SCHOOL of ENGINEERING & APPLIED SCIENCE
UNIVERSITY of VIRGINIA

Ballistic to diffusive heat transfer in molecular building blocks of inorganic/organic multilayers

Patrick E. Hopkins

Associate Professor

Dept. Mech. & Aero. Eng.

University of Virginia

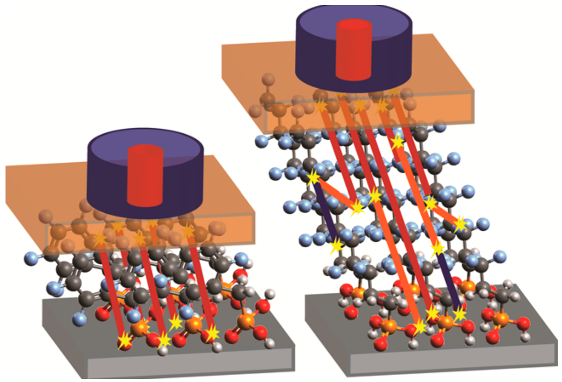
phopkins@virginia.edu

patrickehopkins.com

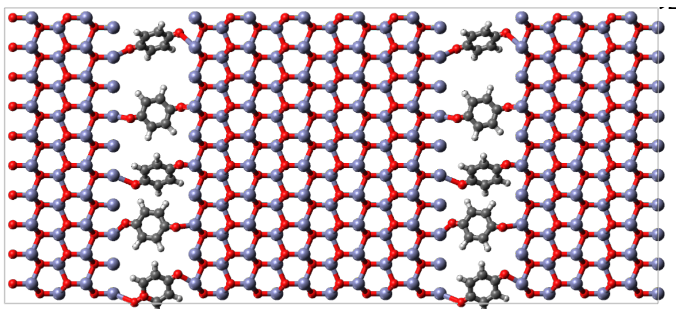
DEPARTMENT OF THE NAVY ONR Science & Technology

SCIENCE TO SHAPE THE FUTURE OF THE ARMY ARMY RESEARCH OFFICE 1951

The students that did the work



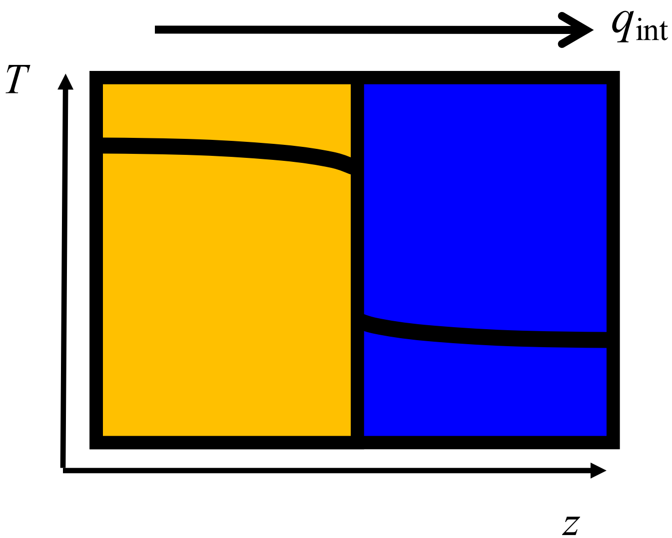
Dr. John T. Gaskins
Sr. Scientist

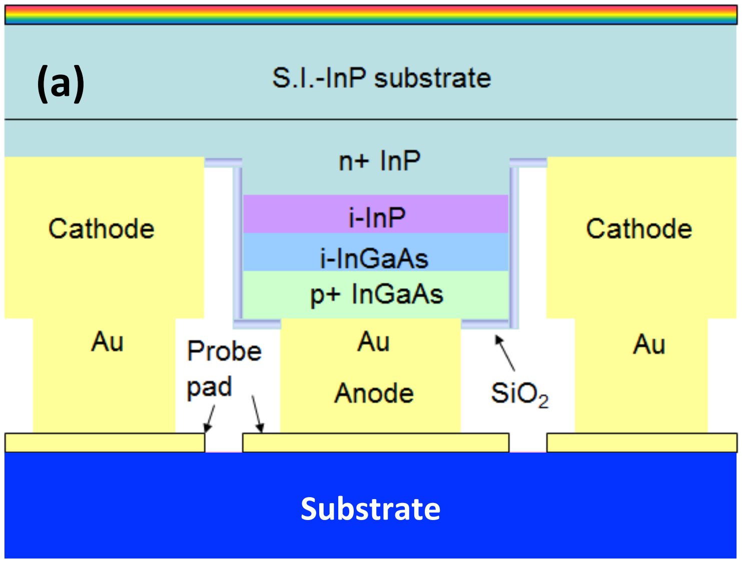


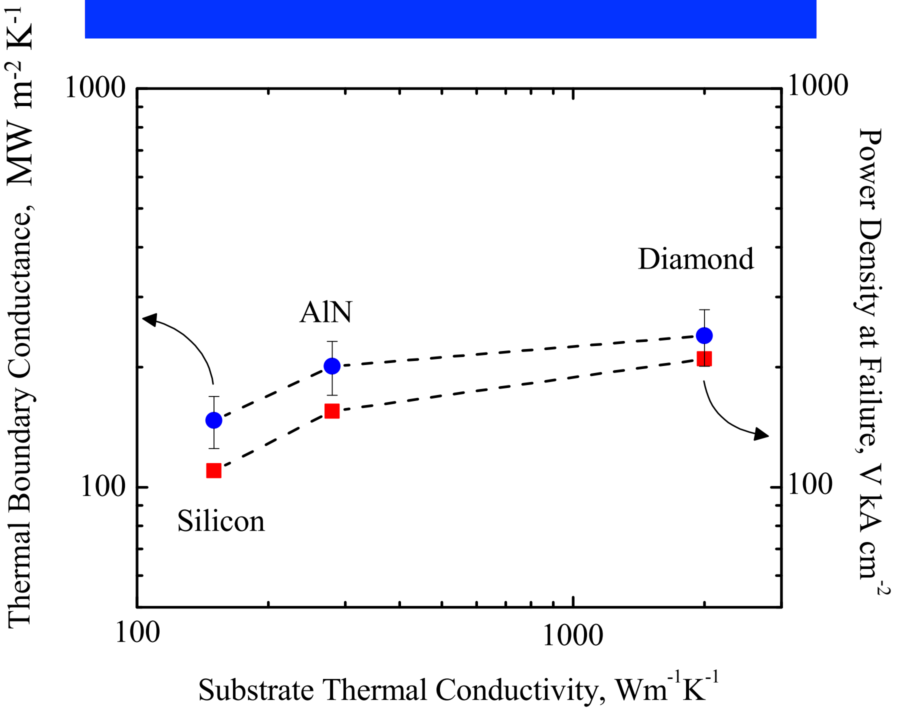
Ashutosh Giri
Ph.D. Student

Thermal boundary conductance

$$q_{\text{int}} = h_{\text{K}} \Delta T = \frac{1}{R_{\text{K}}} \Delta T$$

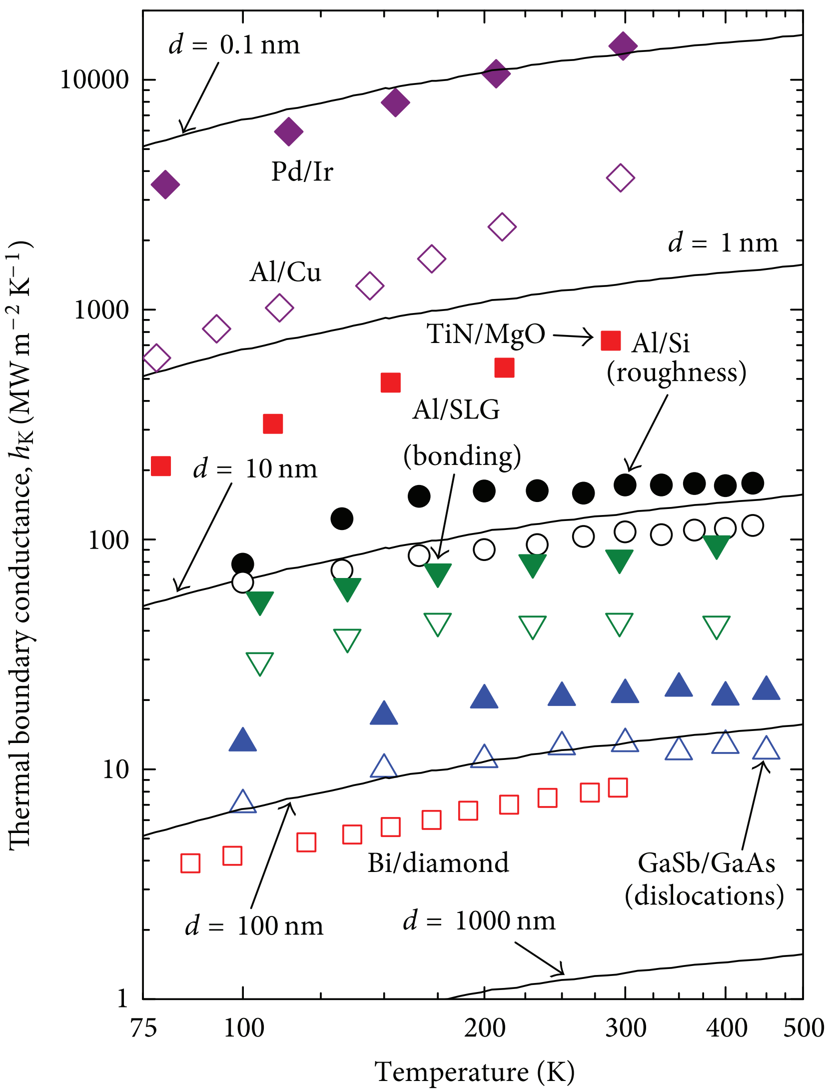




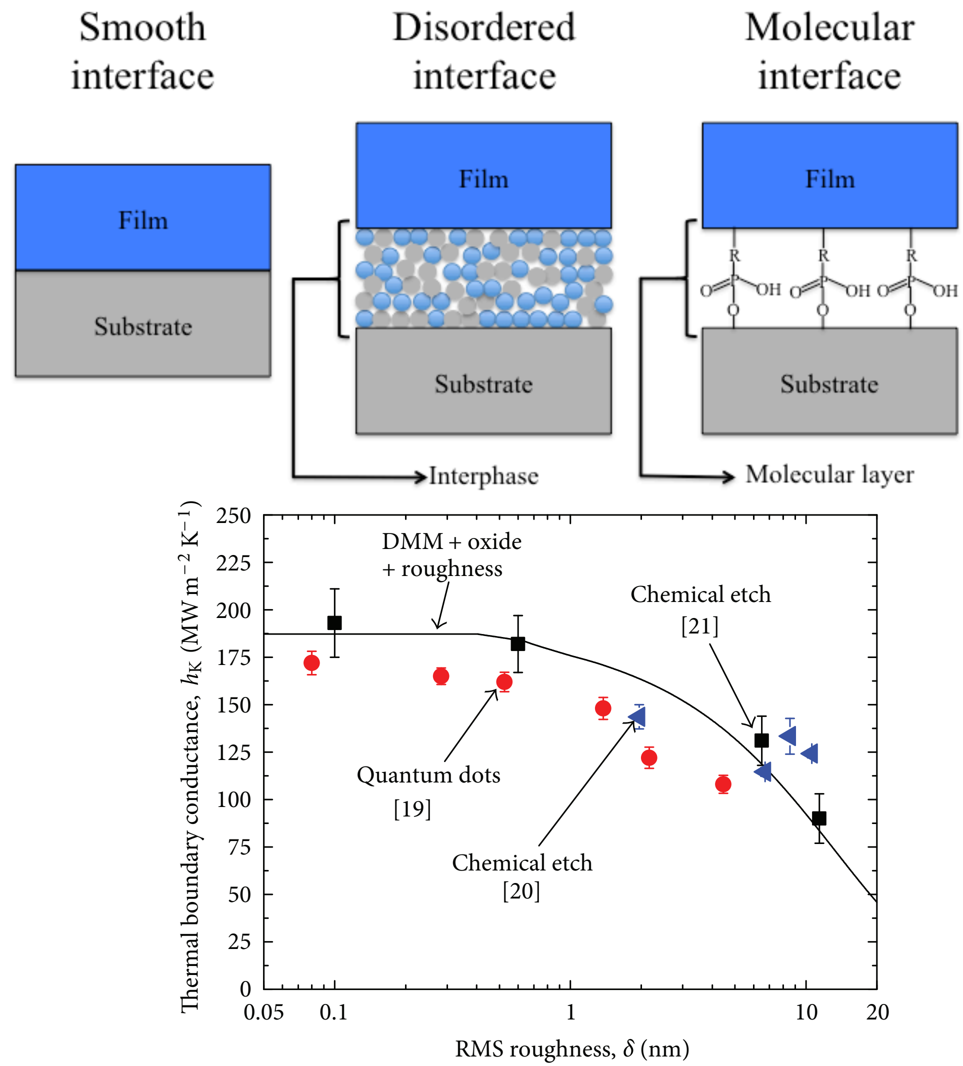


IEEE Photonics **5**, 6800307 (2013)

Defect effects on TBC – "Disordered" interface (inorganic)

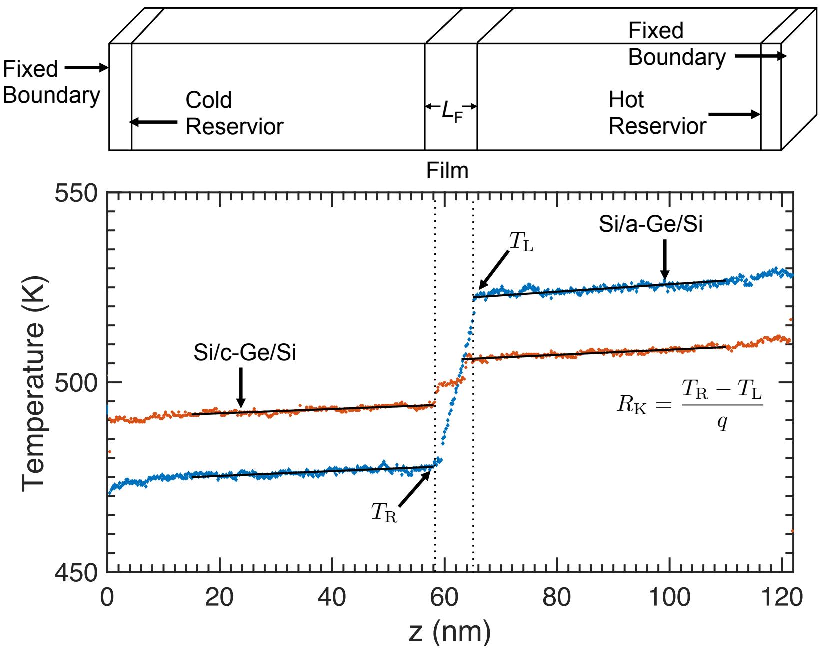


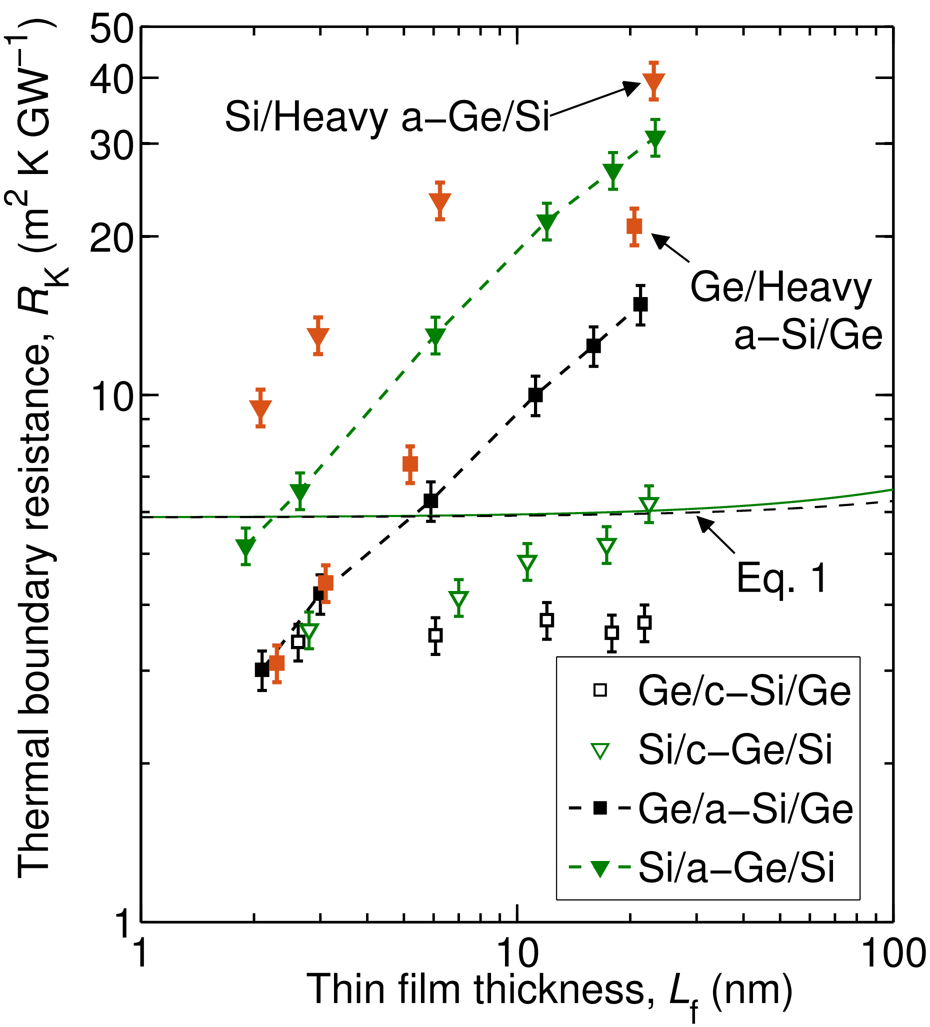
ISRN Mech. Eng. **2013**, 682586 (2013)



PRB **82**, 085307 (2010)
PRB **84**, 035438 (2011)
APL **100**, 111602 (2012)

Ballistic vs. diffusive mechanisms at disordered interfaces



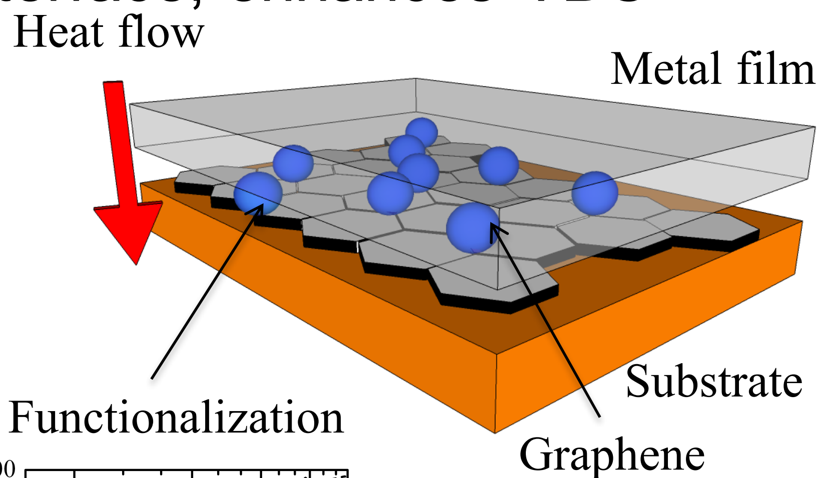


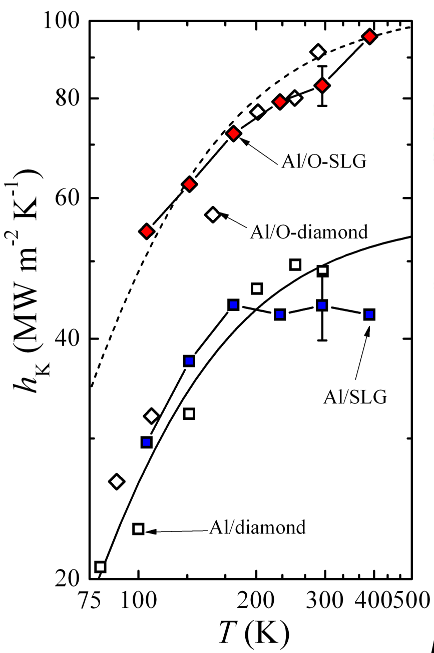
Disorder decreases TBC (increases TBR) when length scale is greater than phonon wavelength

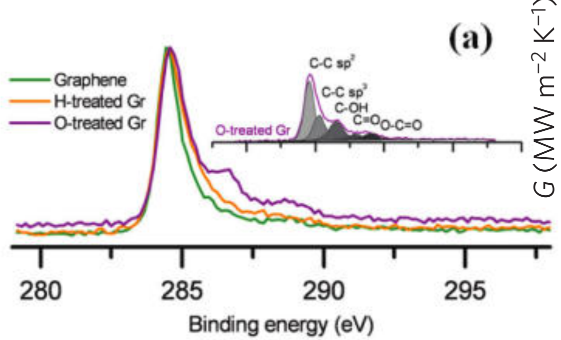
Manuscript under review

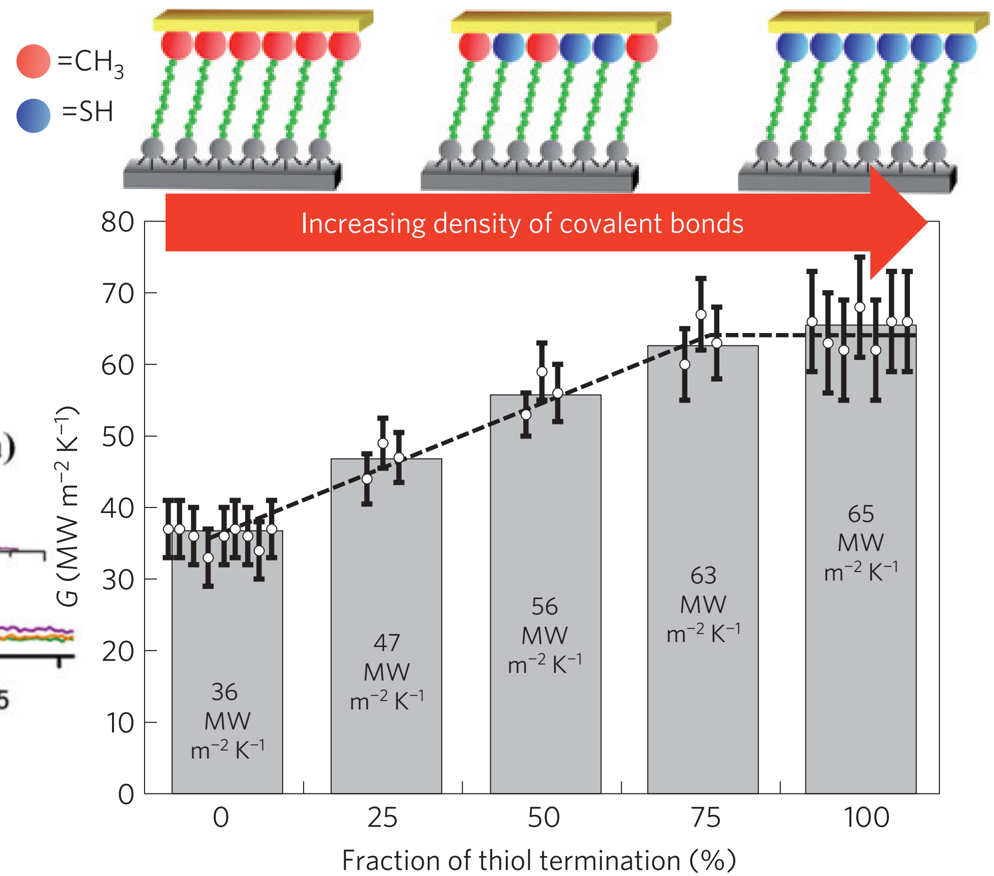
Defect effects on TBC – “Molecular” interface (organic)

Bonding, which can be controlled with surface chemistry at interface, enhances TBC









Nano Lett. **12**, 590 (2012)
Nano Lett. **15**, 4876 (2015)

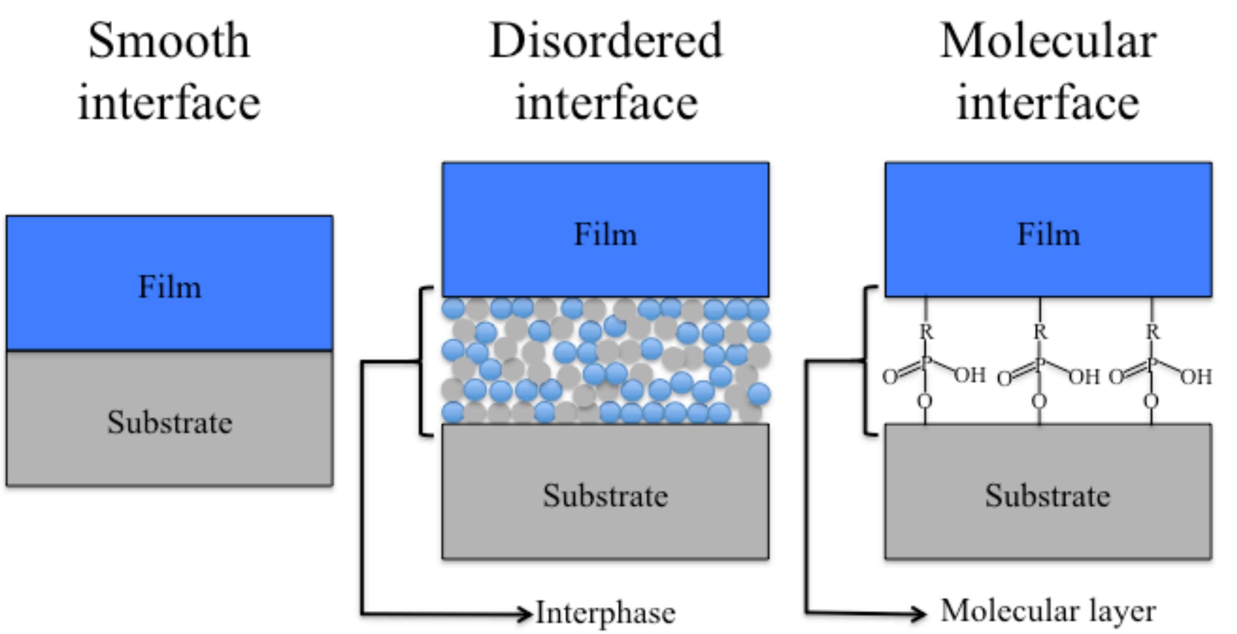
Nat. Mat. **11**, 502 (2012)

Questions motivating this work

•What are the vibrational scattering mechanisms driving heat transfer at and across molecular interfaces?

•How does vibrational energy scatter/transmit across inorganic/molecule interfaces?

•When does scattering ***in*** the molecule at the interface matter?



Outline – Scattering “in” vs. “at” molecular interfaces & TBC

<u>Single interfaces</u>

Metal/phosphonic acid/sapphire

Collab: Sam Graham (GA Tech)

JPCC **119**, 20931 (2015)

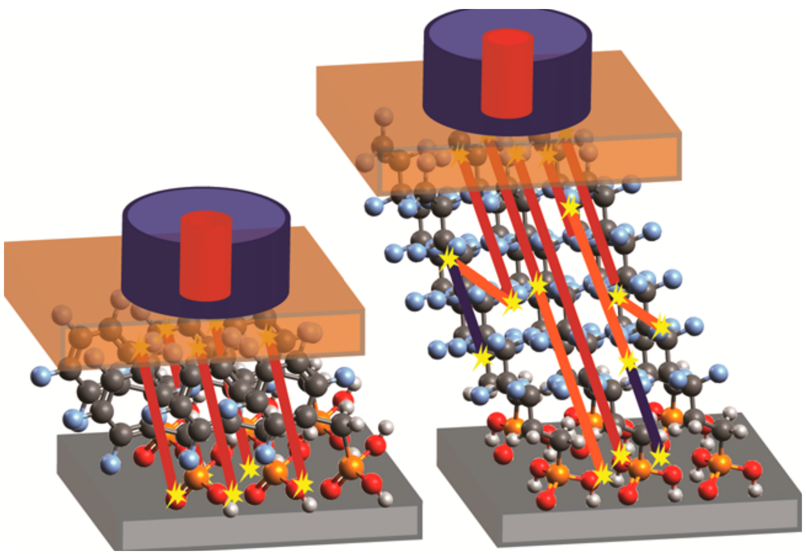
<u>Hybrid structures</u>

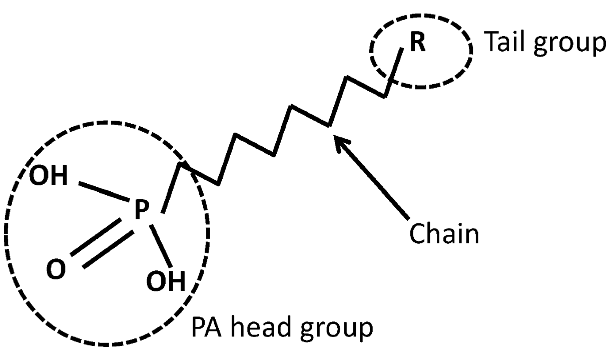
ZnO/HQ or TiO_2/HQ SLs

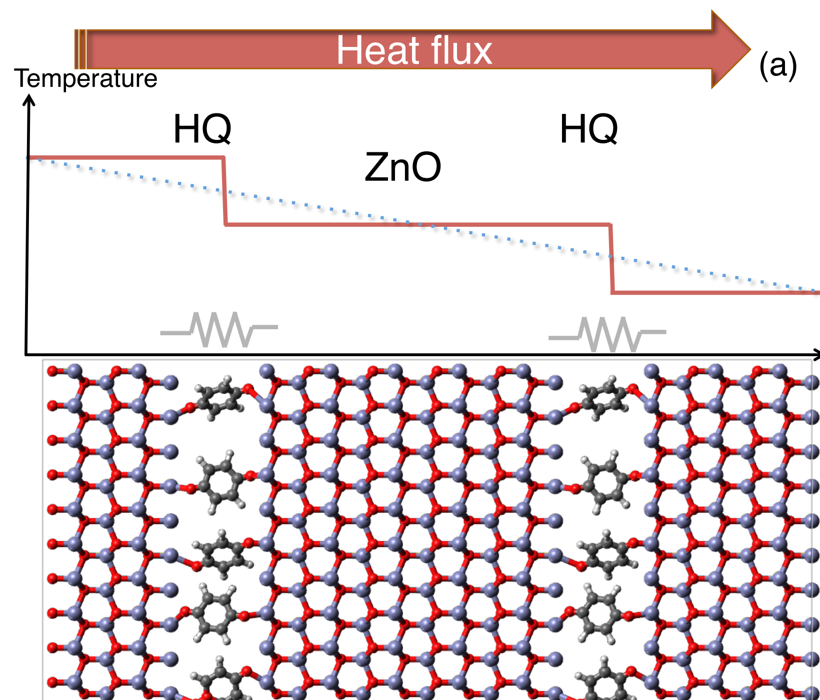
Collab: Maarit Karppinen (Aalto)

Phys. Rev. B **93**, 024201 (2016)

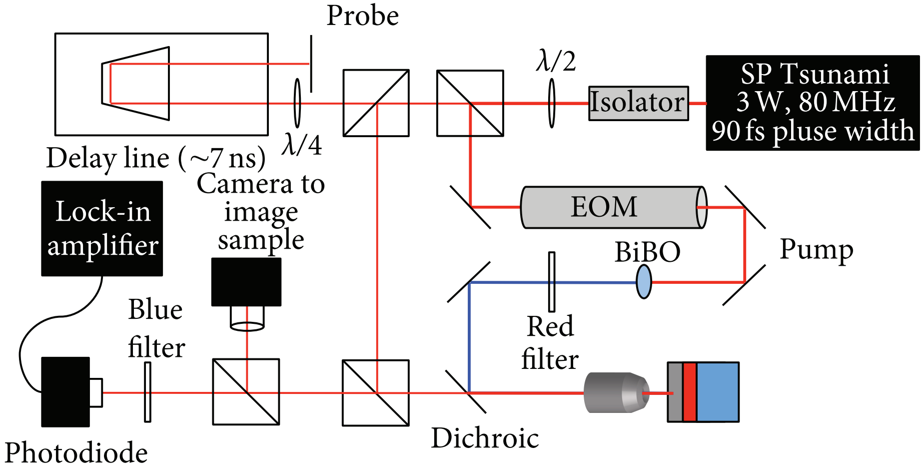
Phys. Rev. B. **93**, 115310 (2016)

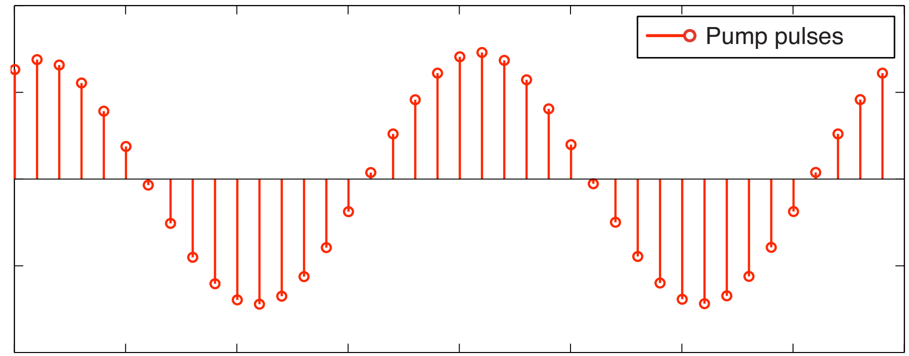


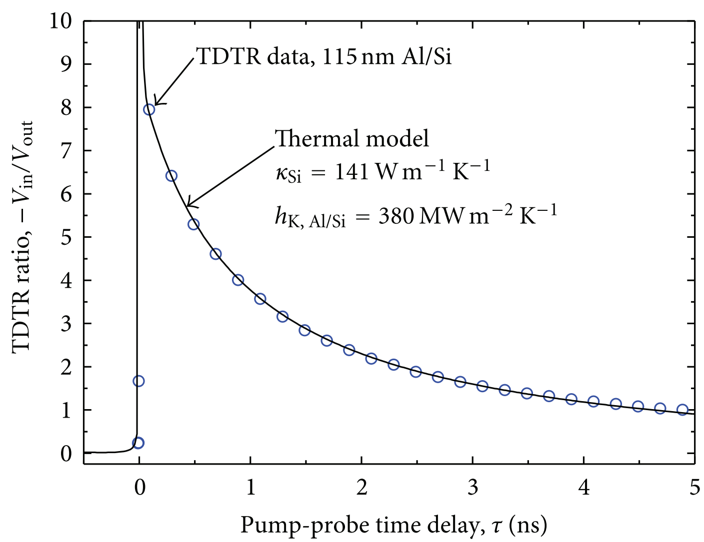




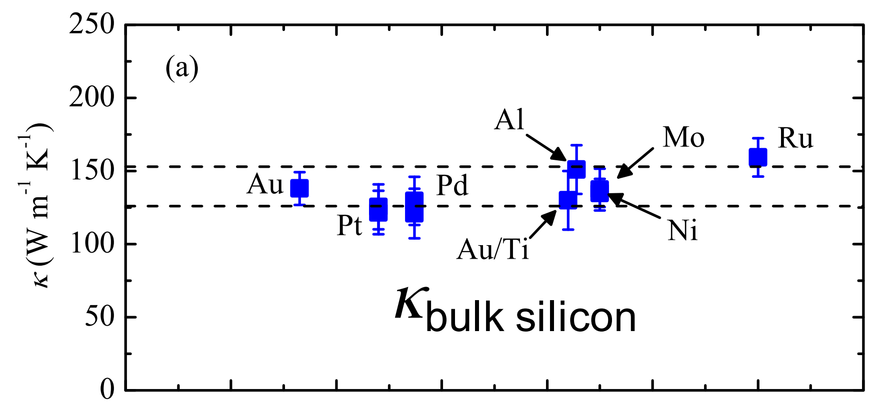
All TBC and κ measurements performed with TDTR







100 ps for heat to diffusive through 100 nm of Al



TDTR Reviews and Analyses

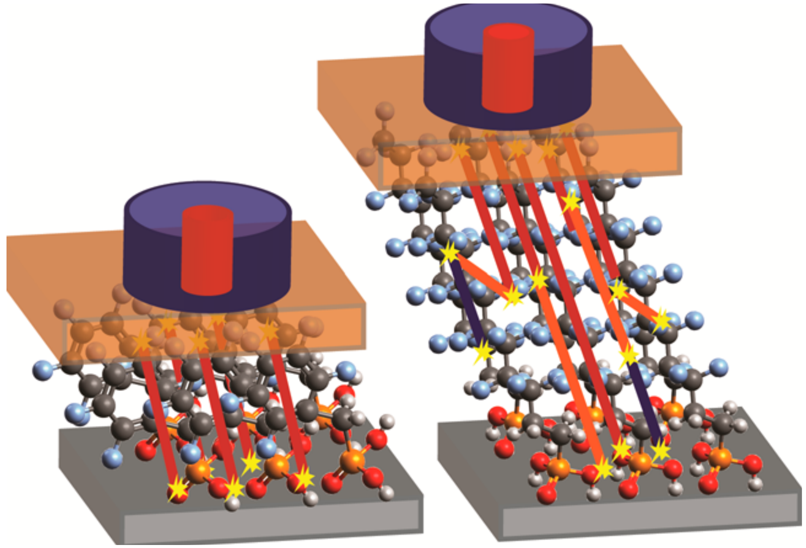
Rev. Sci. Instr. **75**, 5119

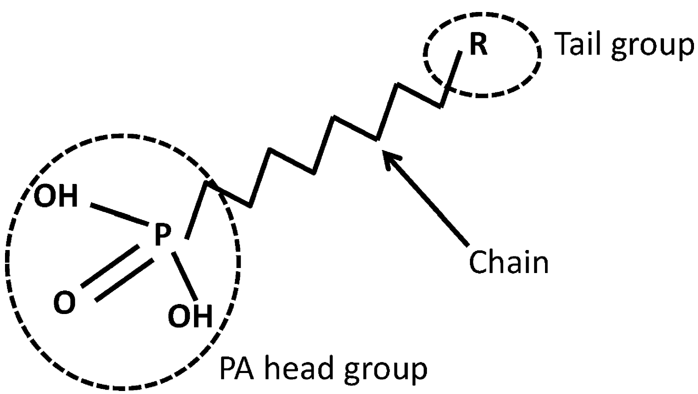
Rev. Sci. Instr. **79**, 114902

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

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

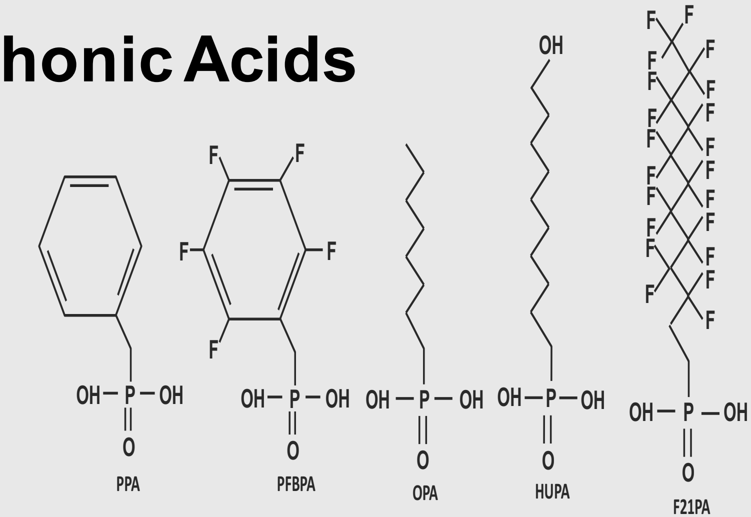
PA's to study molecular scattering at single interface





Metals: Al, Au, Ni

Phosphonic Acids



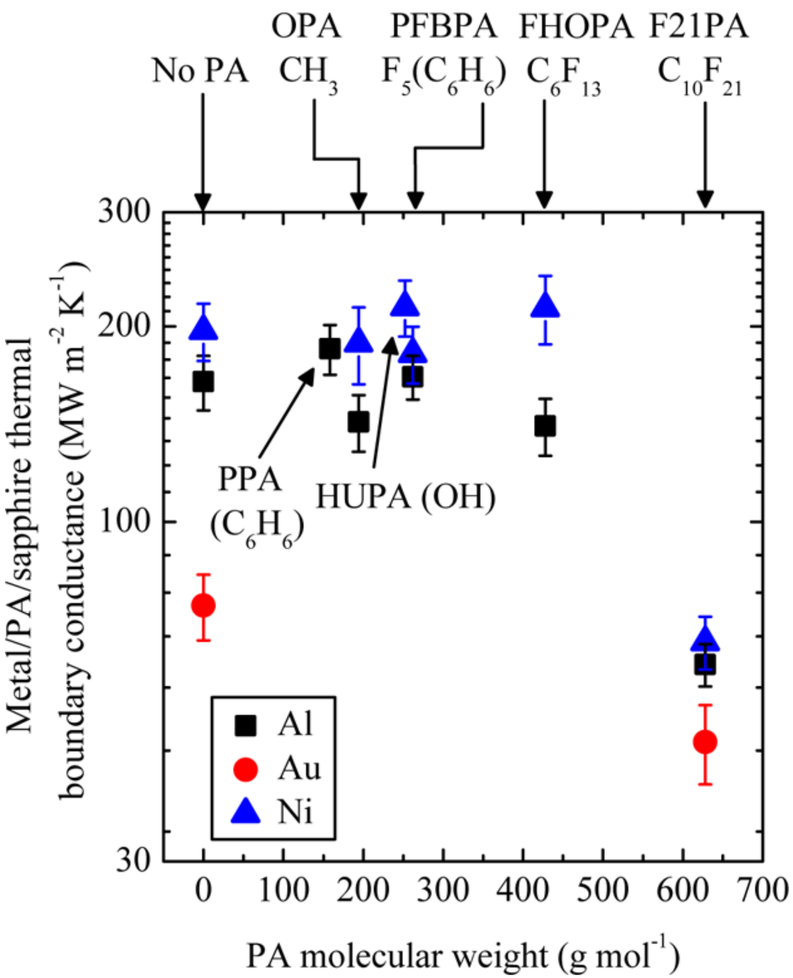
Sapphire substrate
(note: high κ = 35-40 W m^{-1} K^{-1})

JPCC **119**, 20931 (2015)

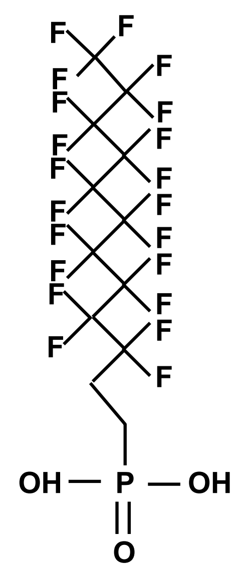
Collaboration

Anu Bulusu, Prof. Sam Graham (GA Tech)

Molecular weight (not length of molecule) affects TBC



- No correlation with length (HUPA~ 1.7 nm, F21PA ~ 2 nm)
- Most noticeable change in TBC with large MW F21PA

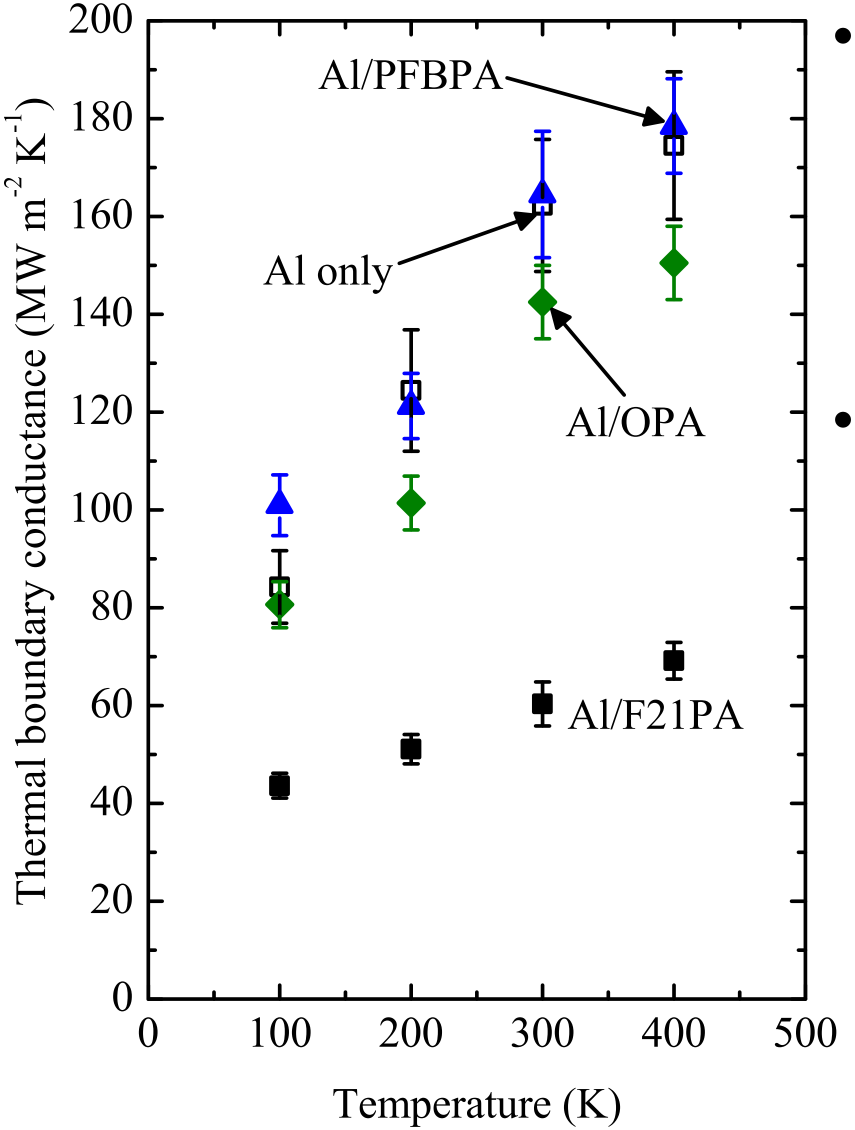


F21PA

JPCC **119**, 20931 (2015)

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

Temperature trends elucidate mechanism



- Similar temperature trends (not including F21PA) suggest no change in phonon scattering mechanisms
- Scattering ***in*** F21PA of vibrations with length scales less than interfacial length scale (consistent with previous discussions)

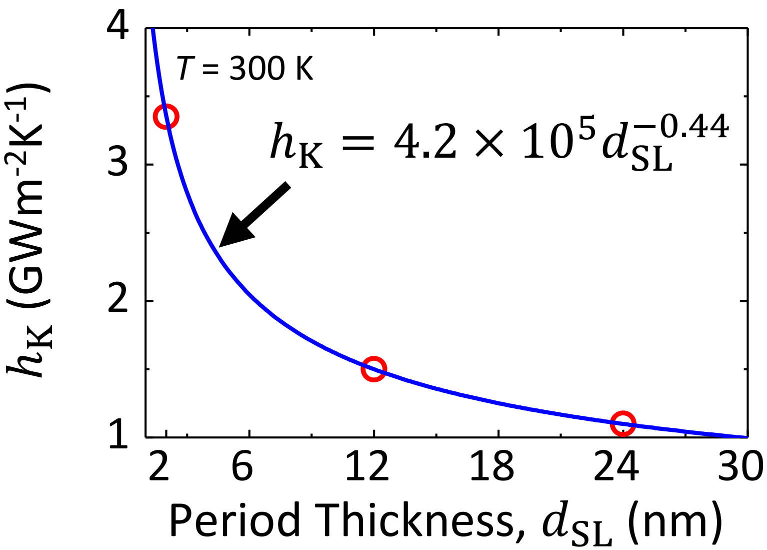
$$\frac{1}{h_{K,total}} = \frac{1}{h_{K,sapphire}} + \frac{1}{h_{F21PA}}$$

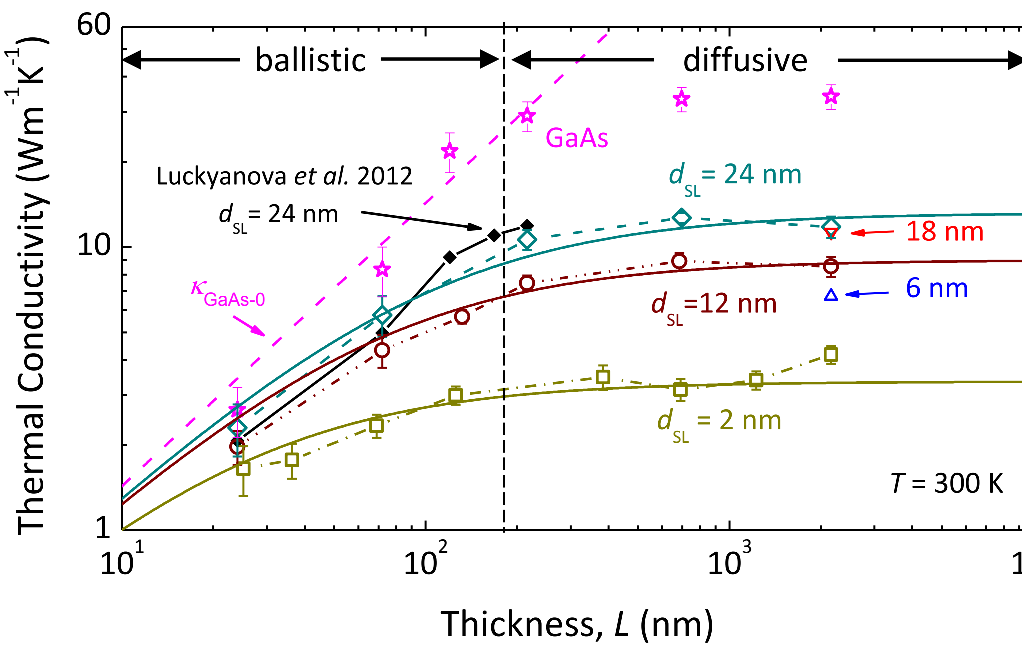
JPCC **119**, 20931 (2015)

Scattering in interfacial region if region is "disordered" and large

How does this translate to nanocomposites/SLs?

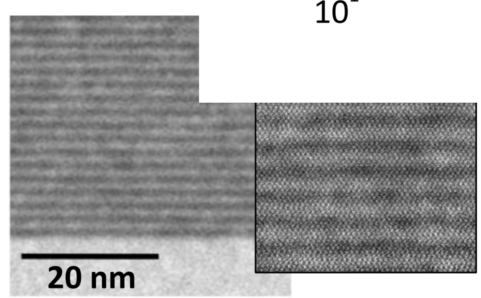
- Single interfaces: length scale of disorder > vibrational wavelength = diffusive scattering in interfacial region
- Single interfaces: length scale of disorder < vibrational wavelength = ballistic transport across interfacial region
- Translates to observations in inorganic SL structures





Manuscript under review

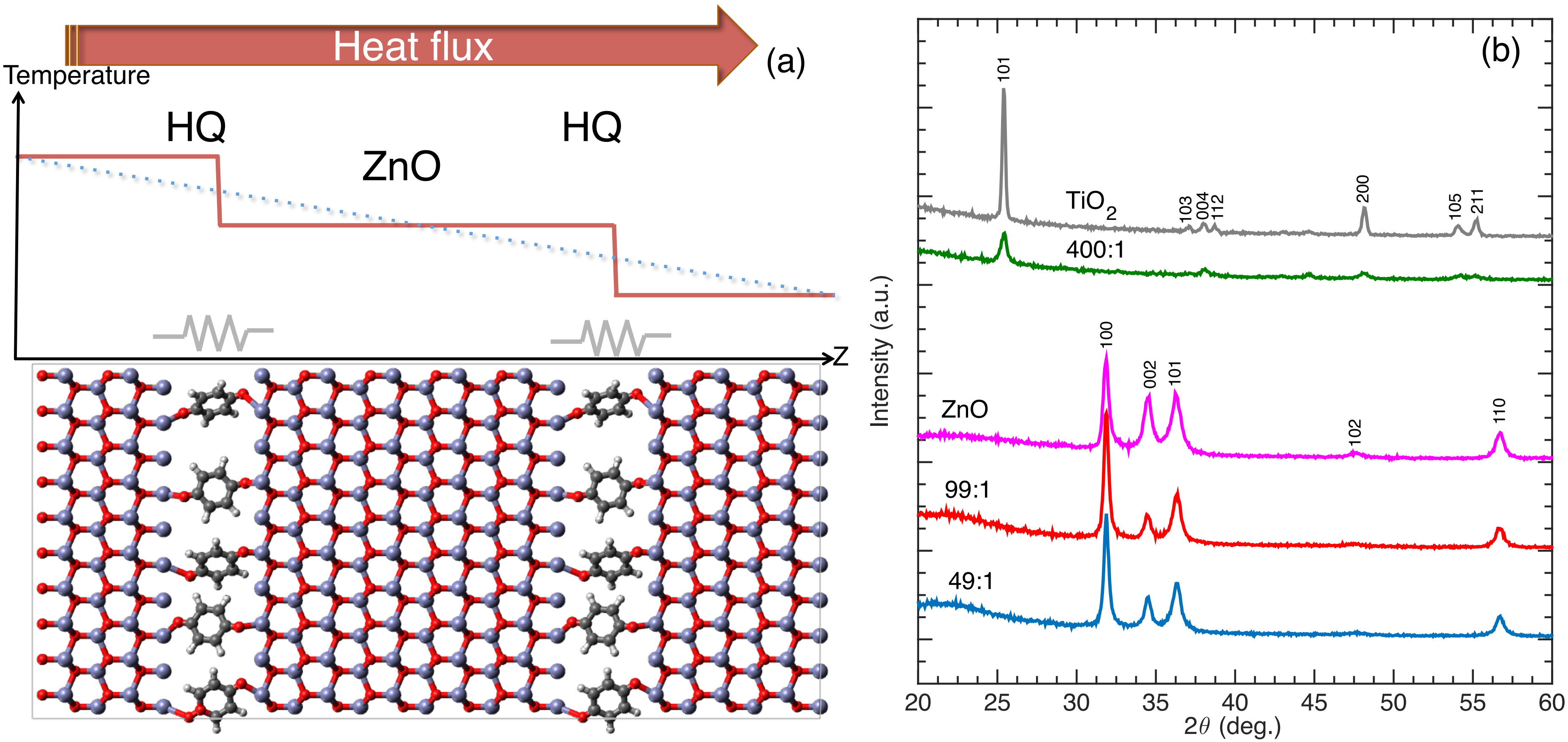
A



d_{SL}= 2 nm

What about organic/inorganic SLs?

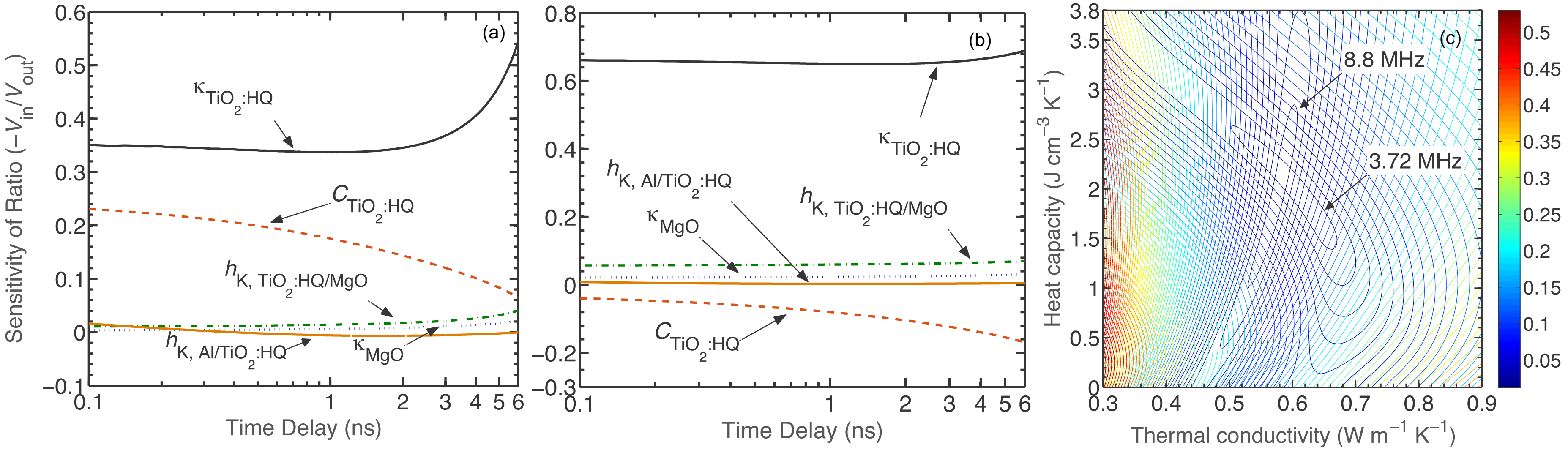
Combined ALD/MLD to reduce κ in oxides



Phys. Rev. B **93**, 024201 (2016)
Phys. Rev. B. **93**, 115310 (2016)

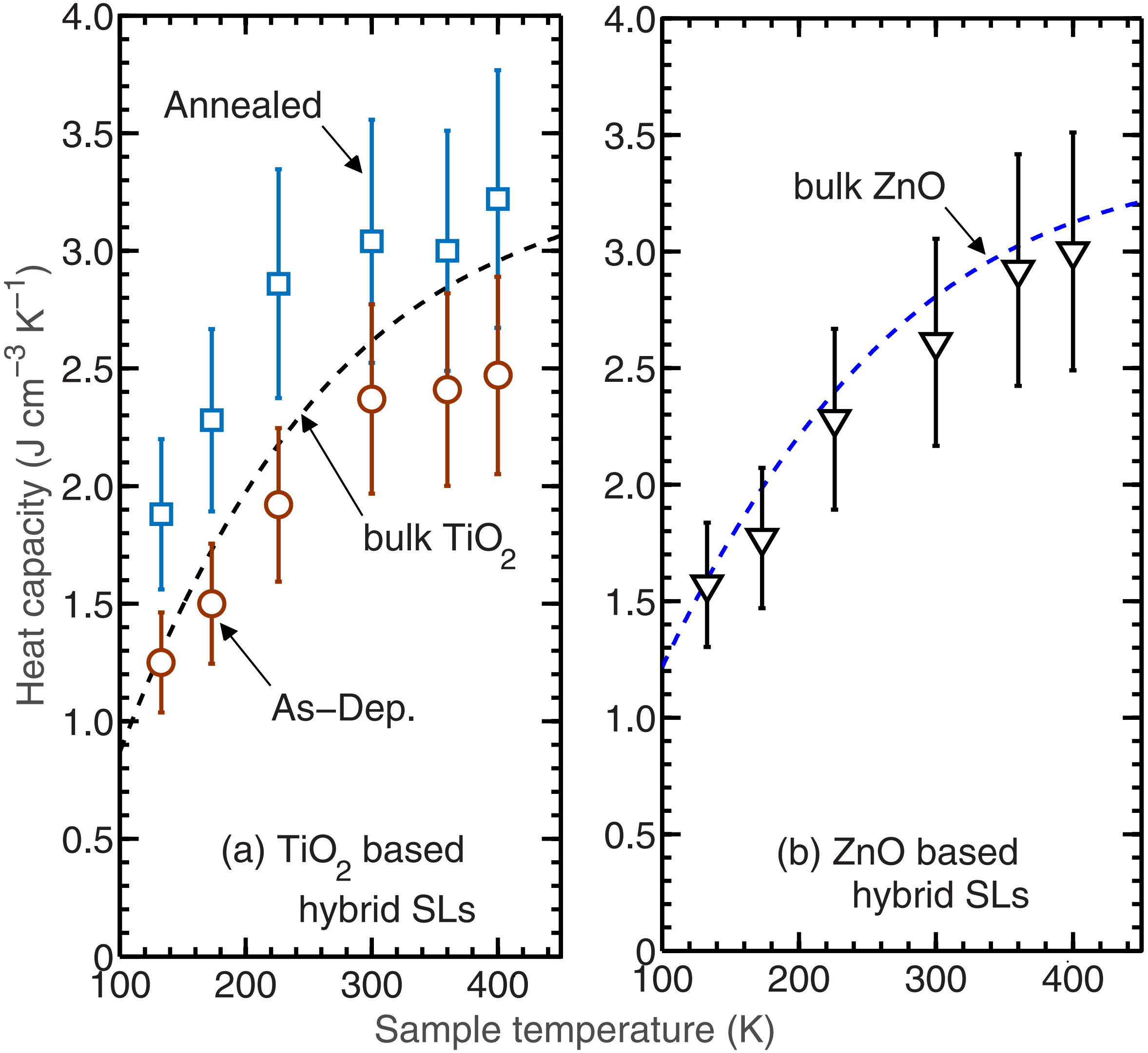
Collaboration
M. Karppinen (Aalto)

Heat capacity of hybrid inorganic/organic materials



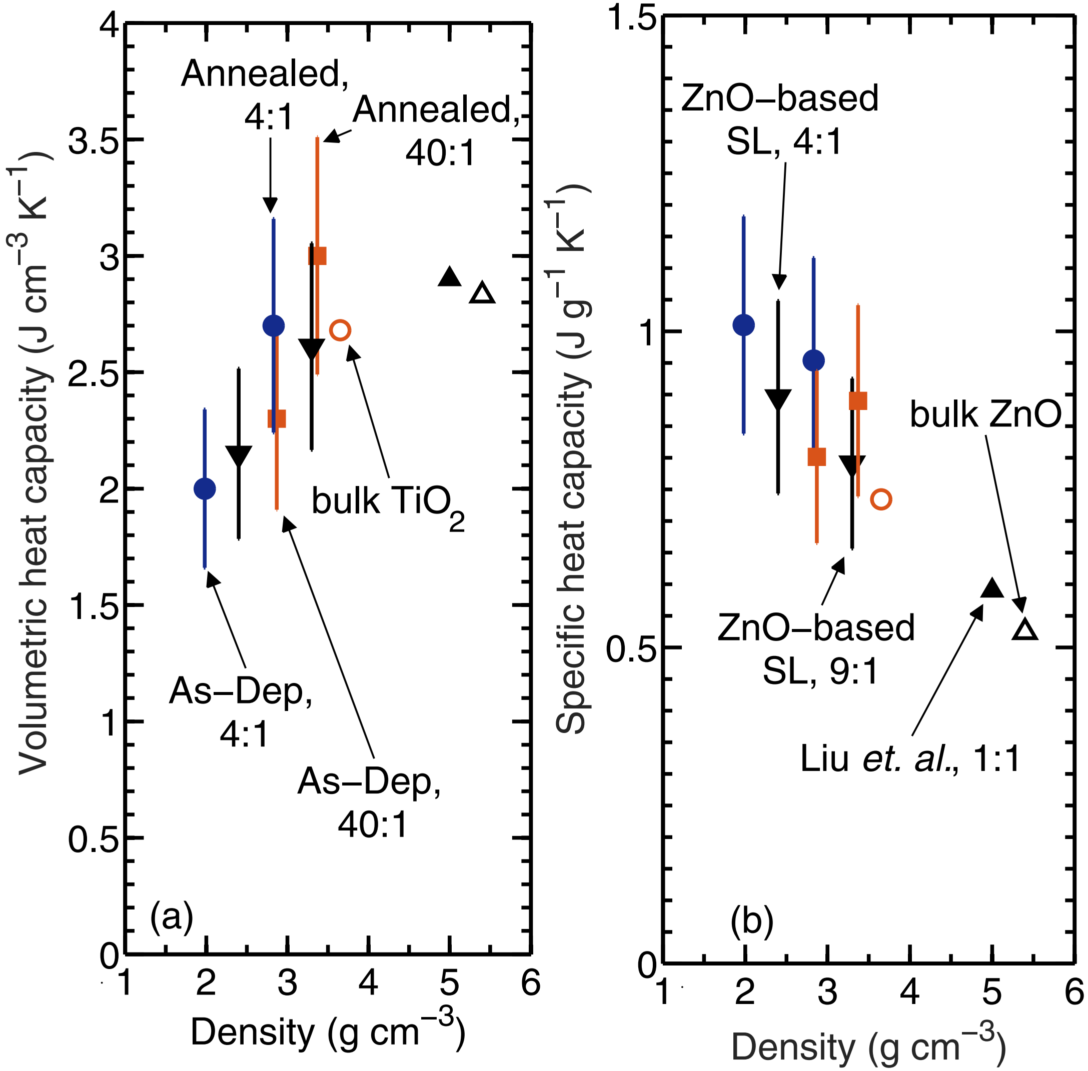
Phys. Rev. B **93**, 024201 (2016)

Heat capacity of hybrid inorganic/organic SLs



Phys. Rev. B **93**, 024201 (2016)

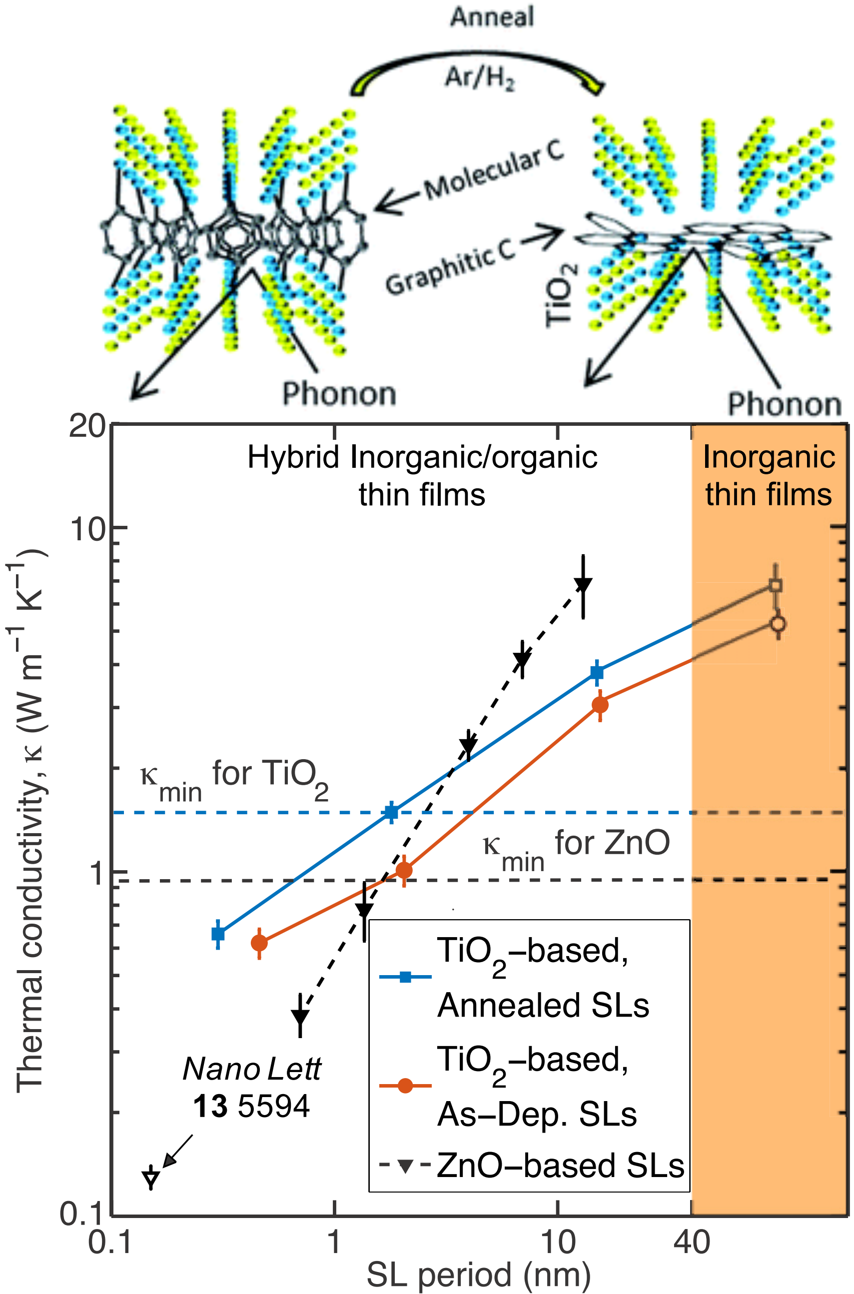
Heat capacity of hybrid inorganic/organic SLs



Phys. Rev. B **93**, 024201 (2016)

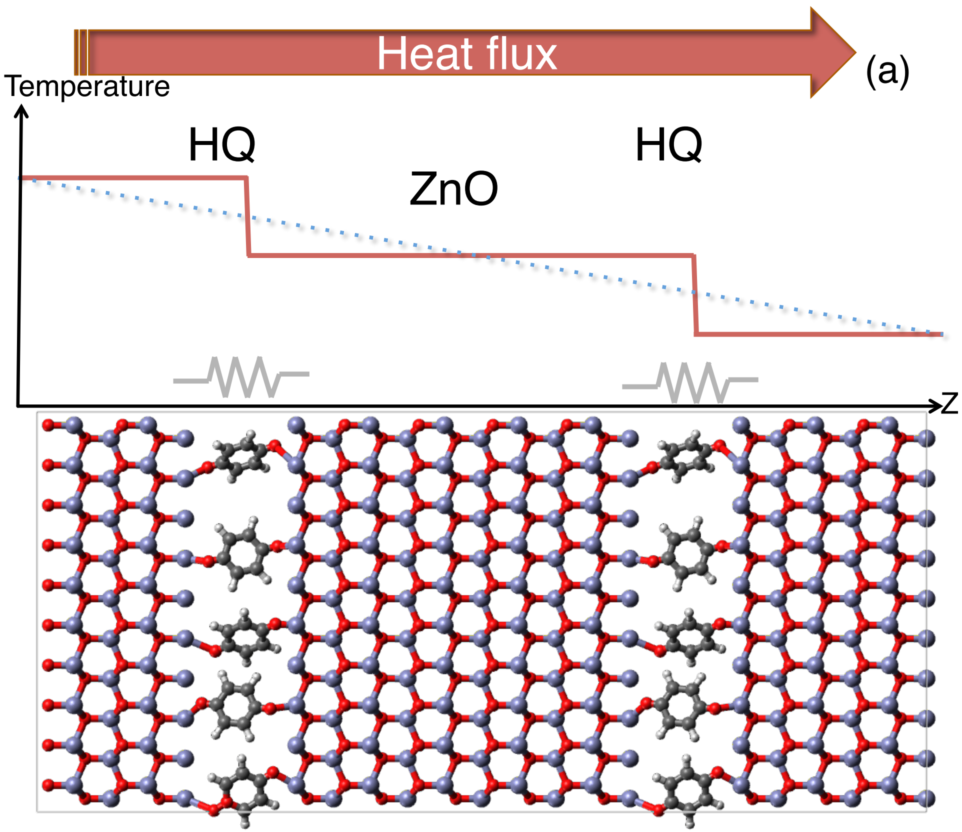
Vibrational scattering at inorganic/organic interface

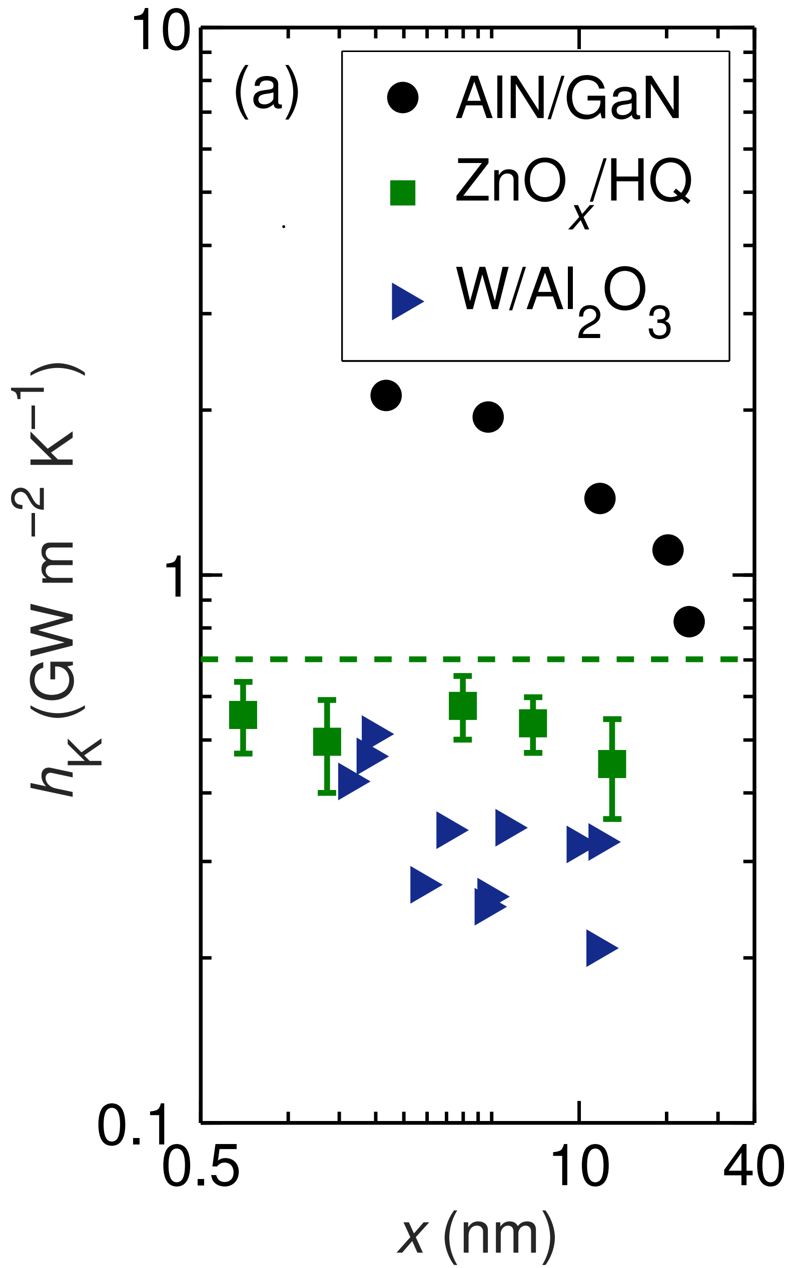
- Phonon scattering at organic/inorganic interface can lead crystalline composites achieving κ less than amorphous phase
- Scattering ***at*** interface, not ***in*** HQ layer
- Let's analyze this in terms of a TBC



Phys. Rev. B **93**, 024201 (2016)
Phys. Rev. B. **93**, 115310 (2016)

TBC in organic/inorganic composites: Ballistic vs. diffusive





Phys. Rev. B **93**, 024201 (2016)

Phys. Rev. B. **93**, 115310 (2016)

TBC in organic/inorganic composites: Ballistic vs. diffusive

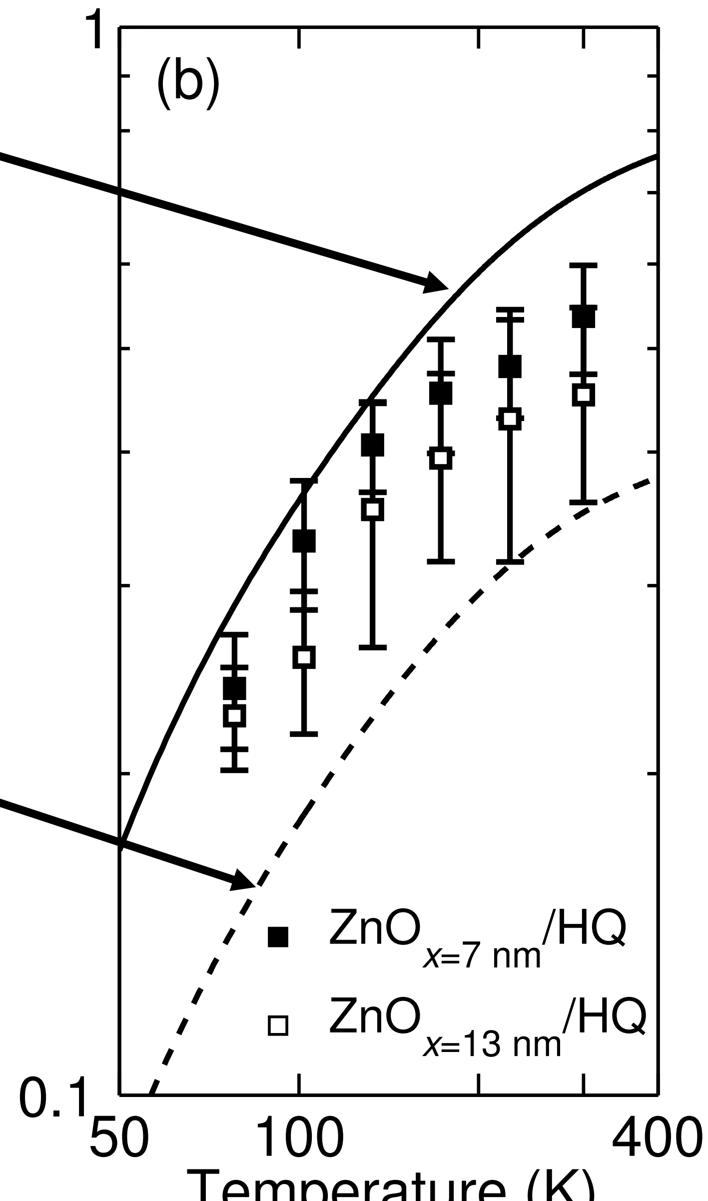
$$\zeta_{1\rightarrow 2} = 1$$

Max possible TBC
(transmission of unity)

$$h_K = \int_\omega q_\omega \zeta_{1\rightarrow 2} \, d\omega$$

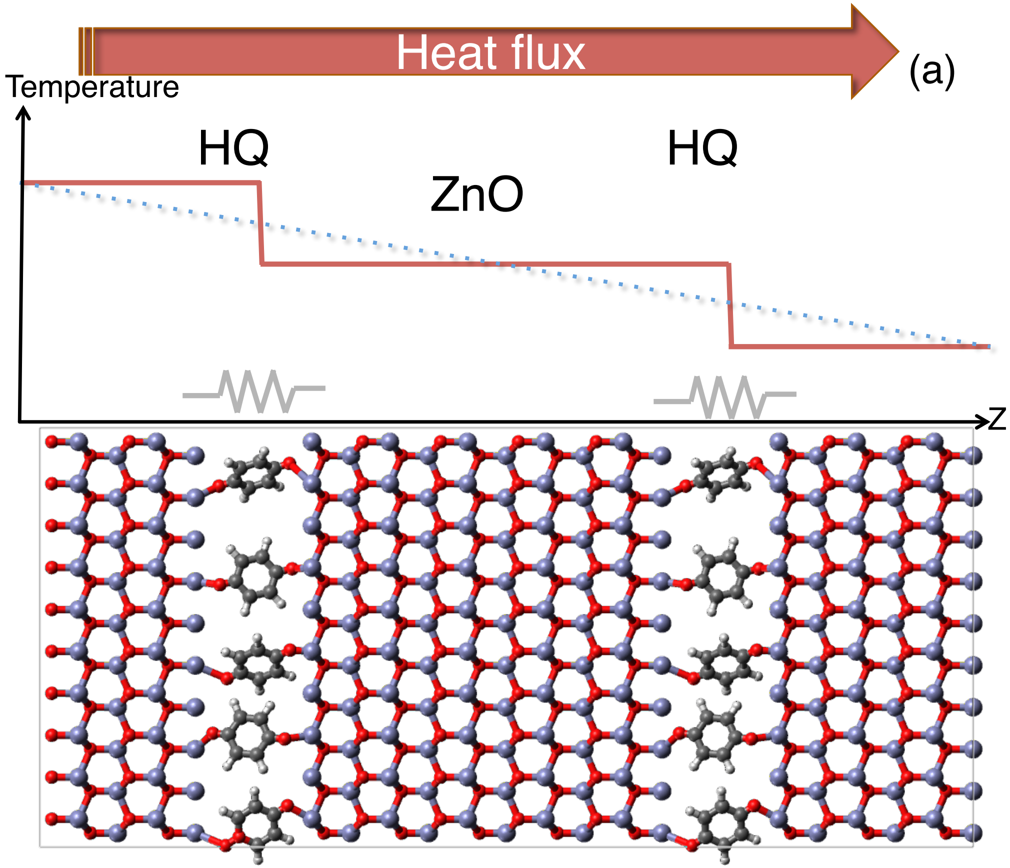
Diffuse mismatch model
(transmission of 50%)

$$\zeta_{1\rightarrow 2} = 0$$



Phys. Rev. B **93**, 024201 (2016)
Phys. Rev. B. **93**, 115310 (2016)

TBC in organic/inorganic composites: Ballistic vs. diffusive



ZnO phonons with wavelengths larger than HQ diameter account for ~80% of heat flux

1) ZnO phonons scatter at ZnO/HQ interface

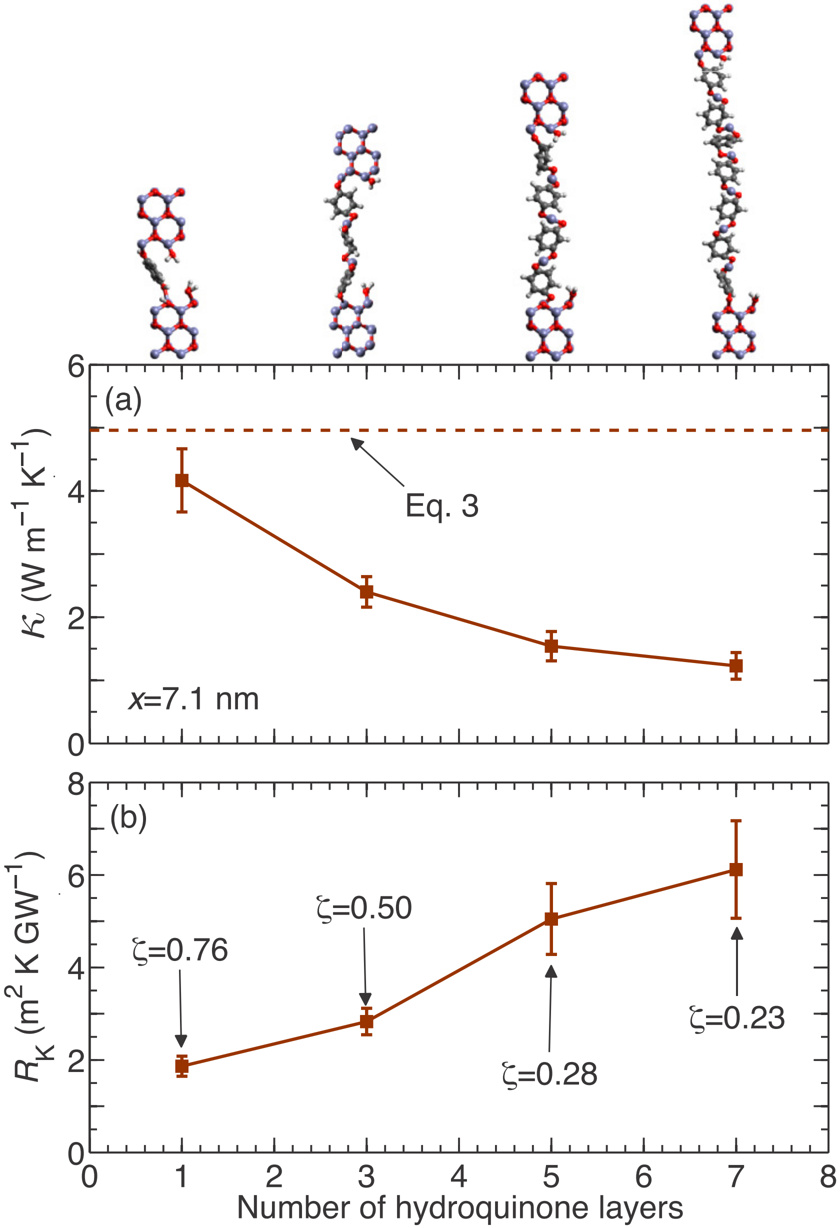
2) ~80% of ZnO phonons transmit across HQ with ζ = 1 (ZnO/ZnO interface)

3) ~20% of ZnO-based vibrations scatter in HQ (can we support this?)

Phys. Rev. B **93**, 024201 (2016)
Phys. Rev. B. **93**, 115310 (2016)

TBC in organic/inorganic composites: Ballistic vs. diffusive

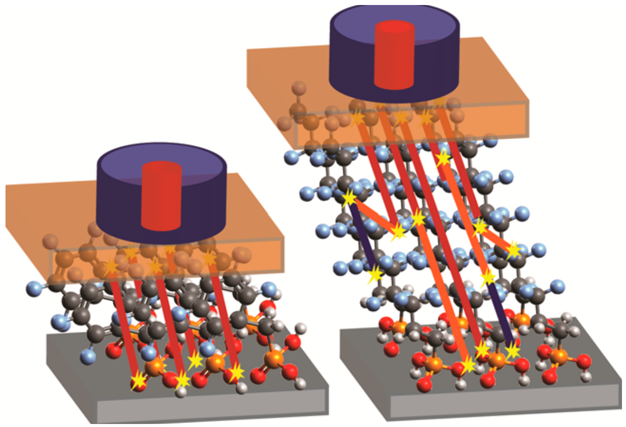
- Increase number of HQ molecules in organic layer, lower κ, lower TBC
- Transmission decreases
- More scattering ***in*** HQ layer as number of HQ molecules increase

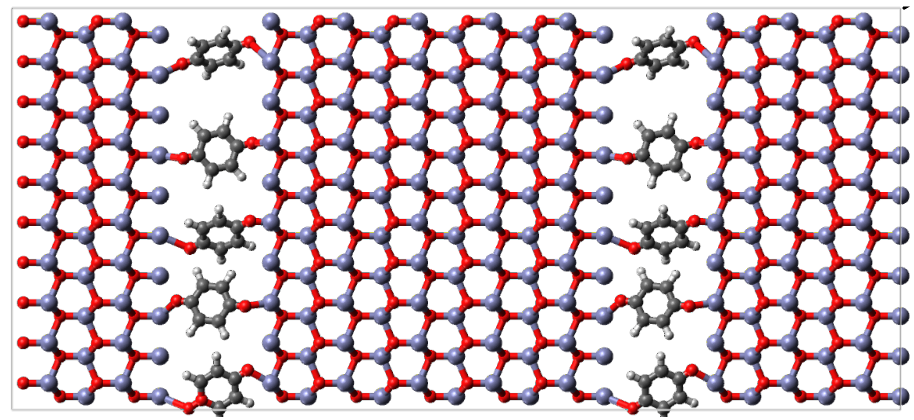


Phys. Rev. B **93**, 024201 (2016)
Phys. Rev. B. **93**, 115310 (2016)

Conclusions

Size of molecule dictates ballistic vs. diffusive heat transfer





<u>Single interfaces</u>

Metal/phosphonic acid/sapphire

Collab: Sam Graham (GA Tech)

JPCC **119**, 20931 (2015)

<u>Hybrid structures</u>

ZnO/HQ or TiO_2/HQ SLs

Collab: Maarit Karppinen (Aalto)

Phys. Rev. B **93**, 024201 (2016)

Phys. Rev. B. **93**, 115310 (2016)