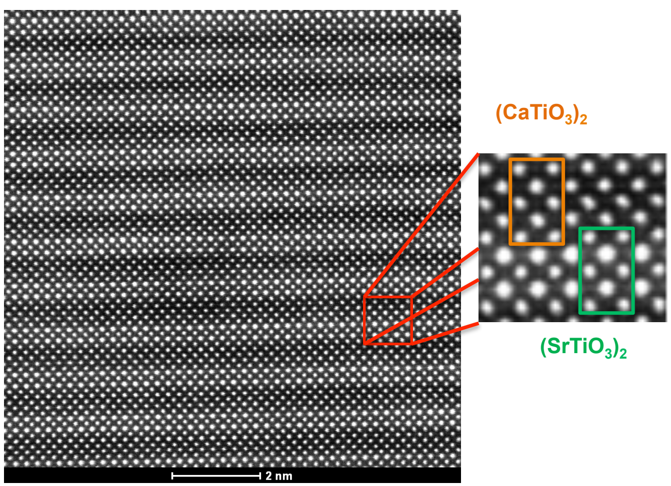


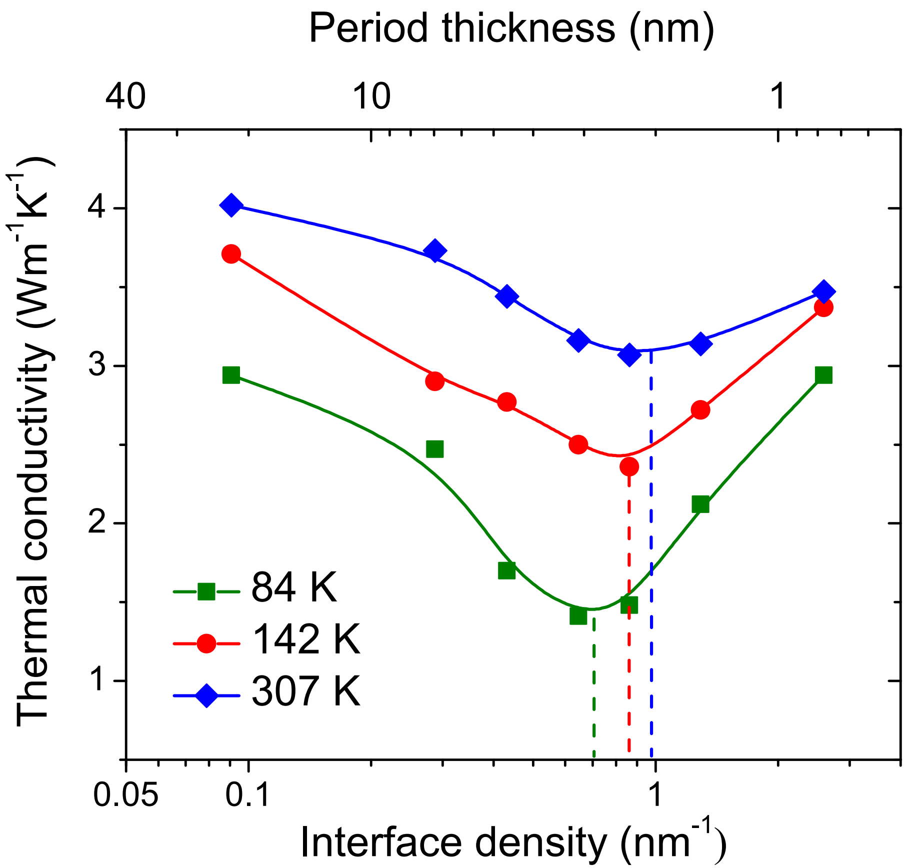
(a = 3.905 Å)
ρ = 5.1 g/cc
v_m = 5.41 km/s

$CaTiO_3$



(a_{pc} = 3.81 Å)
ρ = 3.75 g/cc
v_m = 5.71 km/s



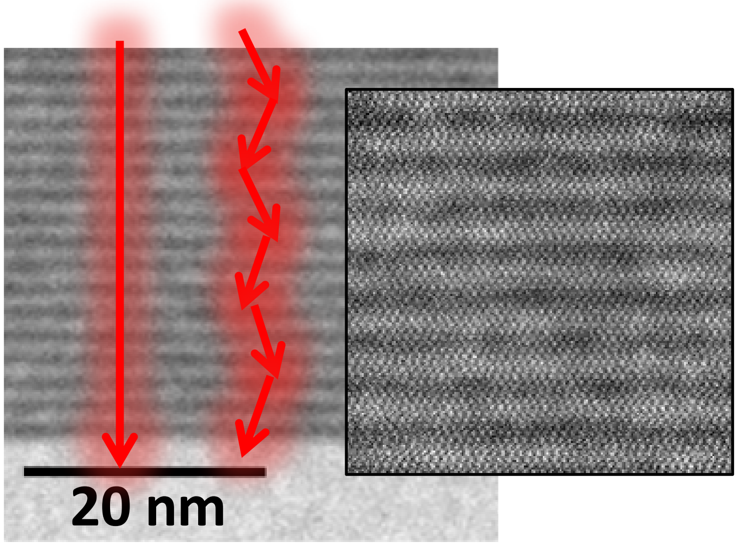


SL design to manipulate coherent phonon transport

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

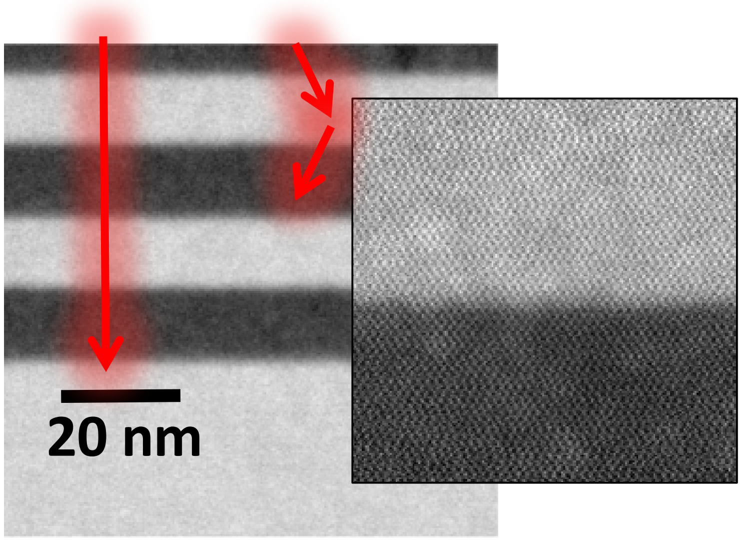
Spectral phonon transport in SLs

(a)



d_{SL} = 2 nm

(b)

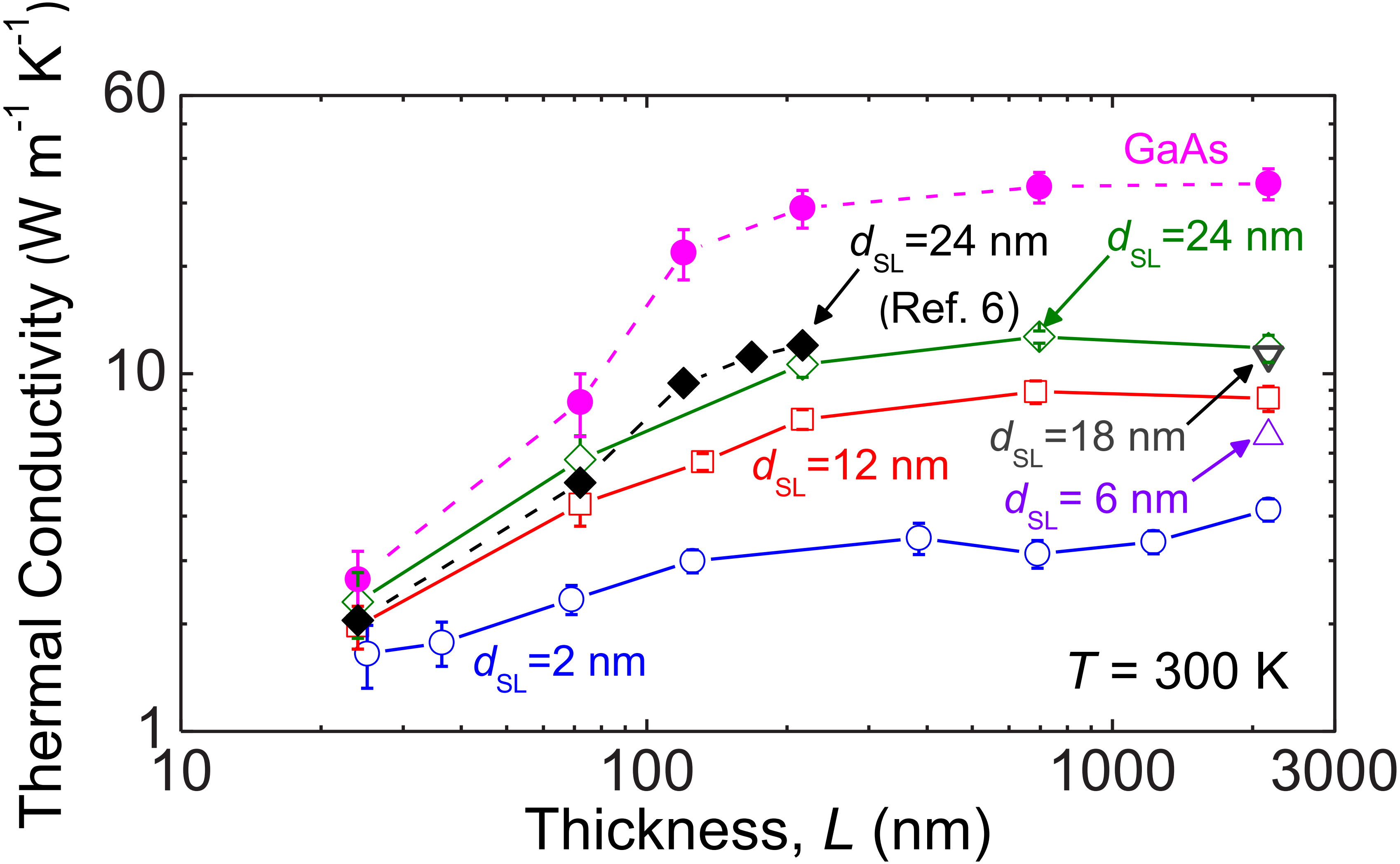


d_{SL} = 24 nm

Do all phonons really scatter at interfaces???

What if wavelength of phonon is >> than periodicity?

Spectral phonon transport in SLs

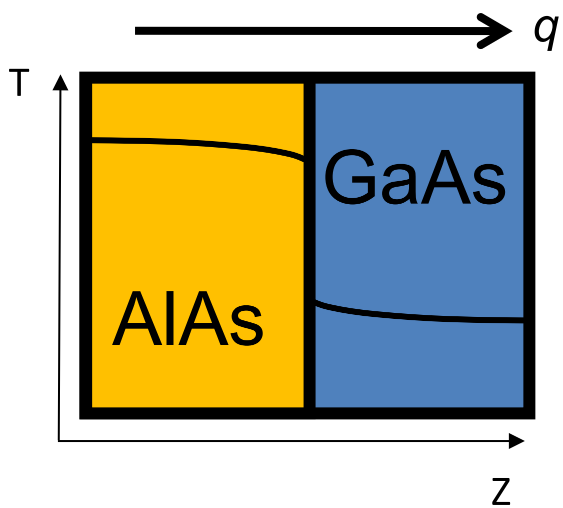


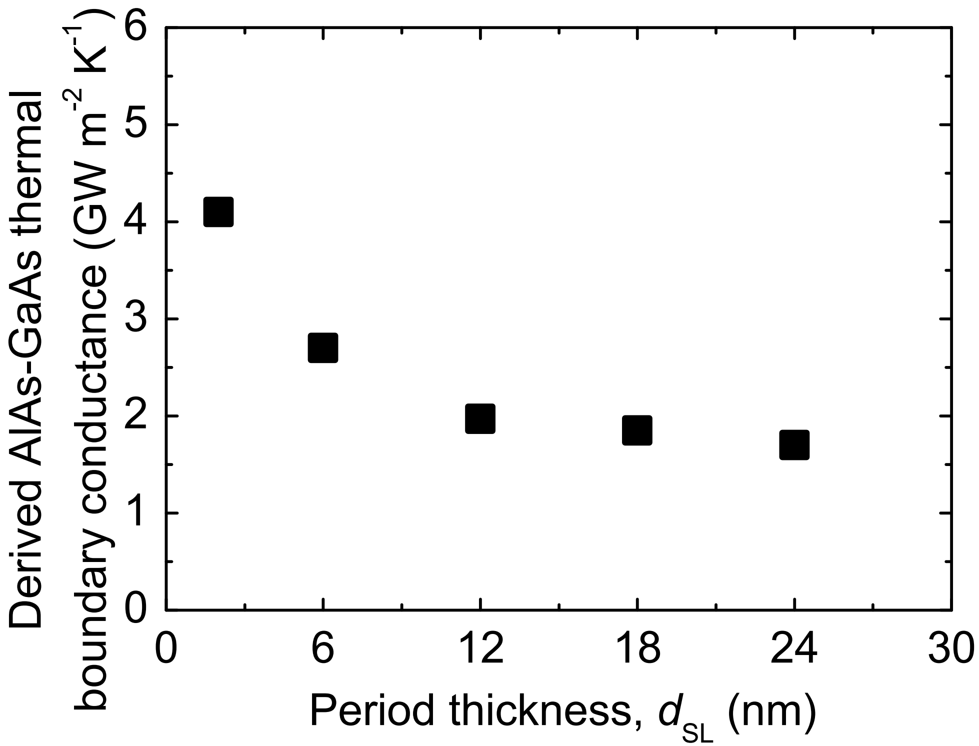
Collaboration: G. Balakrishnan (UNM)

Phys. Rev. B **97**, 085306

TBC at AlAs/GaAs interface

$$q = h_{\mathrm{K}} \Delta T = \frac{1}{R_{\mathrm{K}}} \Delta T$$

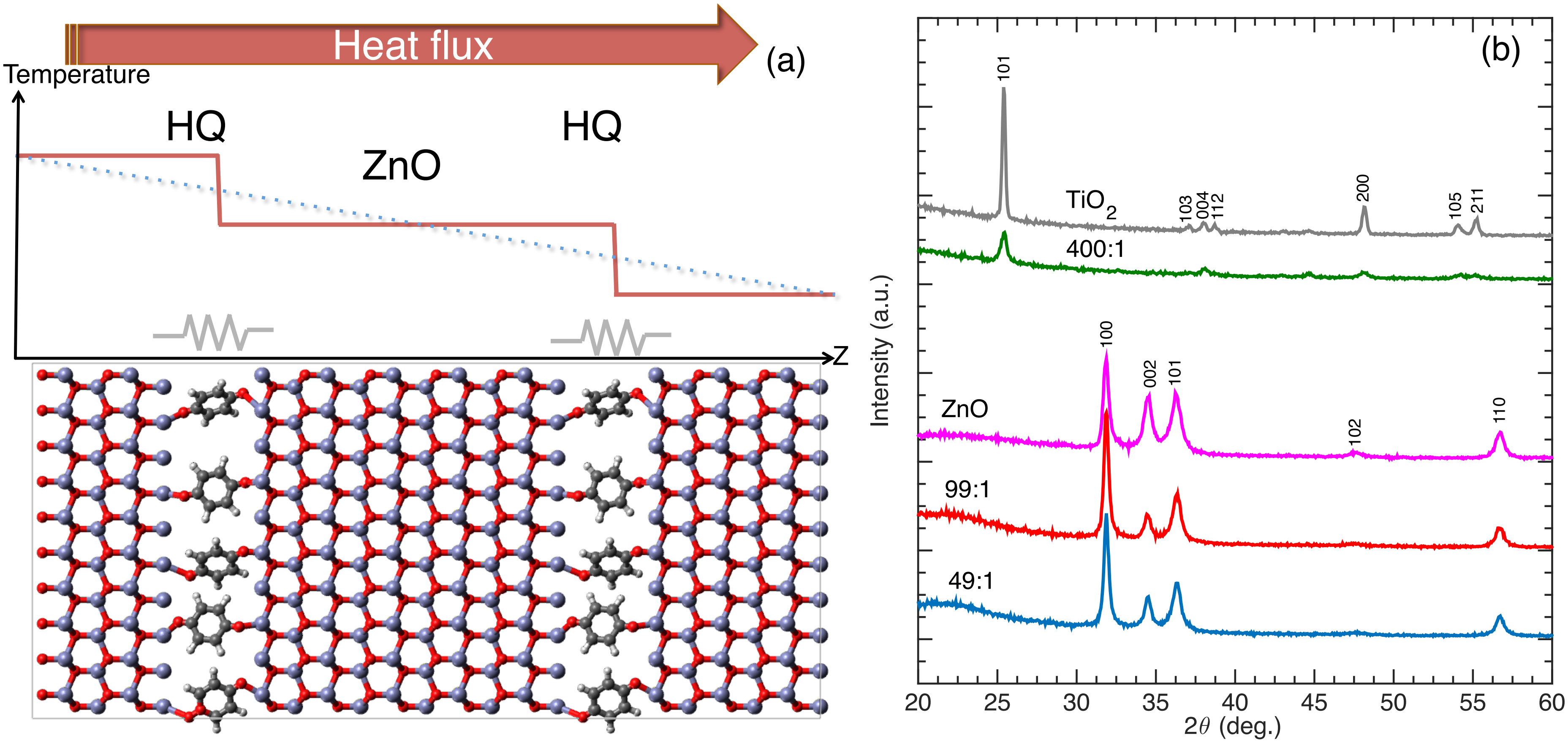




Collaboration: G. Balakrishnan (UNM)

Phys. Rev. B **97**, 085306

Turn to molecular heterostructures

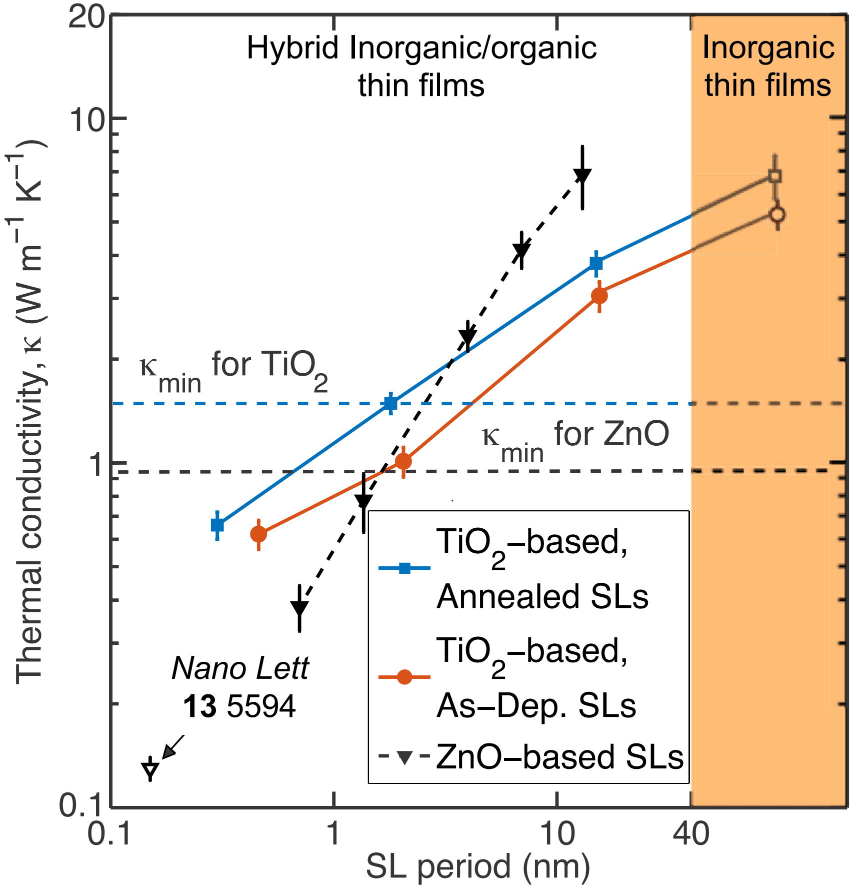


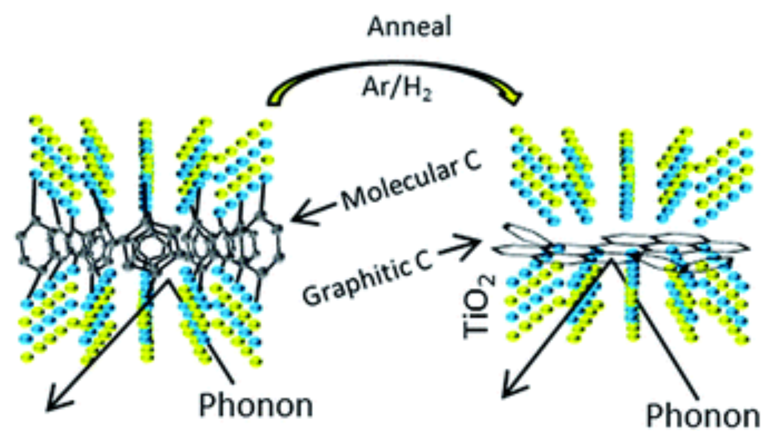
PRB **93**,115310; *PRB* **93**, 024201

Collaboration: M. Karppinen (Aalto) – ALD/MLD growth

Turn to molecular heterostructures

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





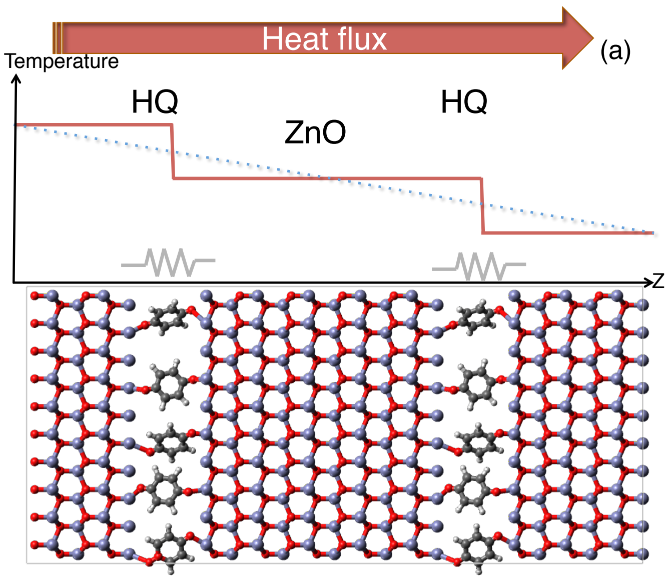
Reductions due to the thermal boundary conductance across organic/inorganic interfaces

PRB **93**,115310; *PRB* **93**, 024201

Collaboration: M. Karppinen (Aalto) – ALD/MLD growth

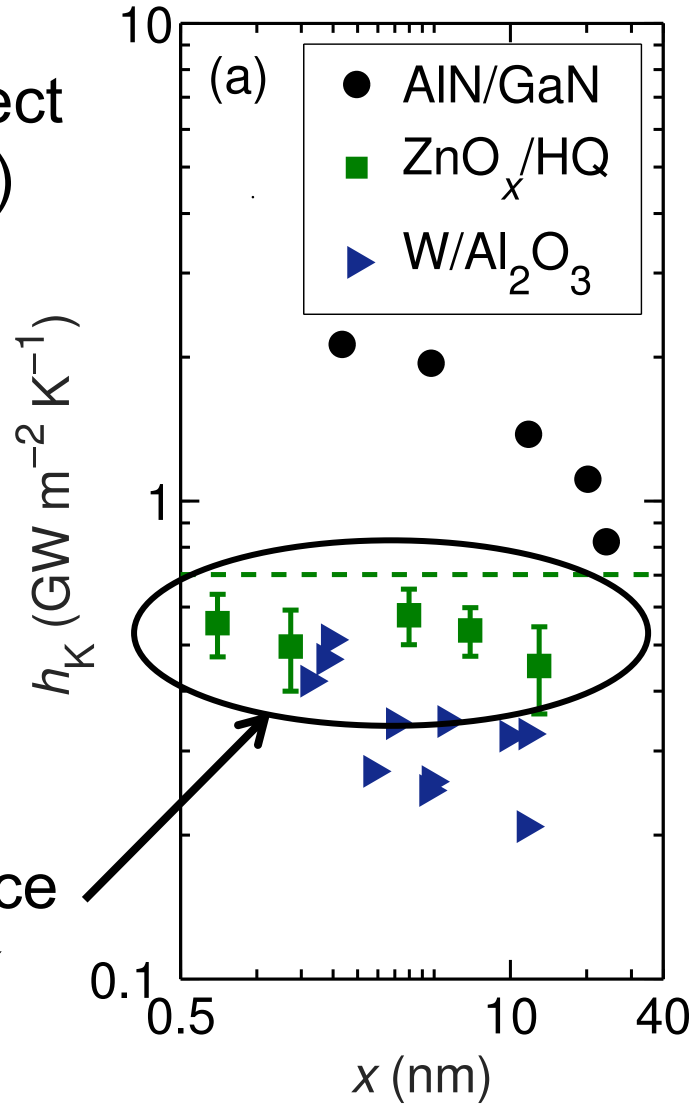
Diffusive phonon scattering at organic/inorganic interface

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



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

Molecular interface constant with *x*

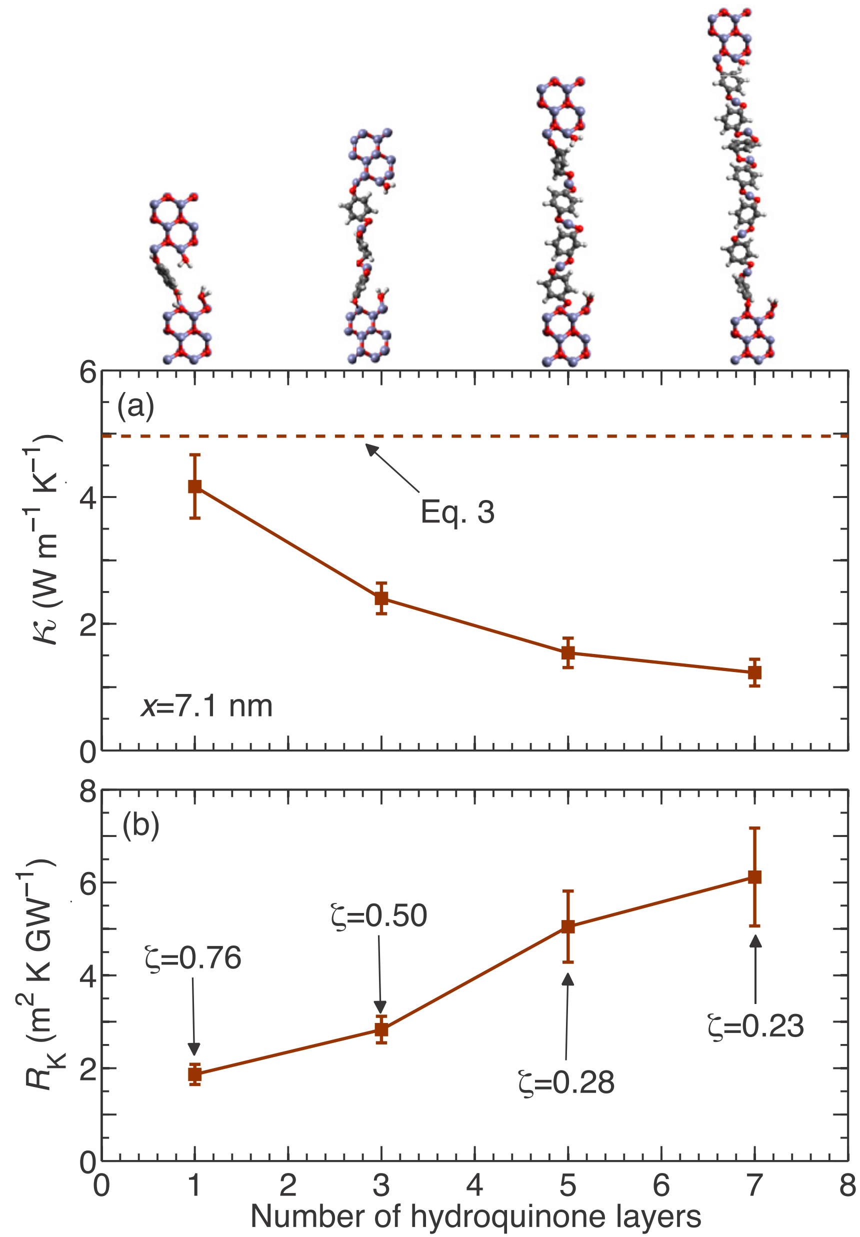


PRB **93**,115310; *PRB* **93**, 024201

Collaboration: M. Karppinen (Aalto) – ALD/MLD growth

Diffusive phonon scattering at organic/inorganic interface

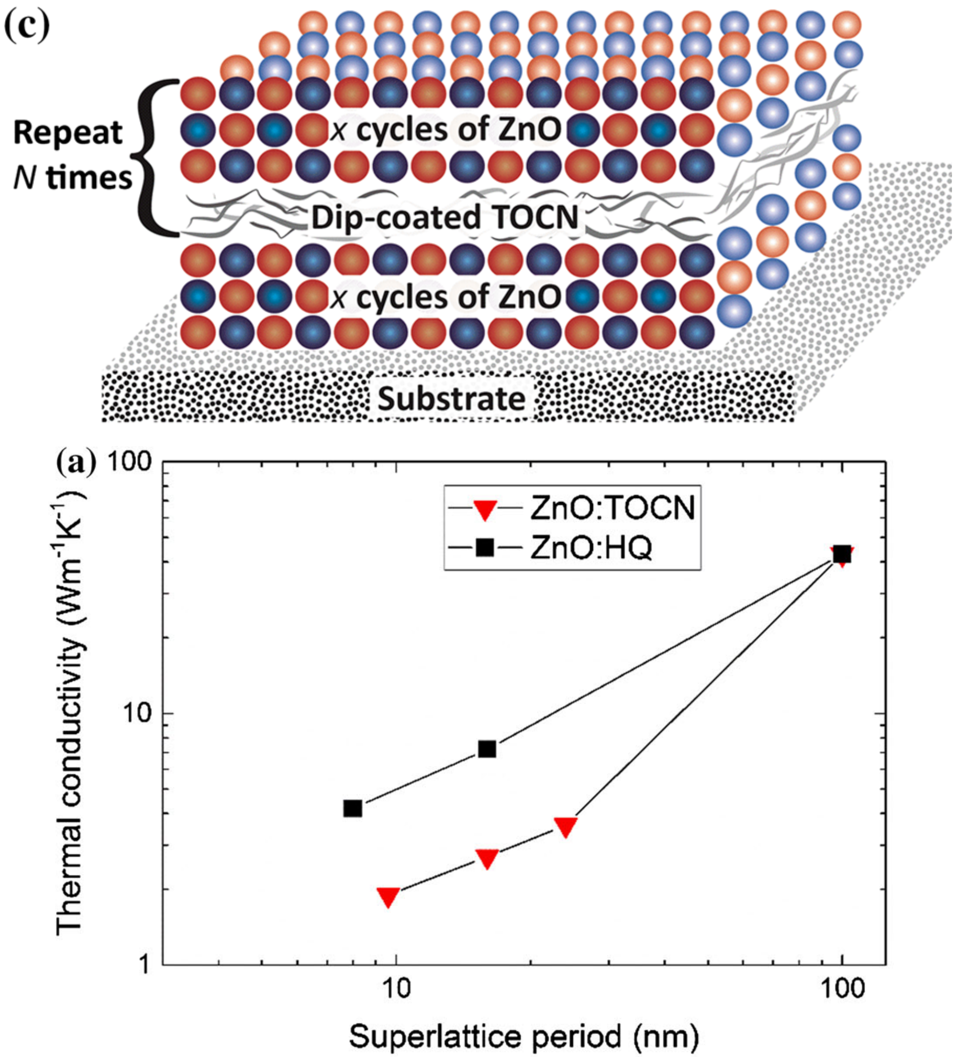
Can use hybrid materials to study diffusive scattering in few molecule thick films



PRB **93**,115310; **Collaboration**: M. Karppinen (Aalto) – ALD/MLD growth

Heat transport mechanisms in novel hybrid materials

ZnO/nanocellulose



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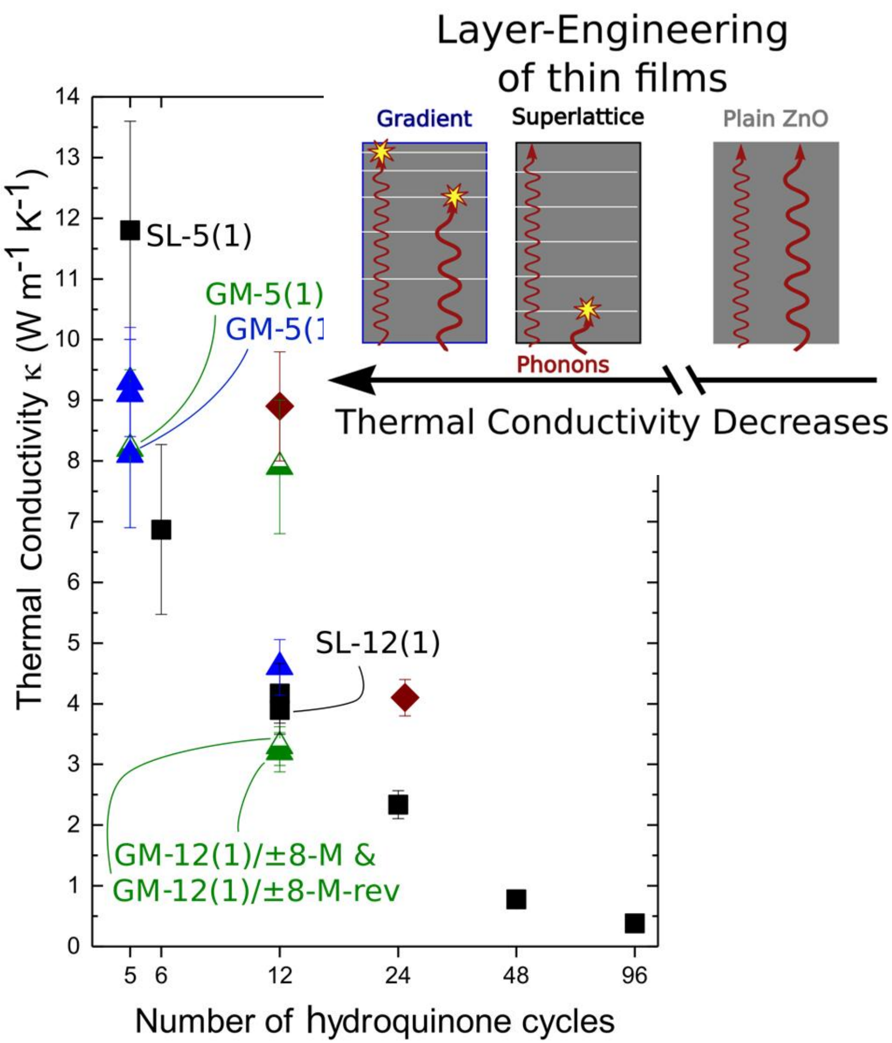
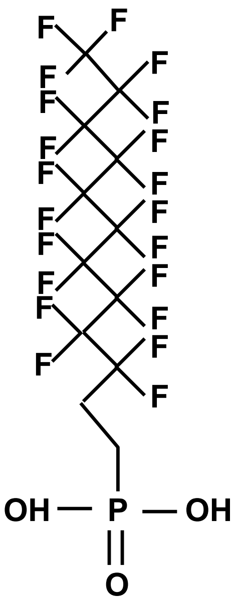
A periodic hybrid "SLs"



Appl. Mat. & Int. (to appear)

Conclusions/outlook – Heterogeneous material interfaces and engineering the chemical bond can lead to novel regimes of vibrational heat transport in materials



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