UVA | SCHOOL of ENGINEERING & APPLIED SCIENCE

Manipulating the chemical bond to control thermal transport in graphene & low dimensional carbon films

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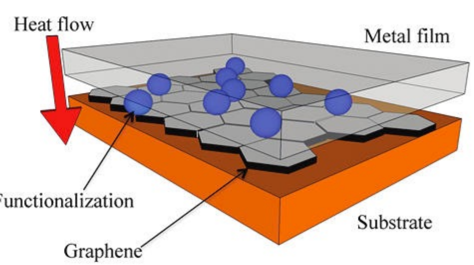
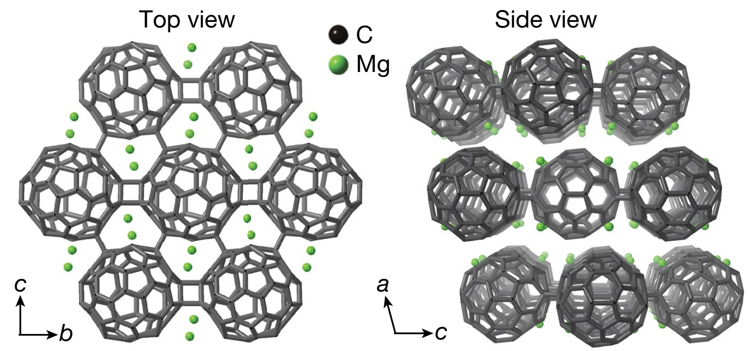
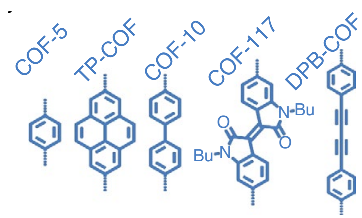
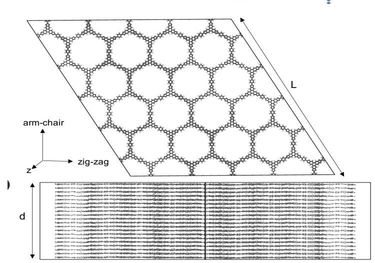
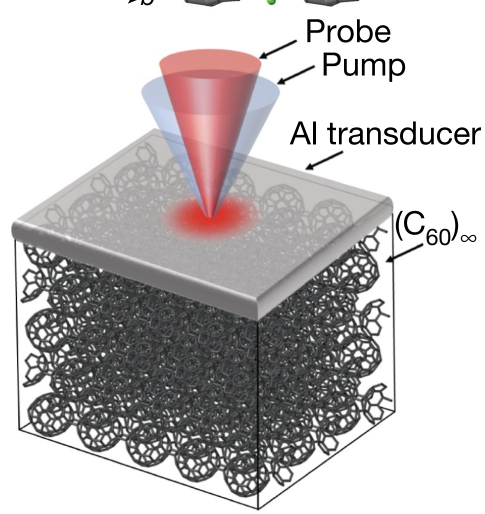
USN ONR
Science & Technology

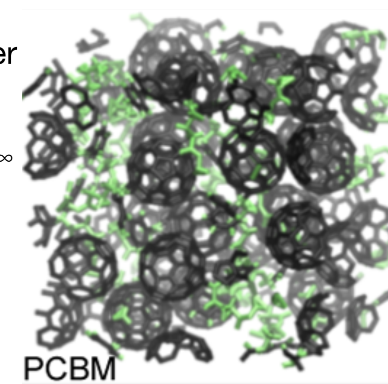




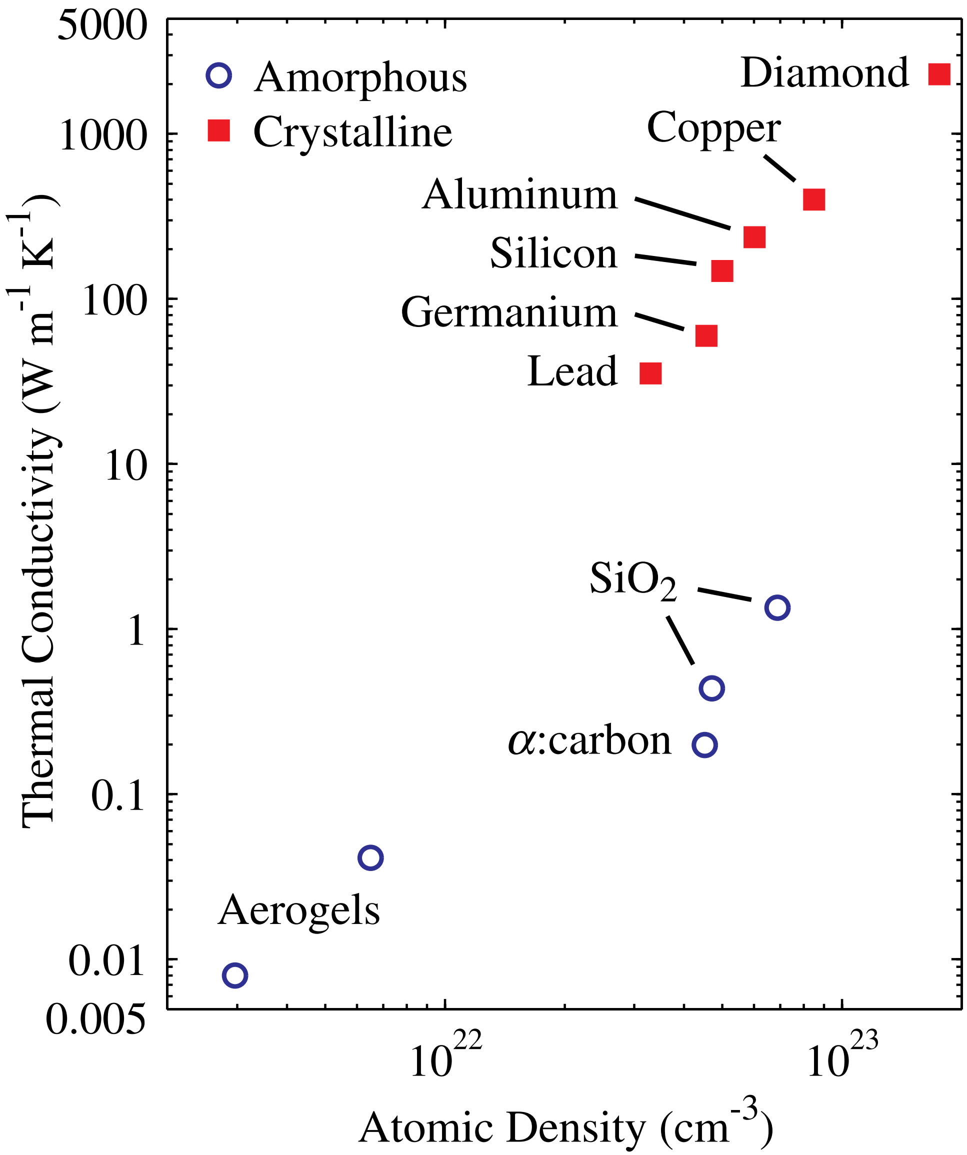








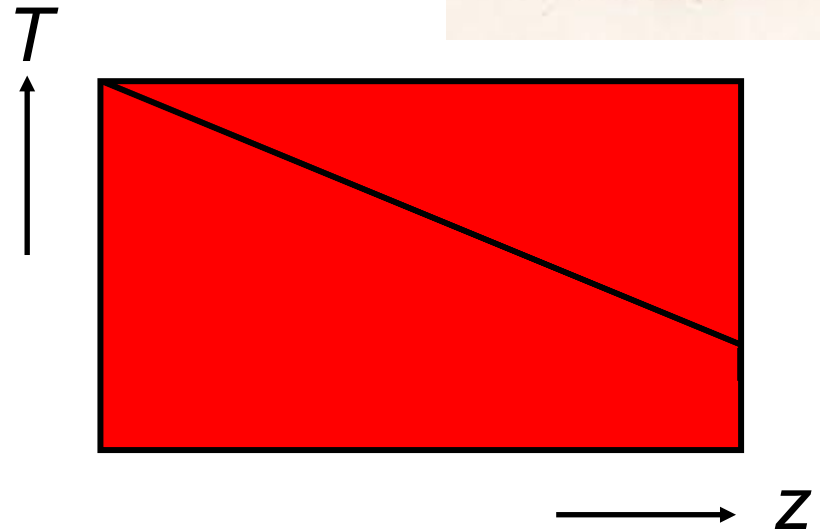
Thermal conductivity of materials – Macro/Microscopic



PRL **110**, 015902 (2013)

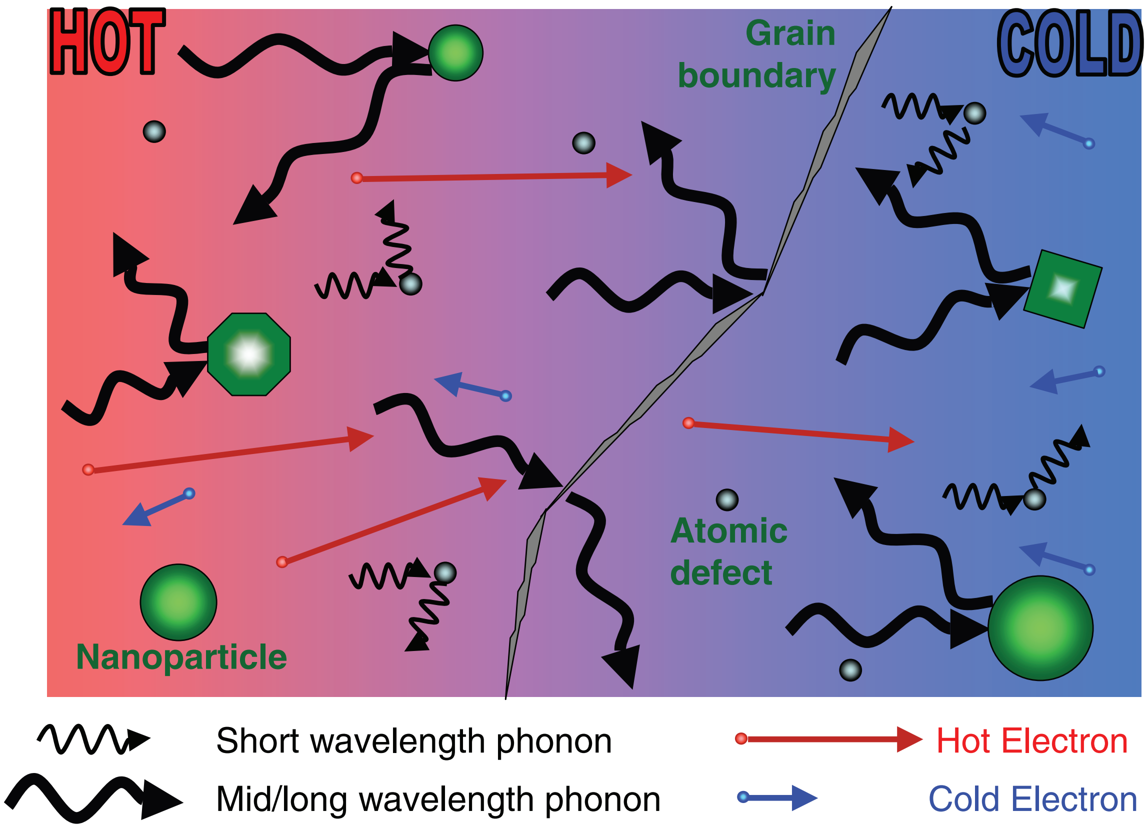
The Fourier Law

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



A nanoscopic view with Kinetic Theory

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



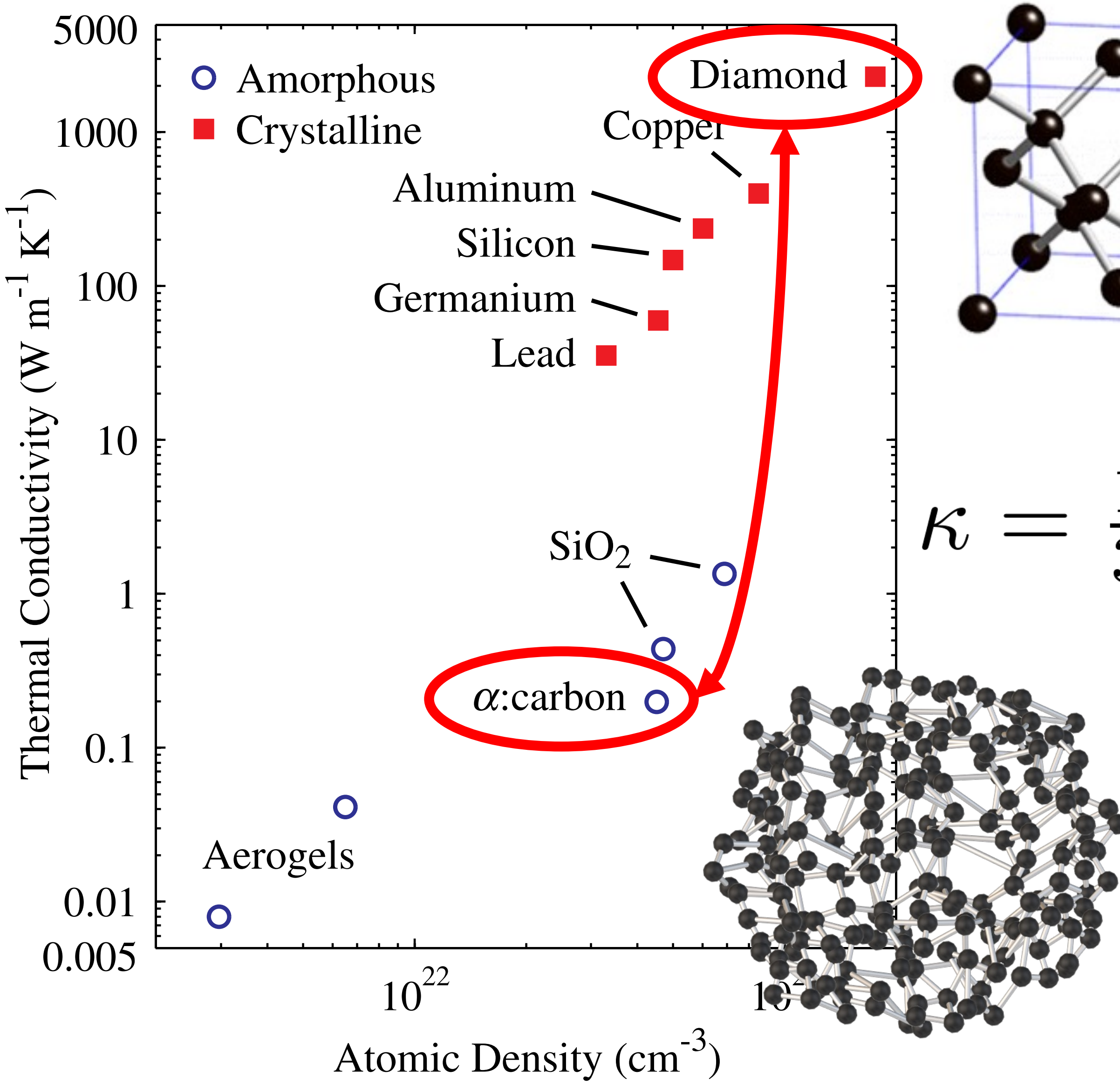
Adv. Mat. **22**, 3970

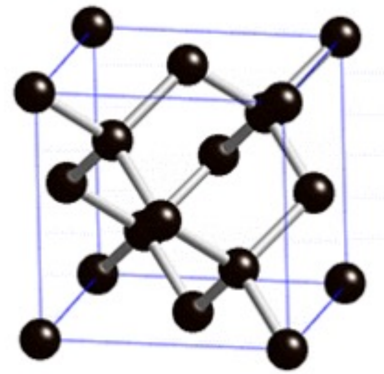
C: Heat capacity
"How much energy electrons/phonons store"

v: Velocity
"How fast the electrons/phonons move"

λ = Mean free path
"How far they move before losing energy/momentum"

Thermal conductivity of materials – Macro/Microscopic

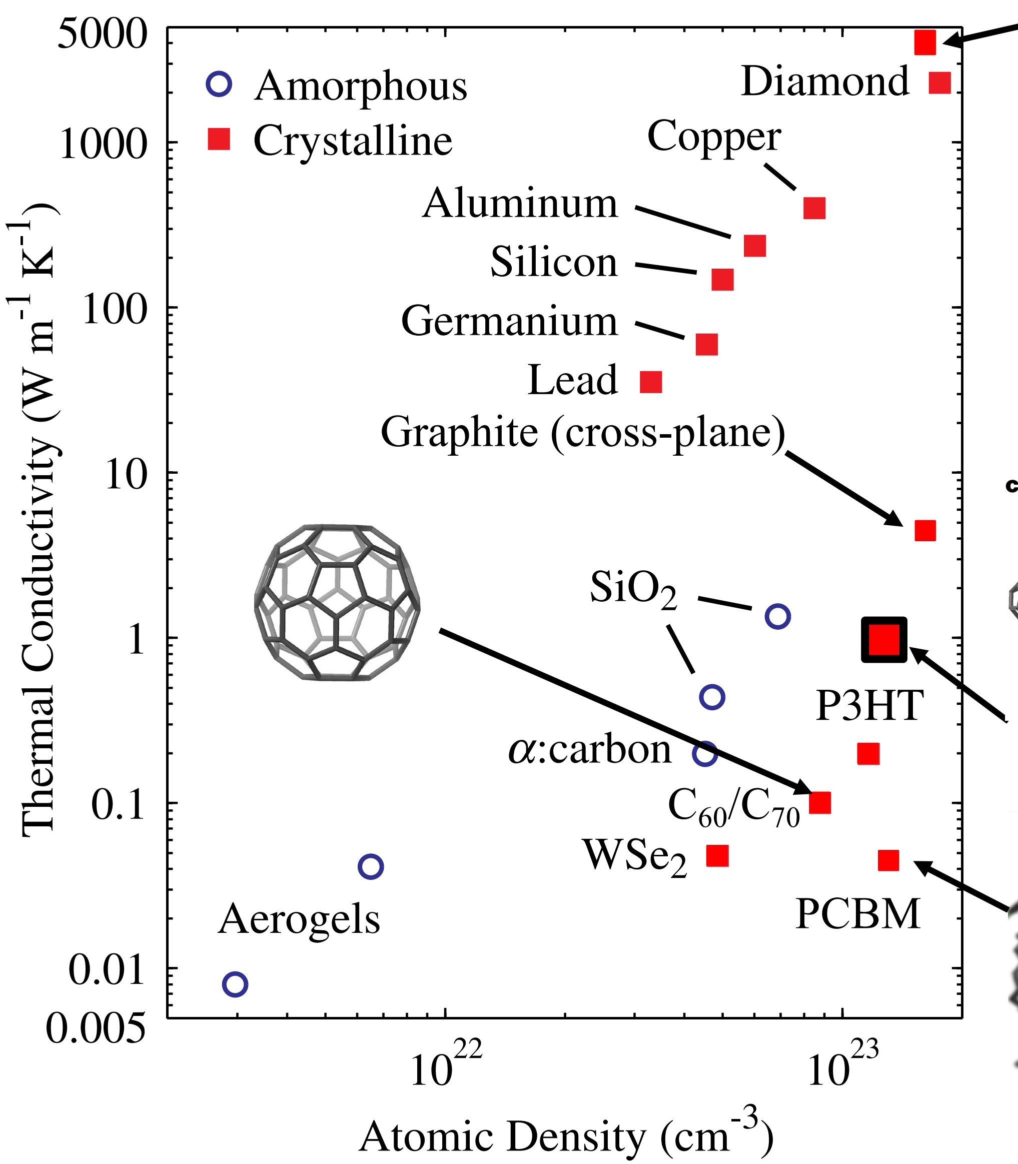


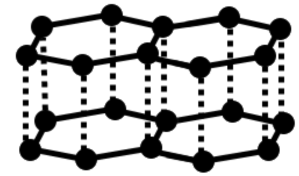


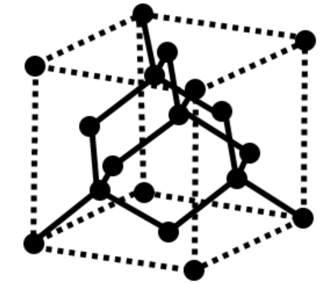
$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

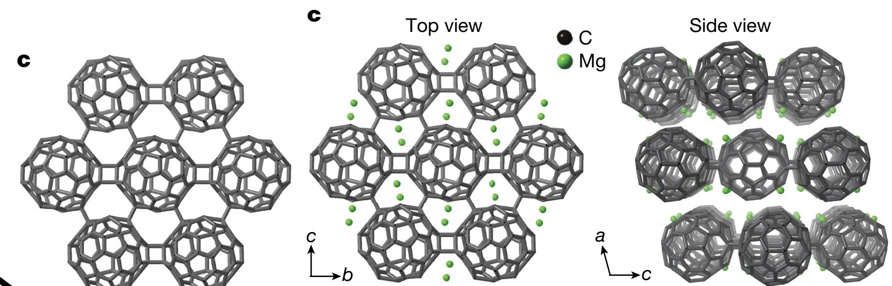
PRL **110**, 015902 (2013)

Thermal conductivity of materials – Nanoscopic

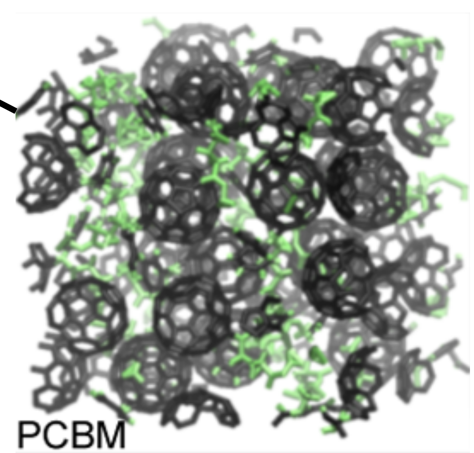



Graphite Structure


Diamond Structure

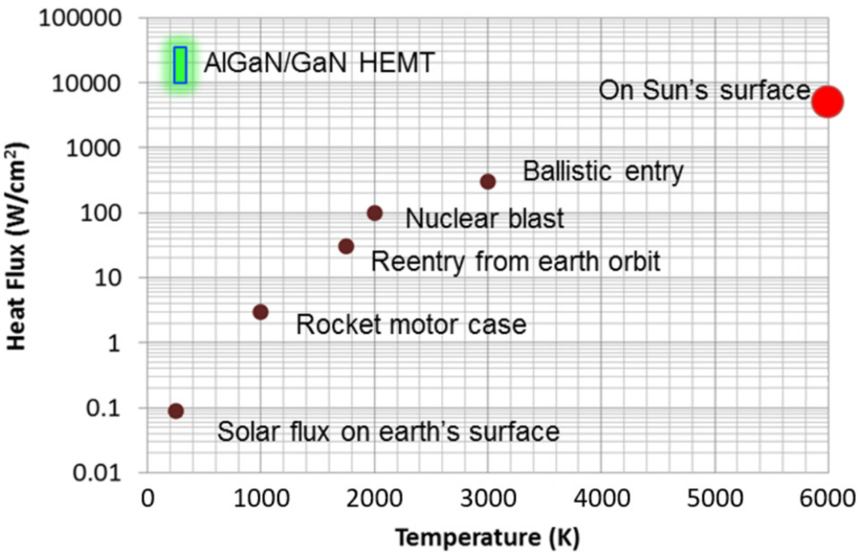


Graphullerene ***Nature*** **613, 71 (2023)**



PRL **110**, 015902 (2013)

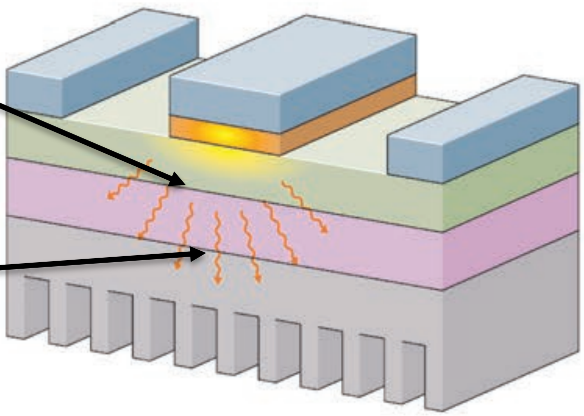
Heat transfer in low dimensional carbon: Why this matters?
Extreme temperatures & gradients in devices & environments



2D materials can help spread the heat

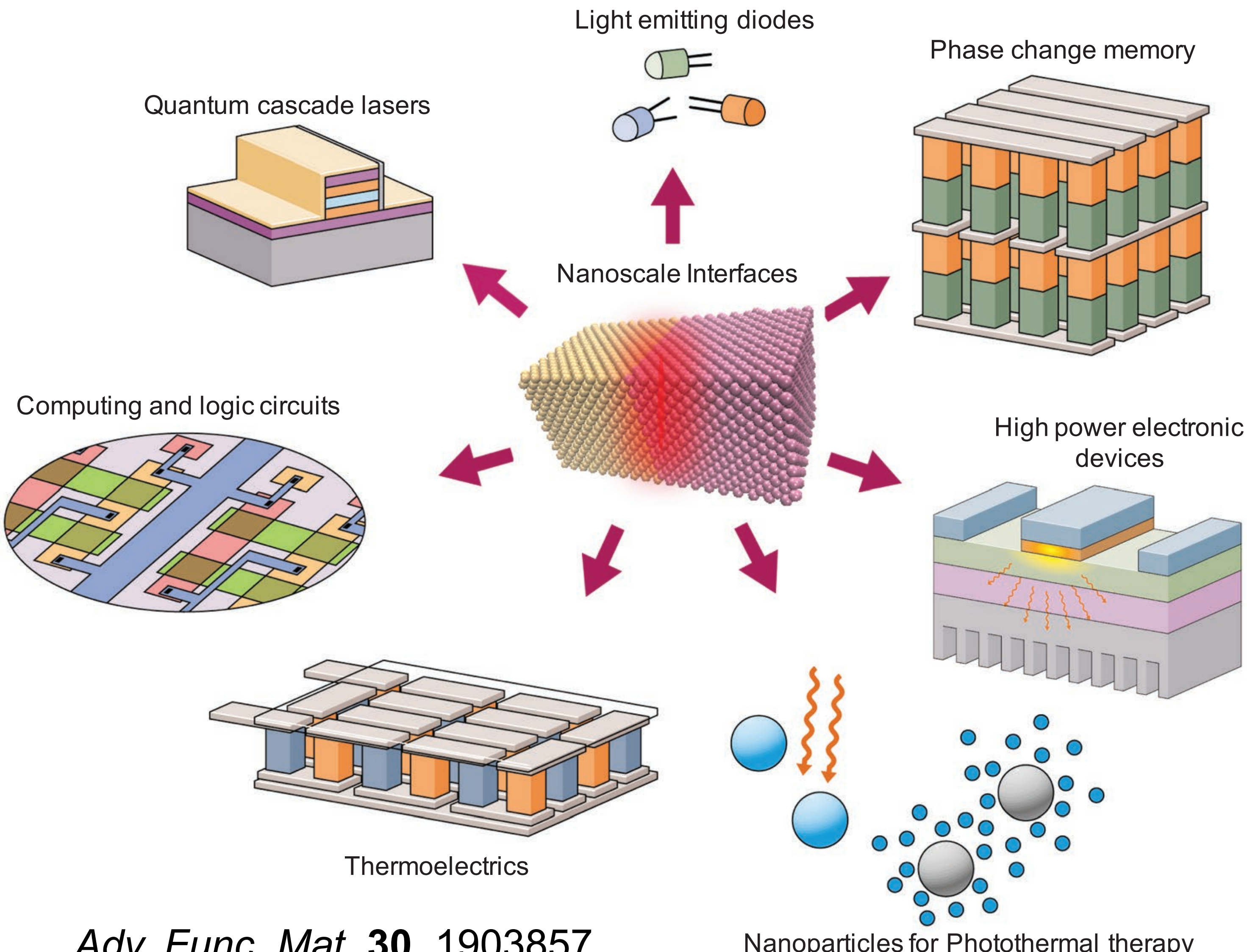
2D material composites as TIMs

High power electronic devices



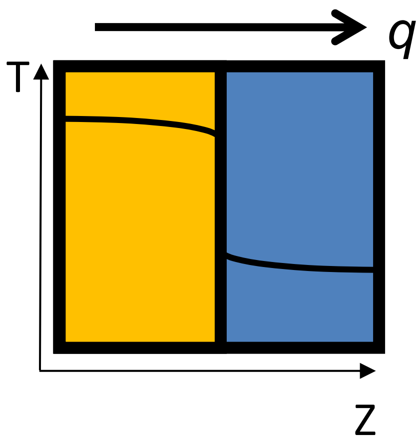
DARPA, *WBG Semi.*; *J. Elec. Pack.* **143**, 020804; *Nature* **601**, 556

Heat transfer in low dimensional carbon: Why this matters? Devices, sensing, extreme temperatures and gradients



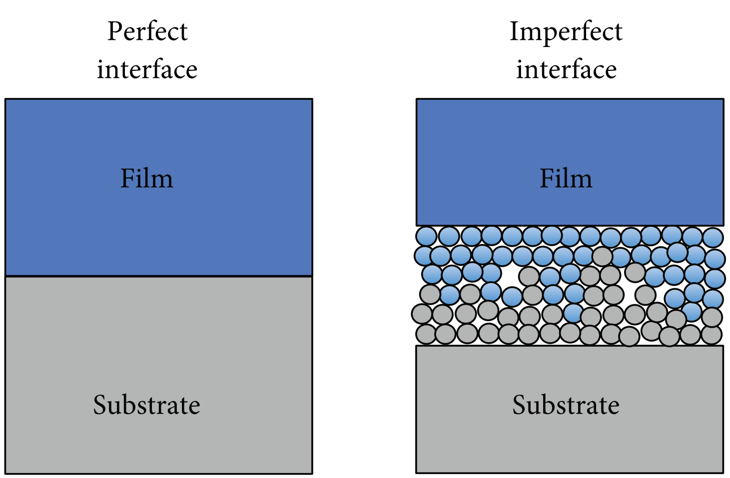
Adv. Func. Mat. **30**, 1903857

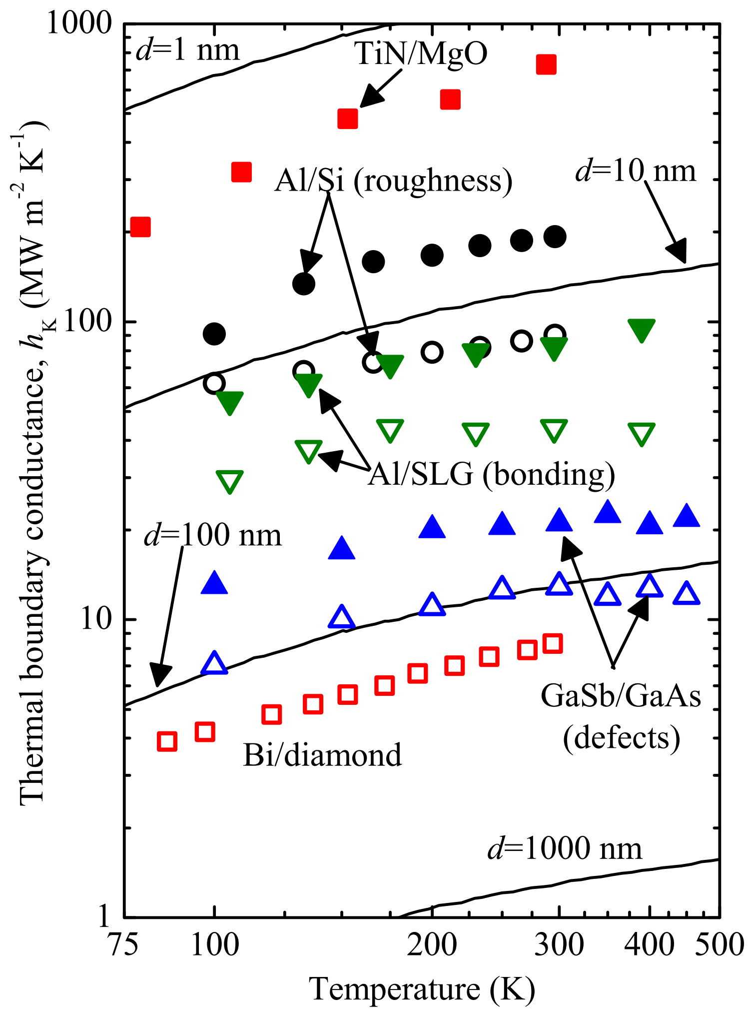
Thermal boundary conductance (TBC)



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

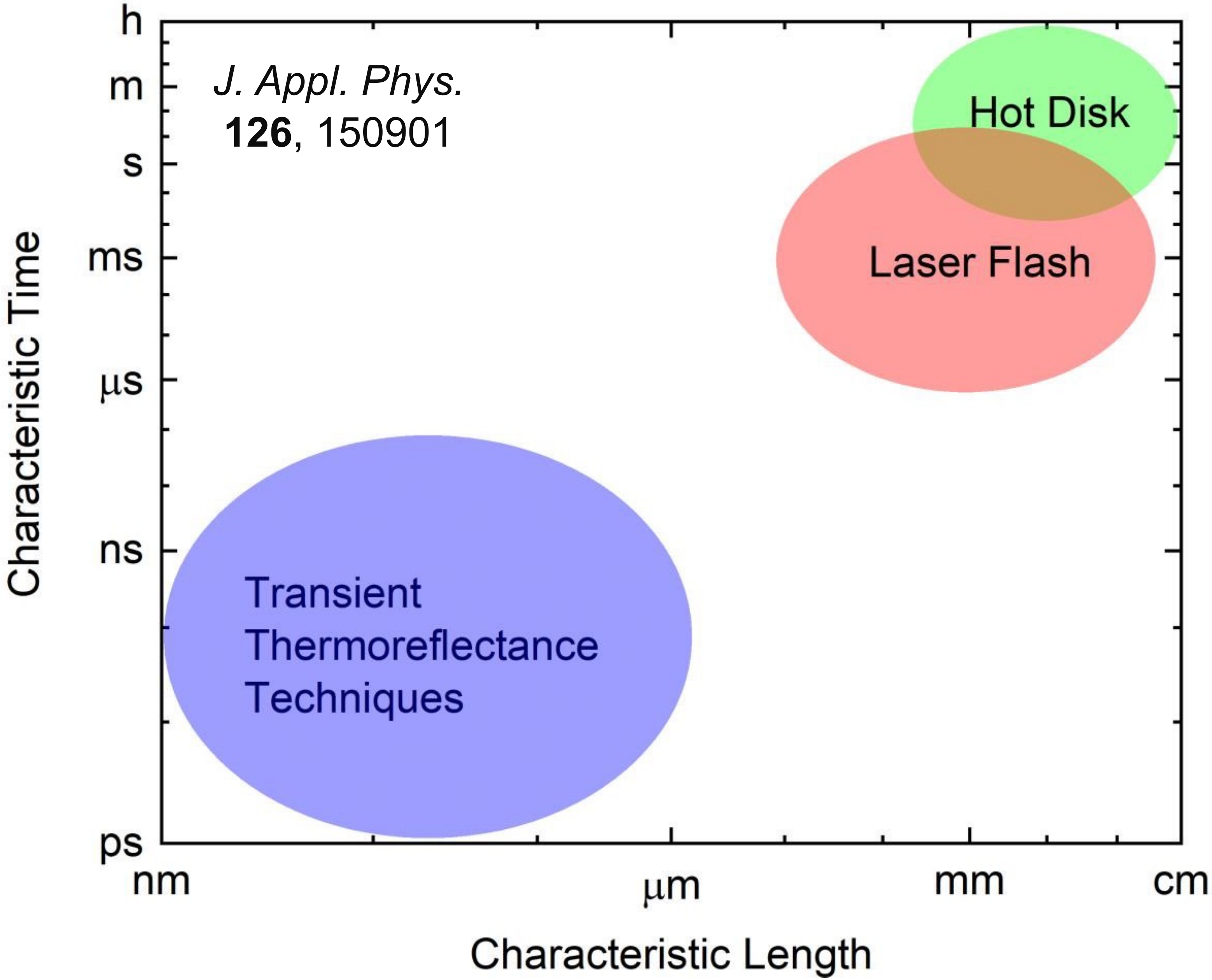
- Disorder typically reduces TBC (increases TBR)
- Not (necessarily) the case with 2D material interfaces





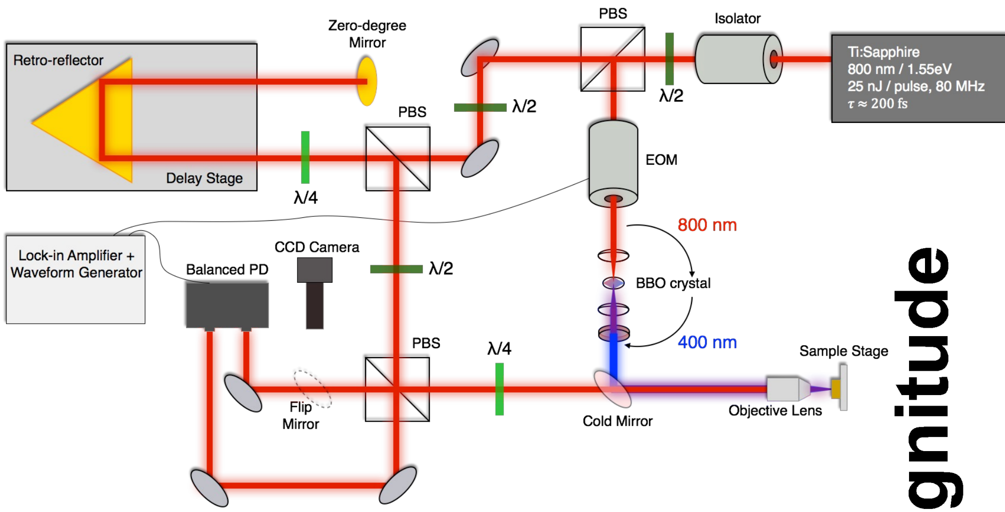
ISRN **2013**, 682586 (2013)

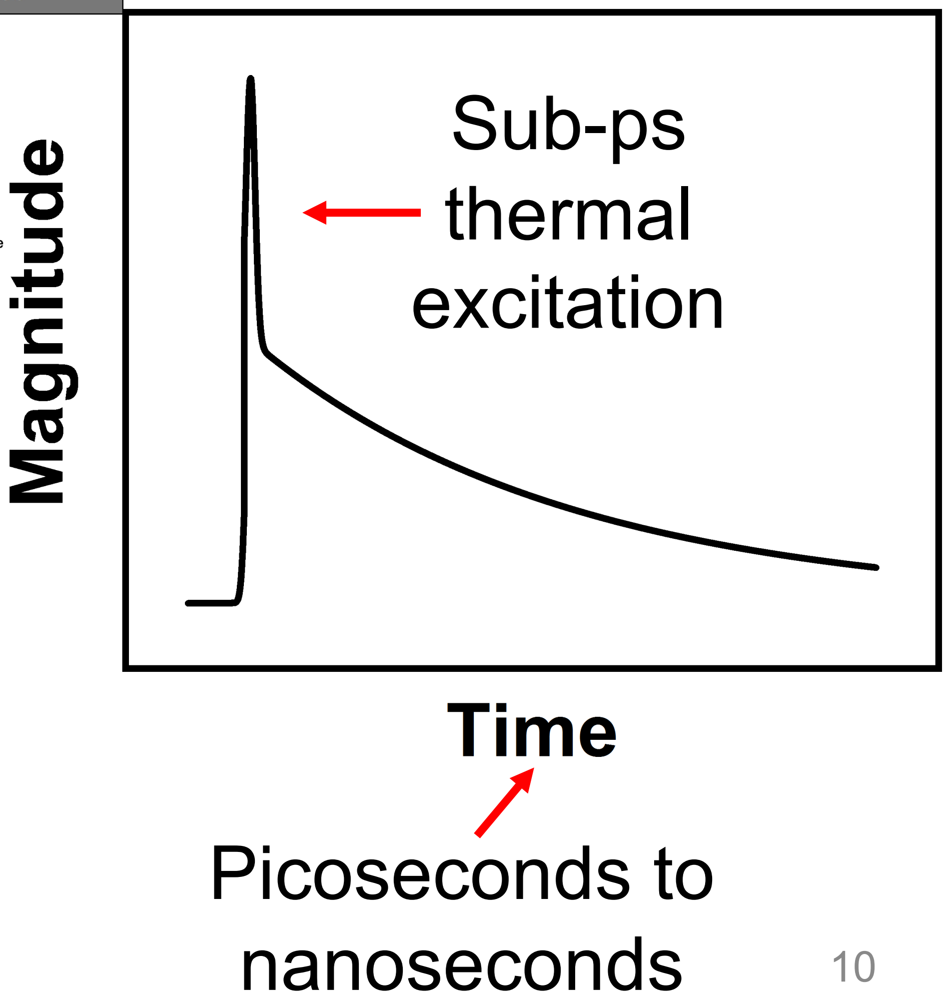
But how do we measure nano to macro HX processes?



Thermal properties of thin films? TDTR

Thin film or "near surface" measurements



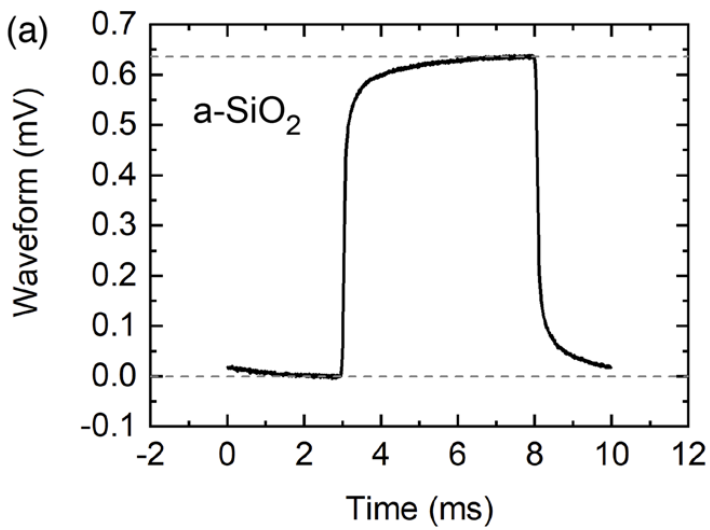


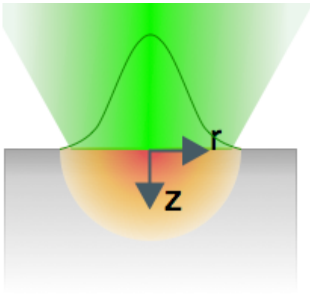
TDTR Reviews and Analyses

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

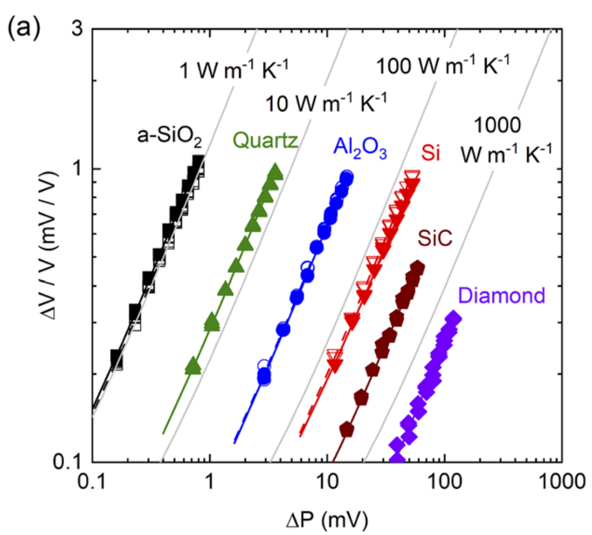
But how do we measure nano to macro HX processes?

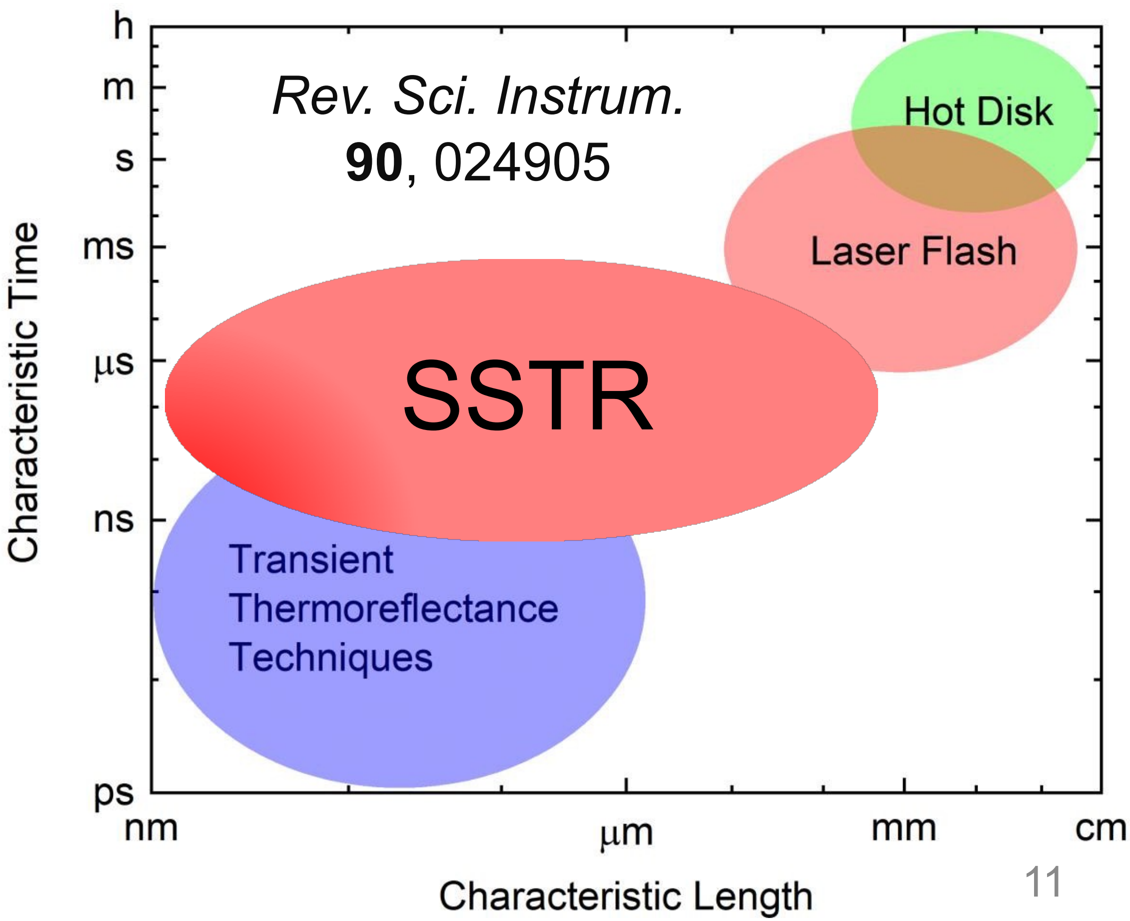
$$Q = -\kappa \nabla T$$





SSTR invented and patented via ONR support

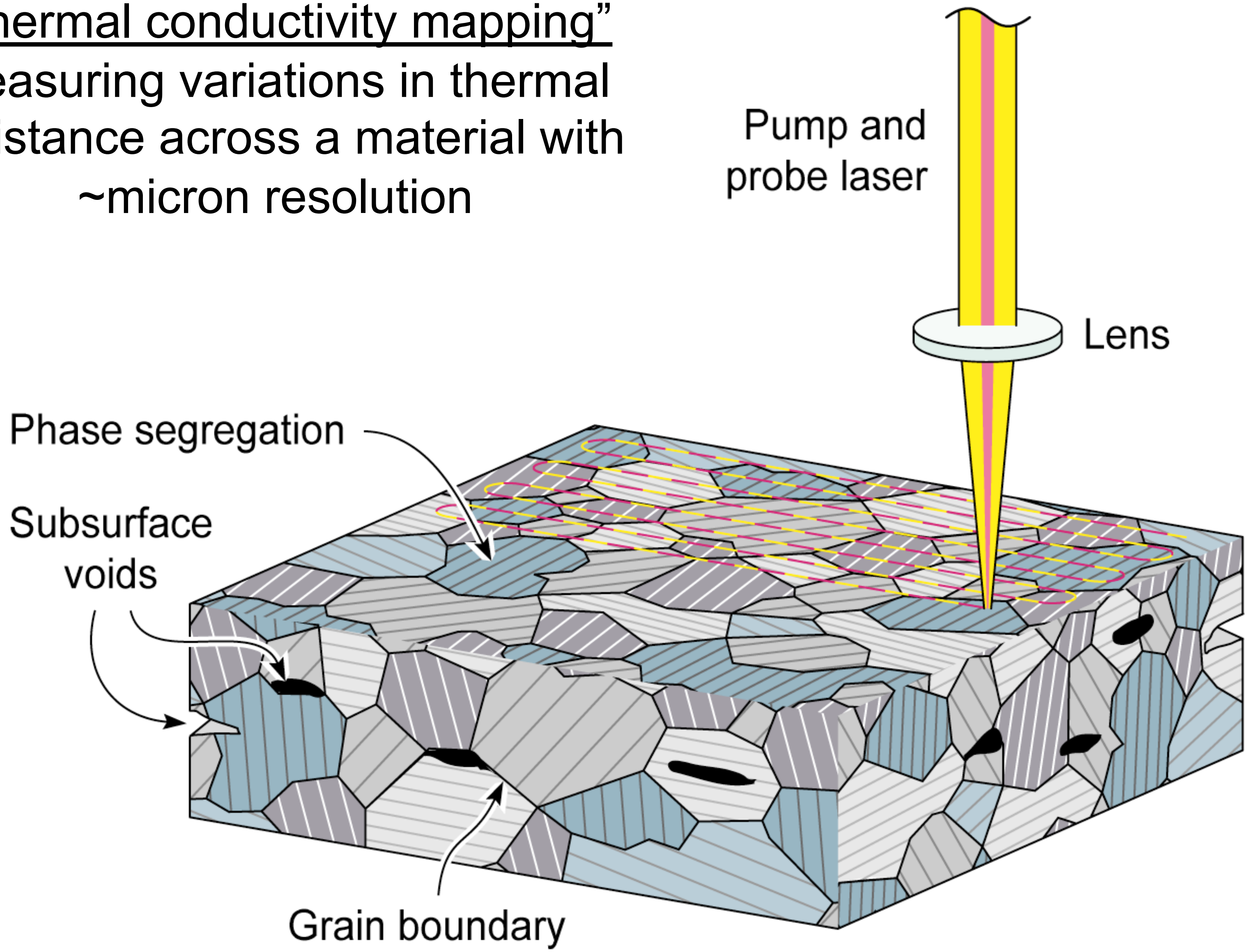




Micron-scale areal resolution for local measurements

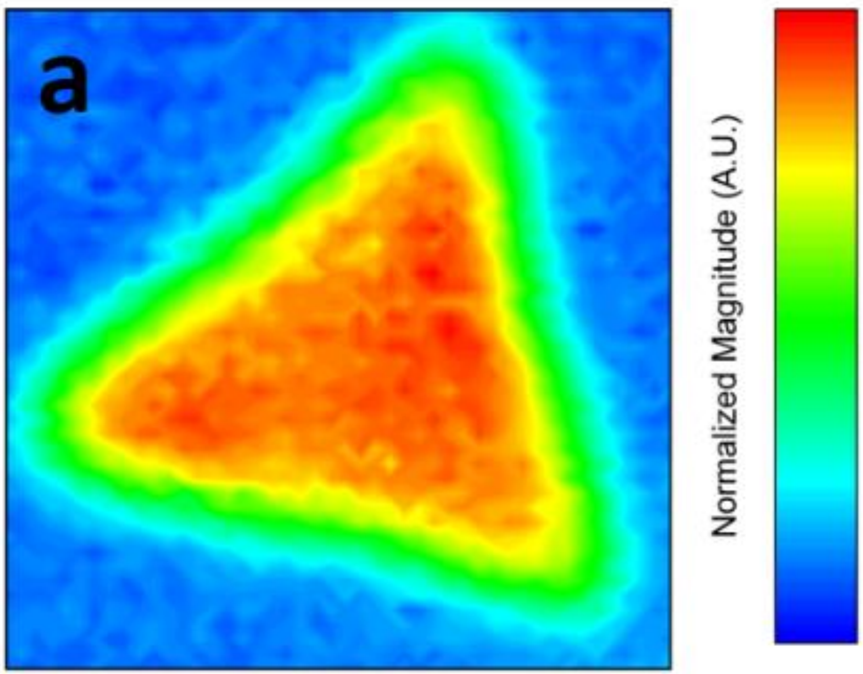
<u>"Thermal conductivity mapping"</u>

Measuring variations in thermal resistance across a material with ~micron resolution

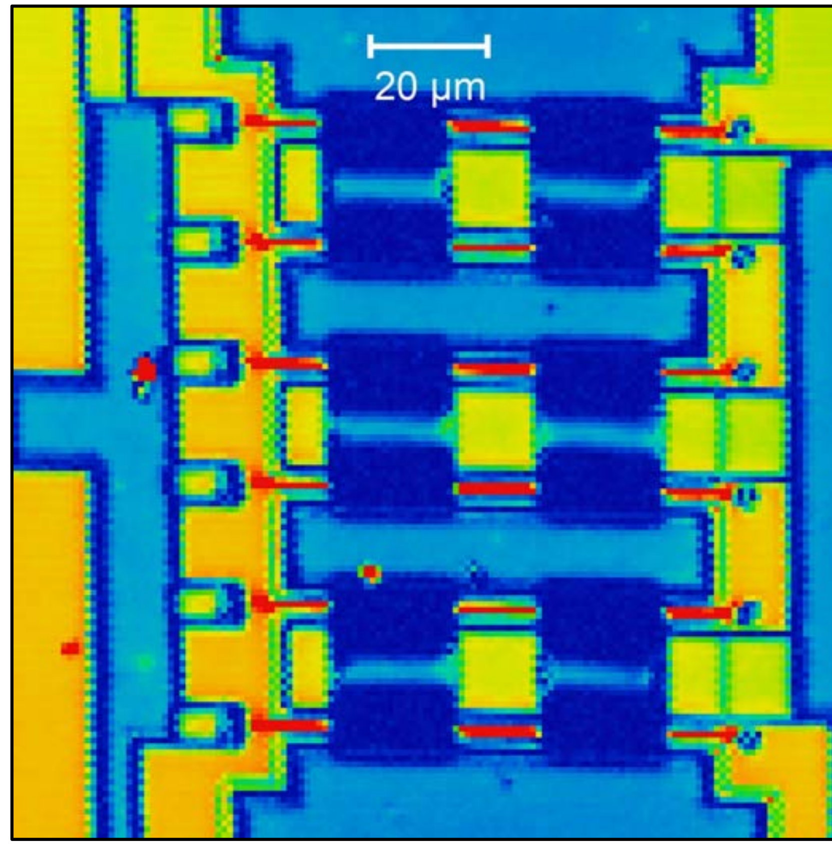


Micron-scale areal resolution for local measurements

Thermal Mapping of Wafers, Devices, etc. w/ Lateral Resolution Down to ~1 micron



WS_2/SiO_2
Adv. Sci. **7**, 2001174 (2020)
Collaboration: Prof. Mauricio Terrones (PSU)



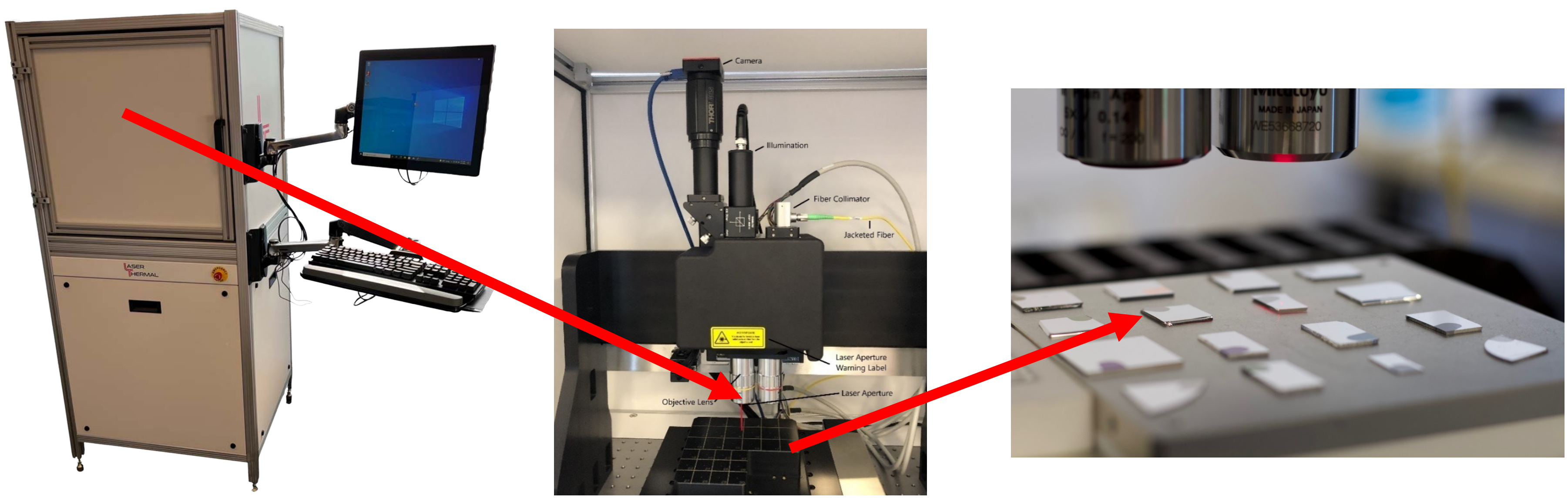
6-finger GaAs pHEMT on a MMIC power amplifier

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

https://Laserthermal.com

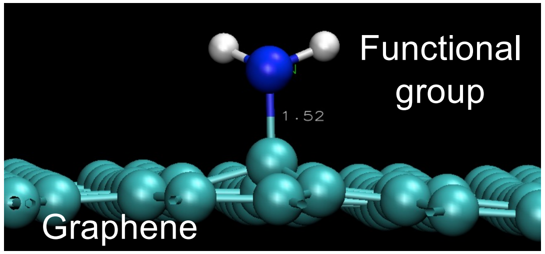
Laser Thermal licensing SSTR IP from UVA, enabling tech transition of invention from ONR funded program to commercial device

LASER THERMAL



Disclosure: Hopkins co-Founder of LT, Inc.

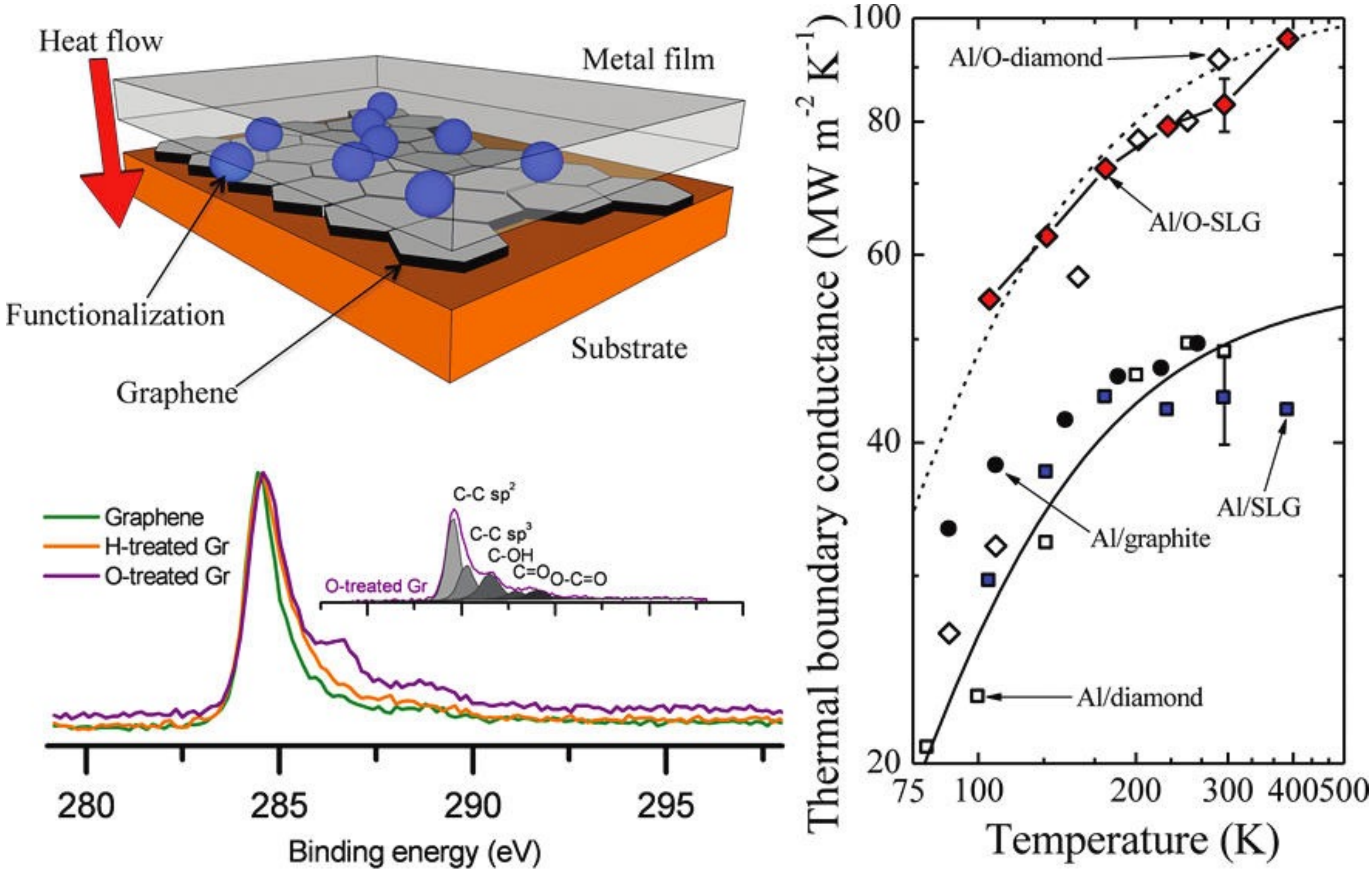
Chemical functionalization of graphene with plasmas



Functional groups covalently bound to graphene
Reversible after anneal

Appl. Phys. Lett. **96**, 231501
Dr. Lock and Dr. Walton’s (NRL) prior work

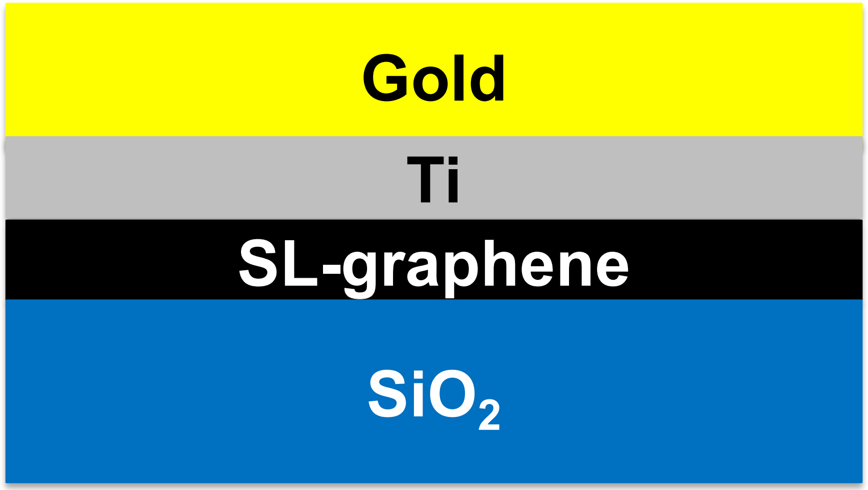
Thermal conductance at functionalized SLG interfaces

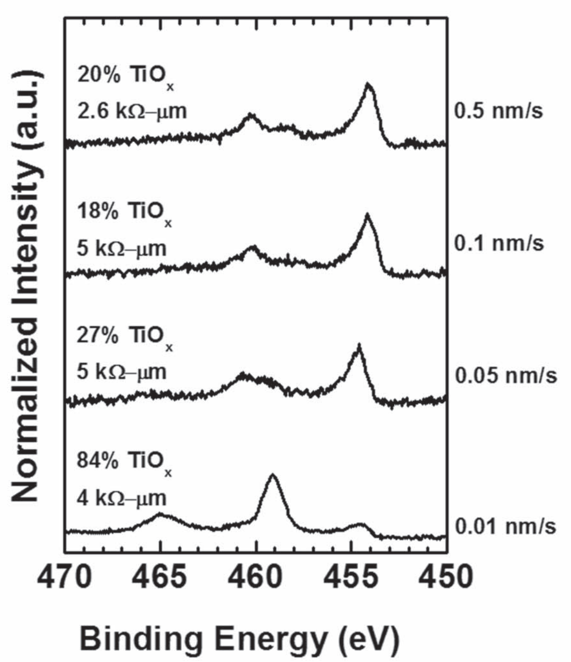


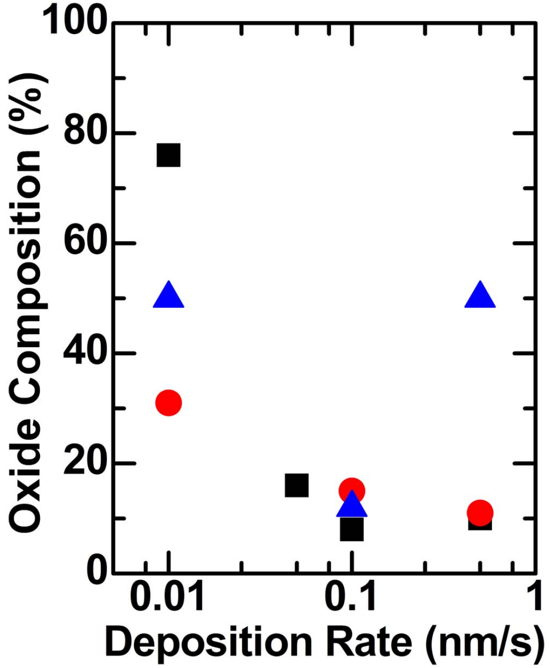
Nano Letters **12**, 590 (2012)

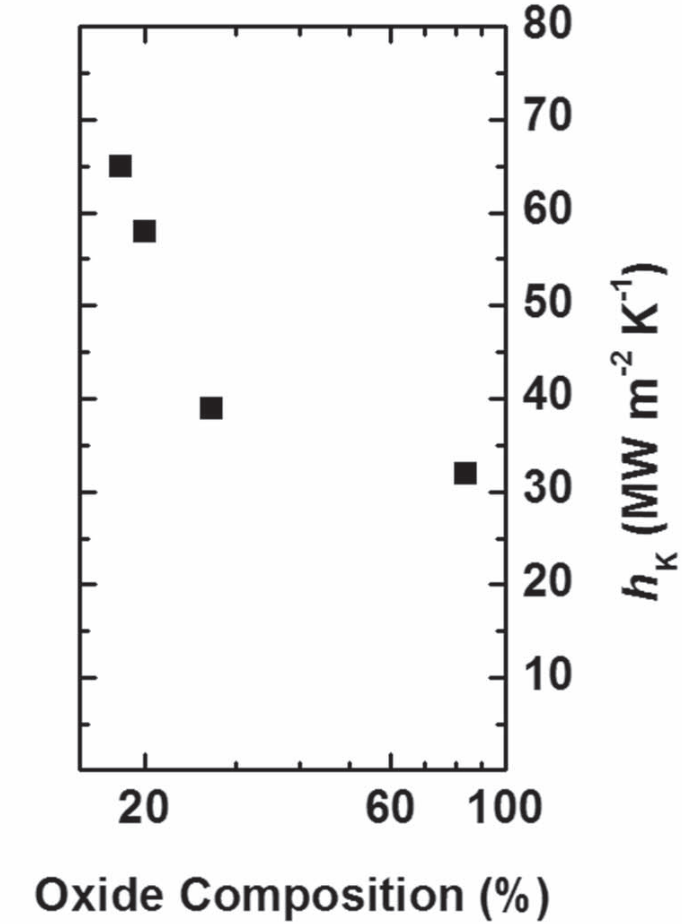
Collaboration Dr. Scott Walton (NRL)

Metal stoichiometry effects on TBC at graphene contacts





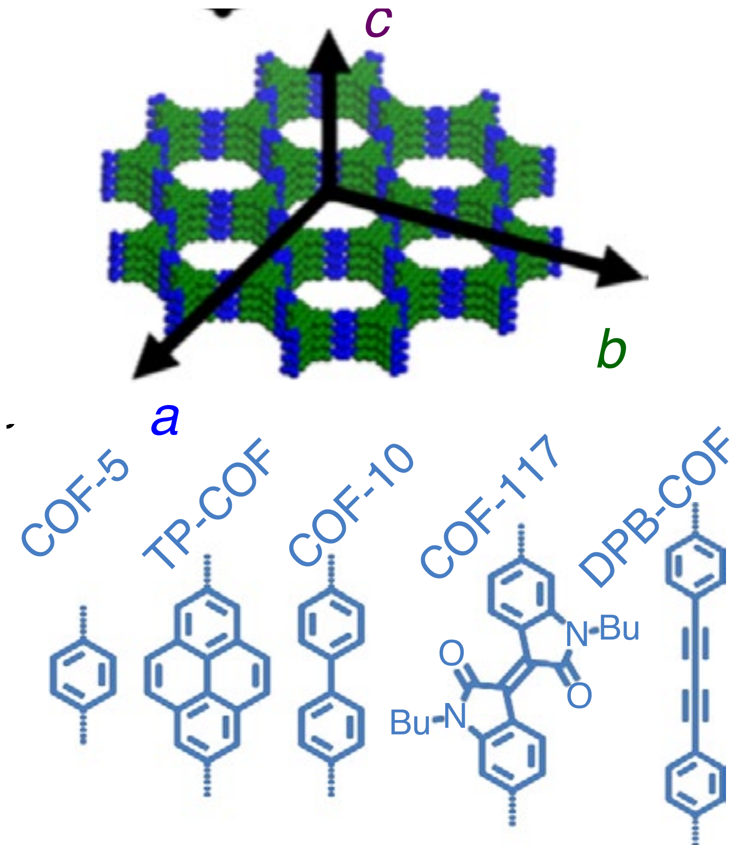


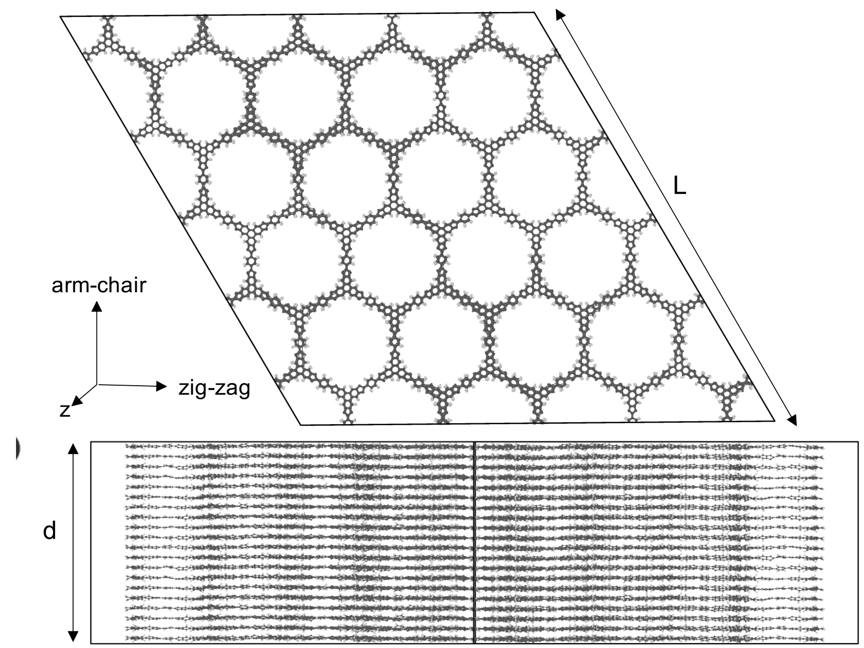


Nanotechnology **29**, 145201 (2018)
Collaboration: Prof. Stephen McDonnell

Covalent organic frameworks (COFs)

Highly porous structure offer low *k*, with strong covalent bonds and light masses



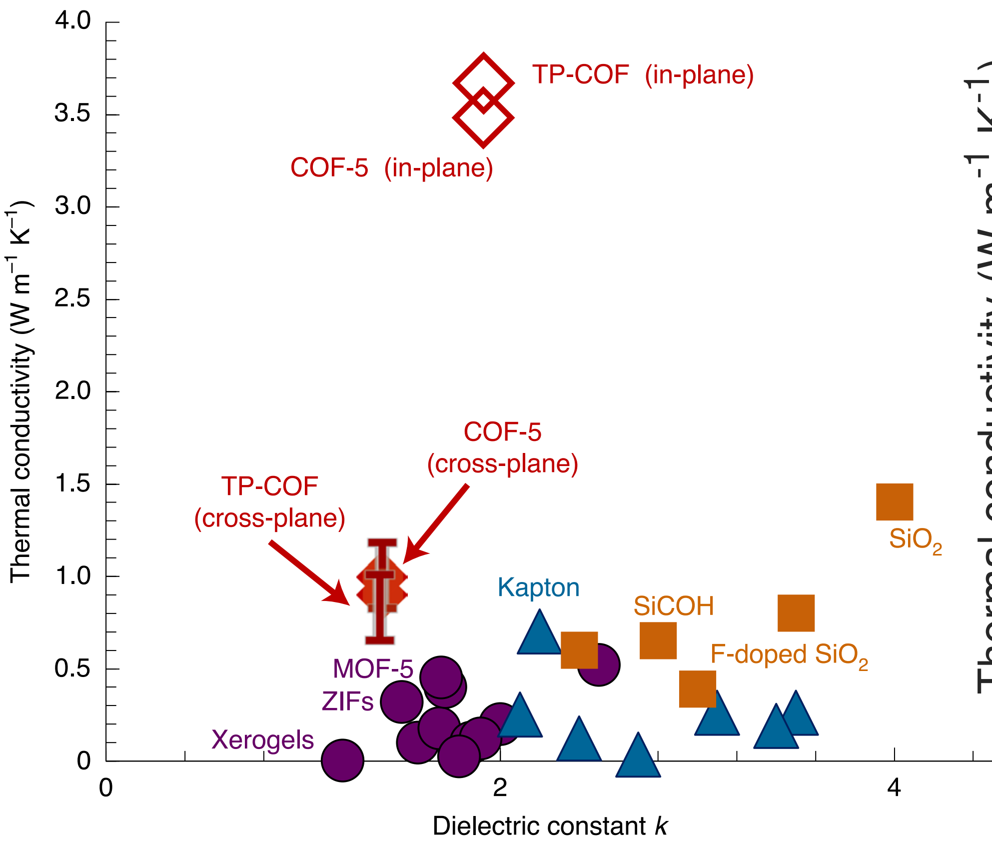


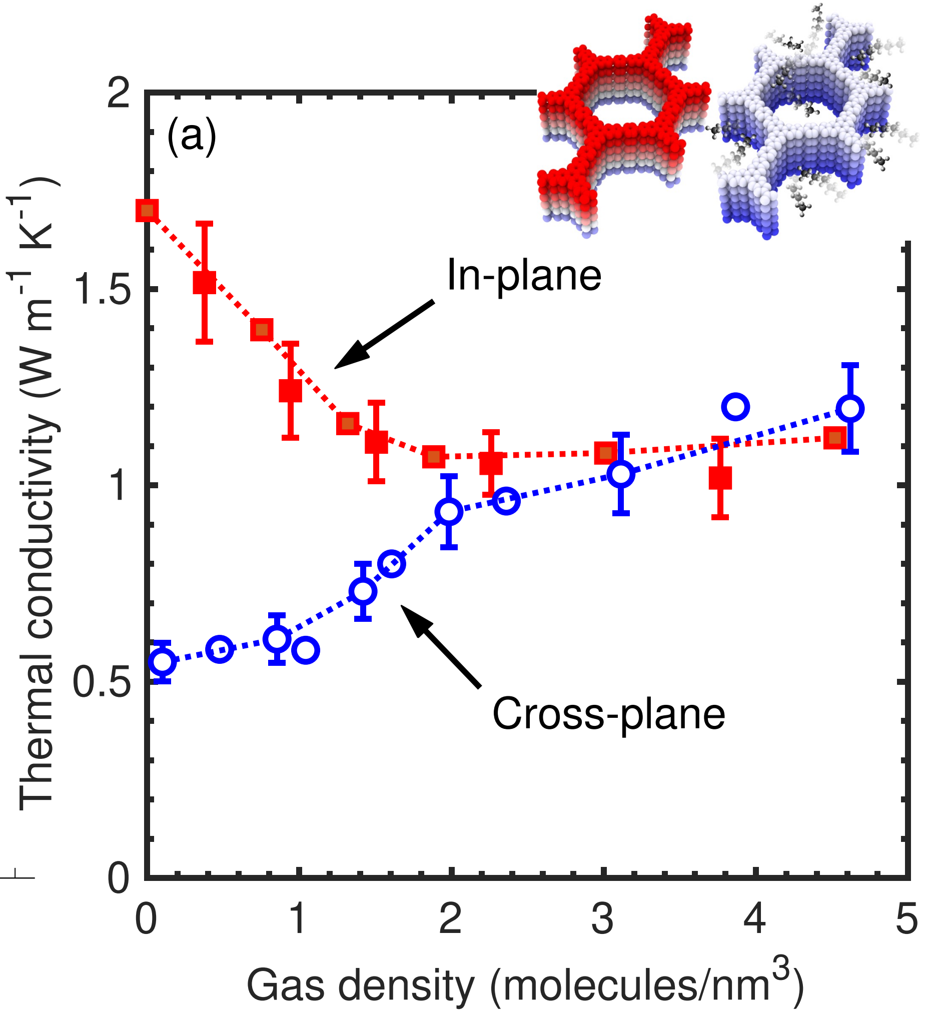
Collaboration: Prof. Will Dichtel (NW) and Prof. Ash Giri (U. Rhode Island)

Nat. Mat. **20**, 1142 (2021); *Nano Lett* **21**, 6188 (2021)

ACS Nano **16**, 2843 (2022); *JPCC to appear*

Increased thermal conductivity, low dielectric constant, functional tuning based on gas adsorption





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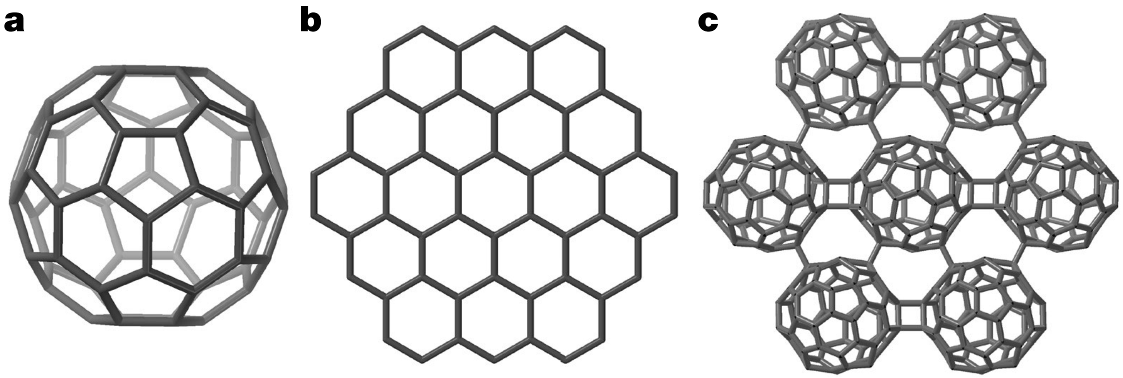
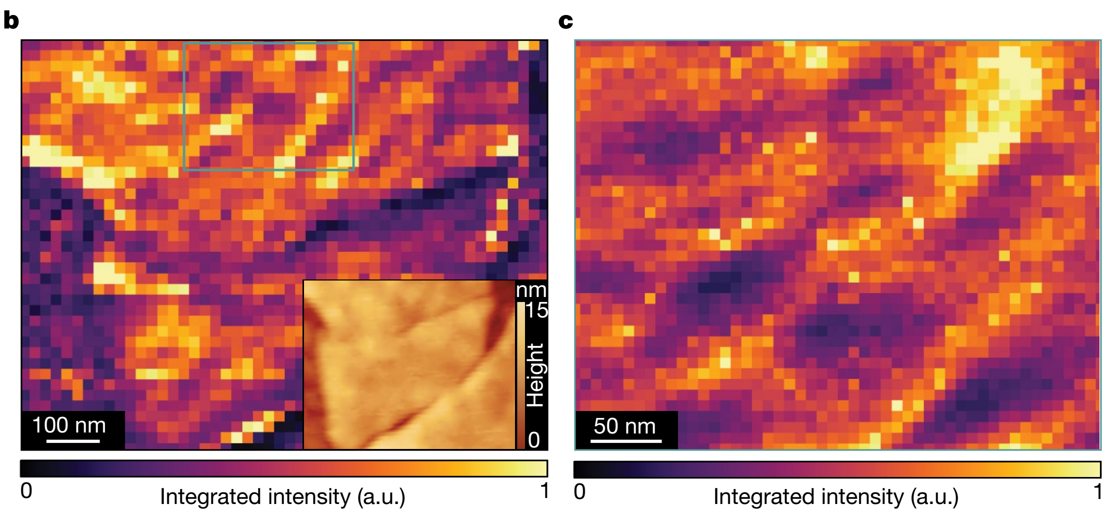
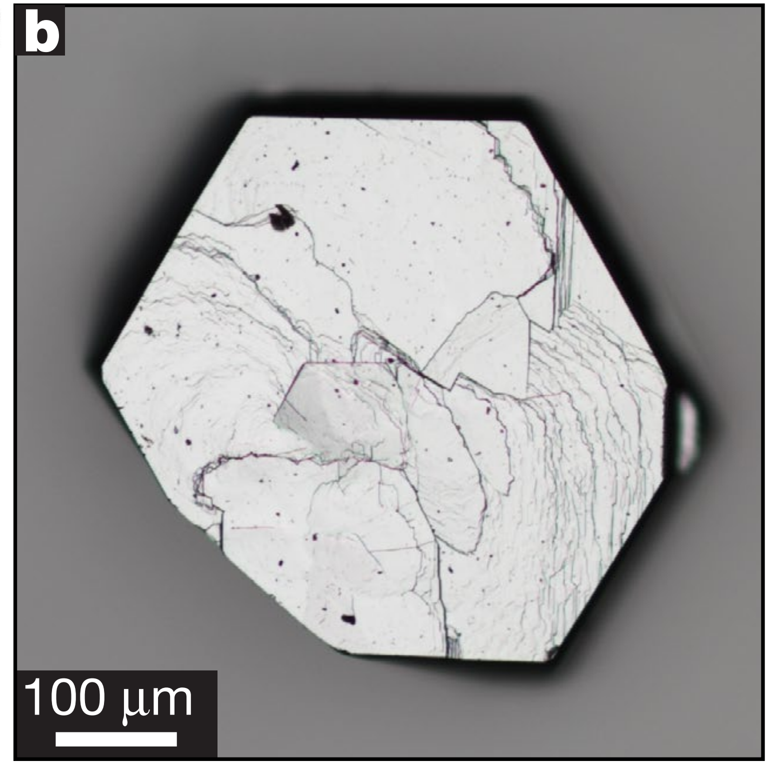
Graphullerene: a two-dimensional crystalline polymer of C_{60}







Nature **613**, 71 (2023)

Elena Meirzadeh[1✉], Austin M. Evans[1,2], Mehdi Rezaee[3], Milena Milich[4], Connor J. Dionne[5], Thomas P. Darlington[6], Si Tong Bao[1], Amymarie K. Bartholomew[1], Taketo Handa[1], Daniel J. Rizzo[7], Ren A. Wiscons[8], Mahniz Reza[9], Amirali Zangiabadi[10], Natalie Fardian-Melamed[6], Andrew C. Crowther[9], P. James Schuck[6], D. N. Basov[7], Xiaoyang Zhu[1], Ashutosh Giri[5], Patrick E. Hopkins[4,11,12], Philip Kim[13], Michael L. Steigerwald[1✉], Jingjing Yang[1✉], Colin Nuckolls[1✉] & Xavier Roy[1✉]

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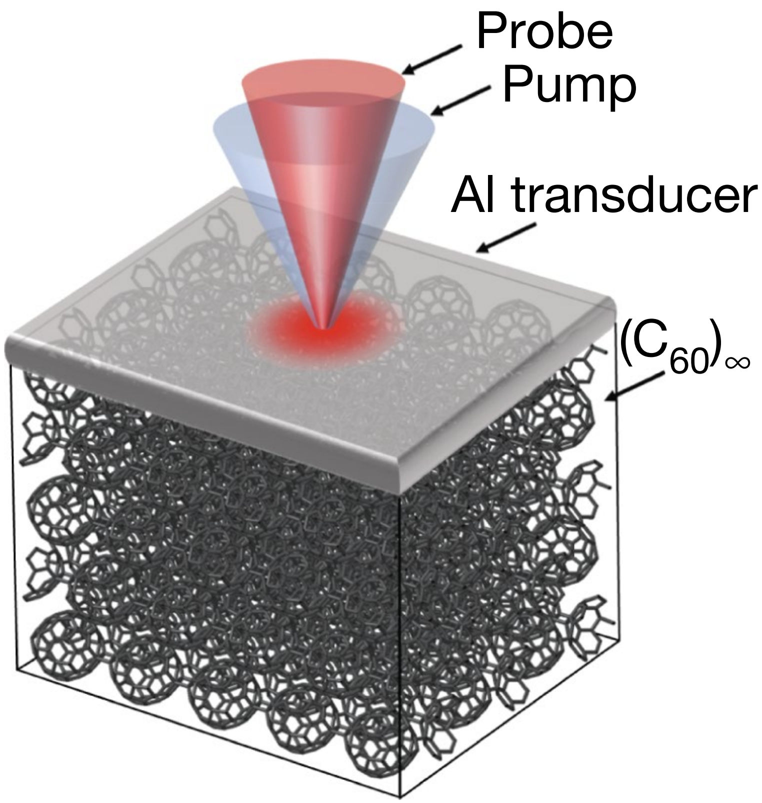

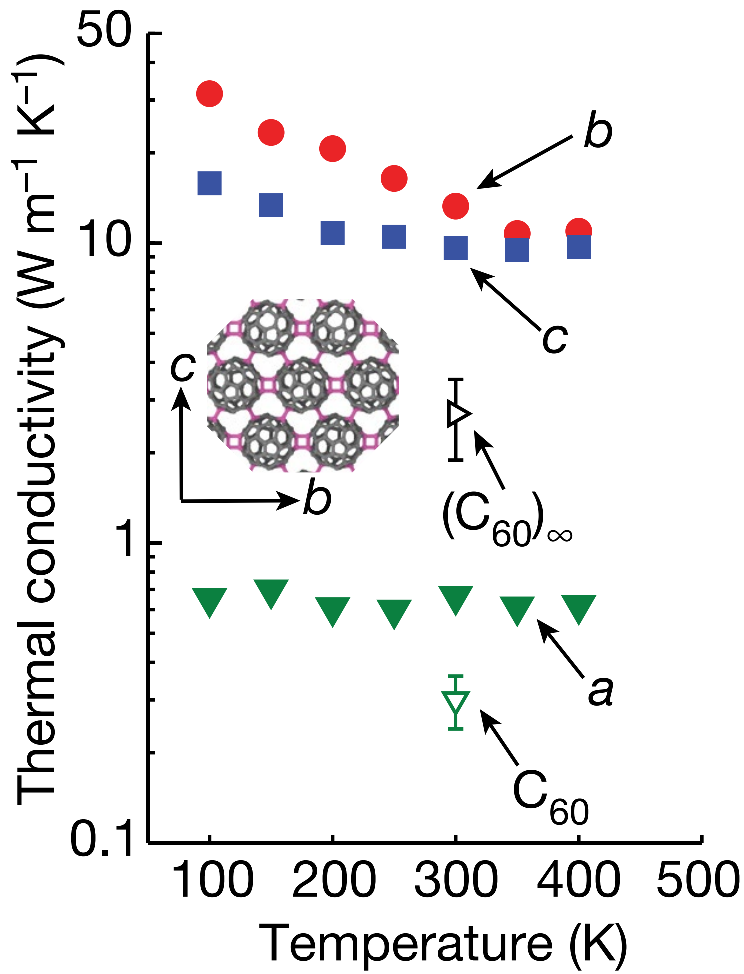

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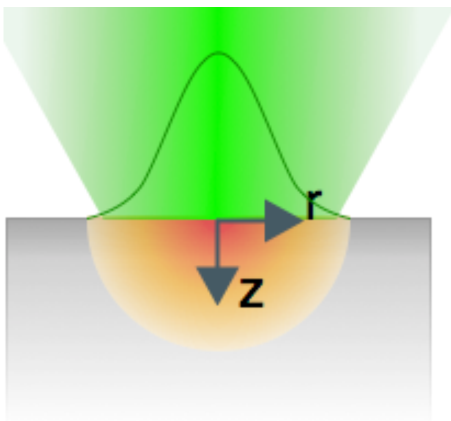
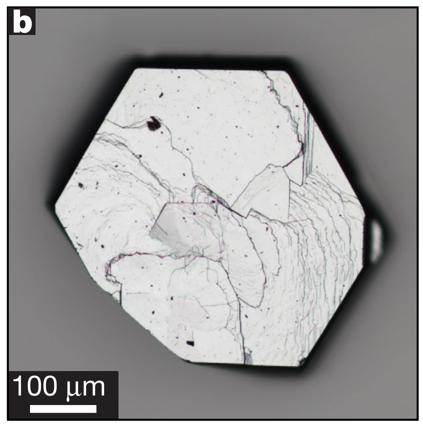
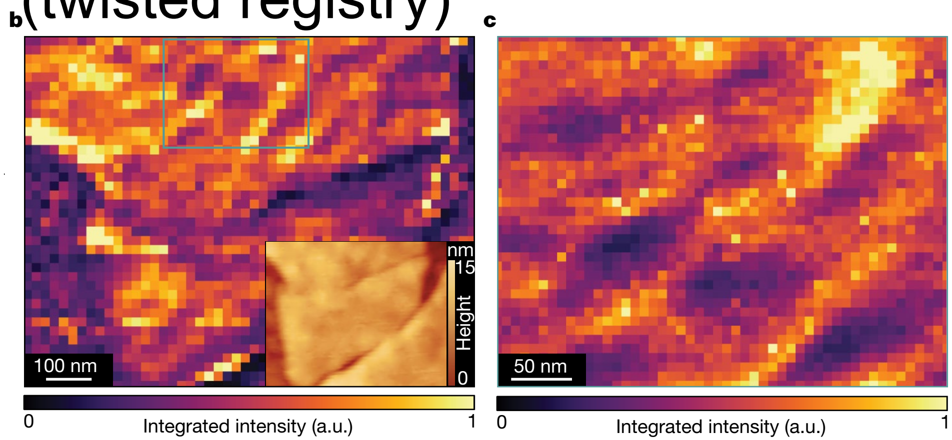
But what are we measuring?

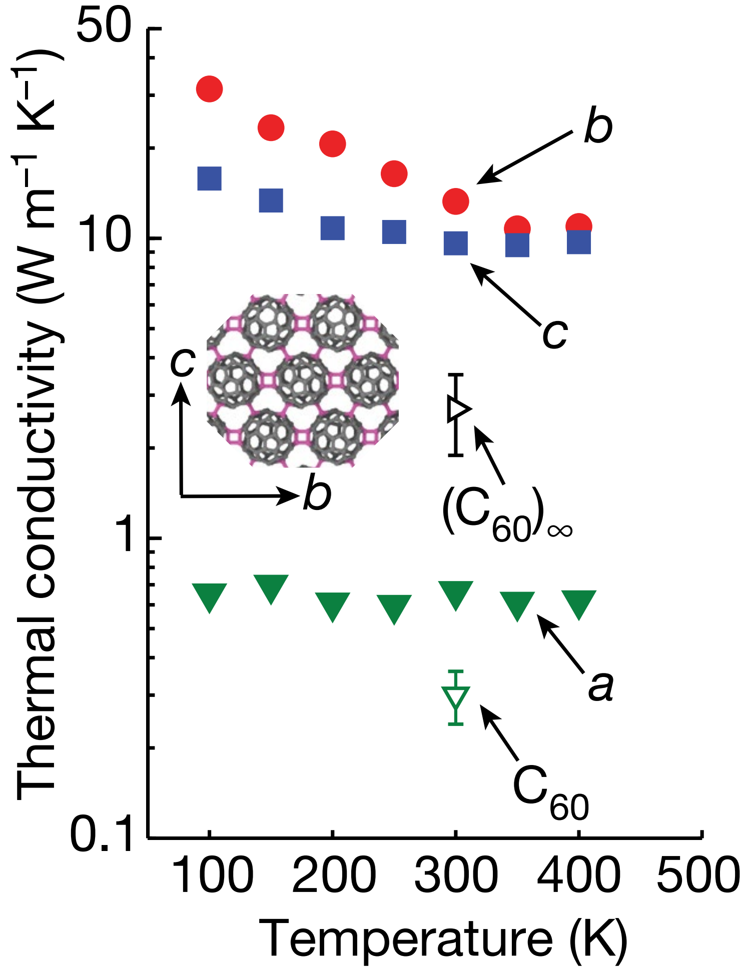
$$\text{radius} \approx 2\,\mu\text{m}$$





Nano-PL: note linear domains (twisted registry)

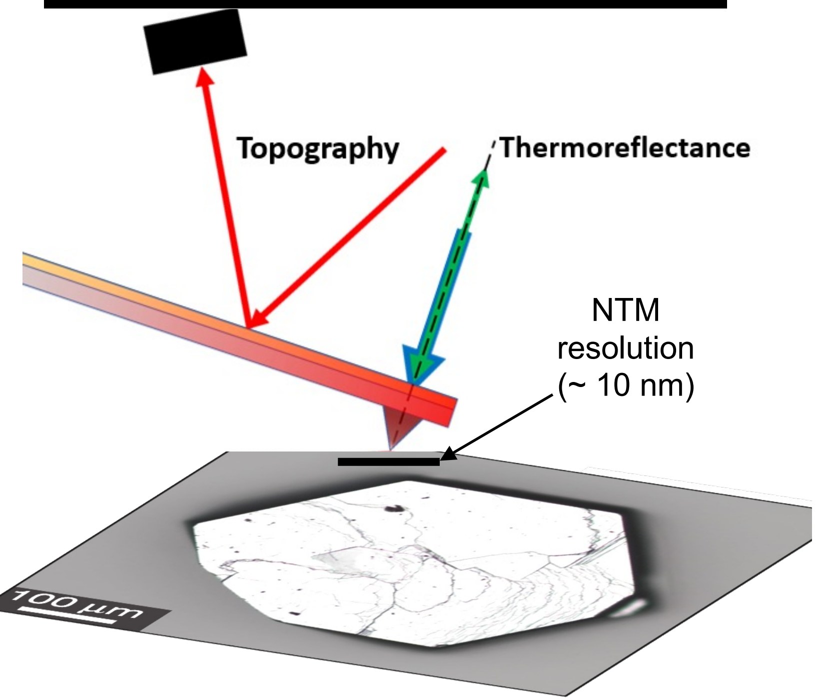




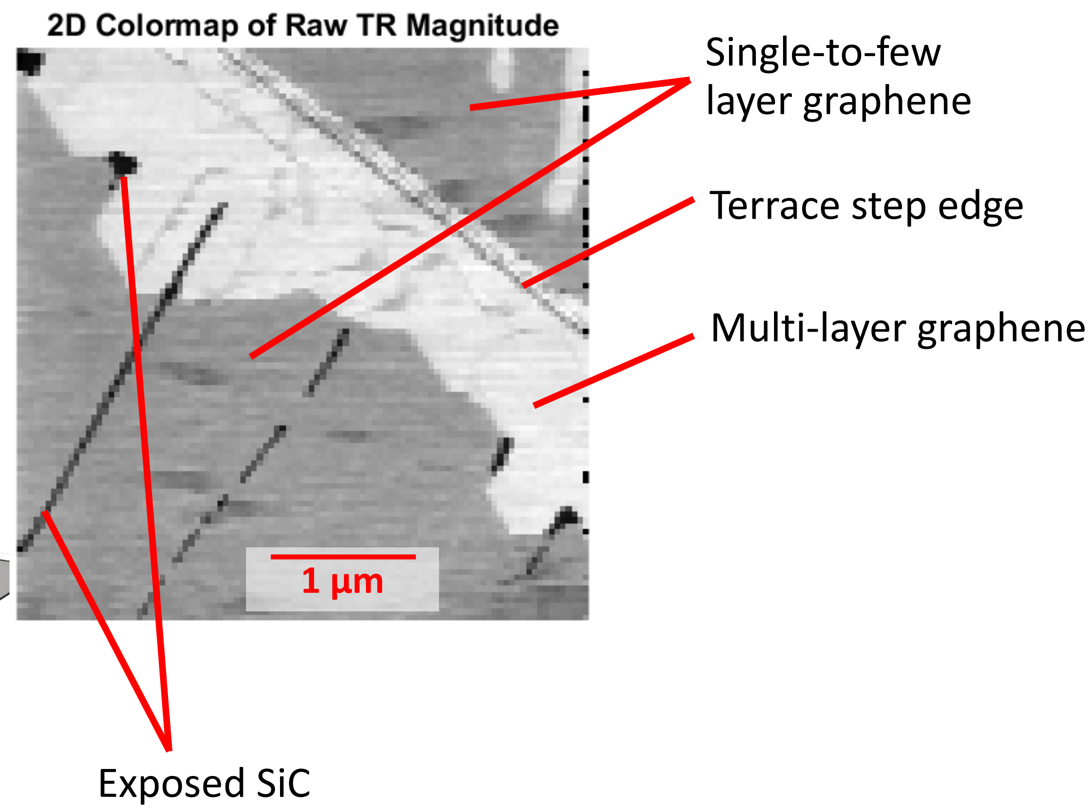
$$\kappa_{\text{measure}} = \sqrt{\kappa_z \kappa_r} \approx 2.6\,\text{W}\,\text{m}^{-1}\,\text{K}^{-1}$$

Resolving nanoscale thermal resistances: NTM

LASER THERMAL



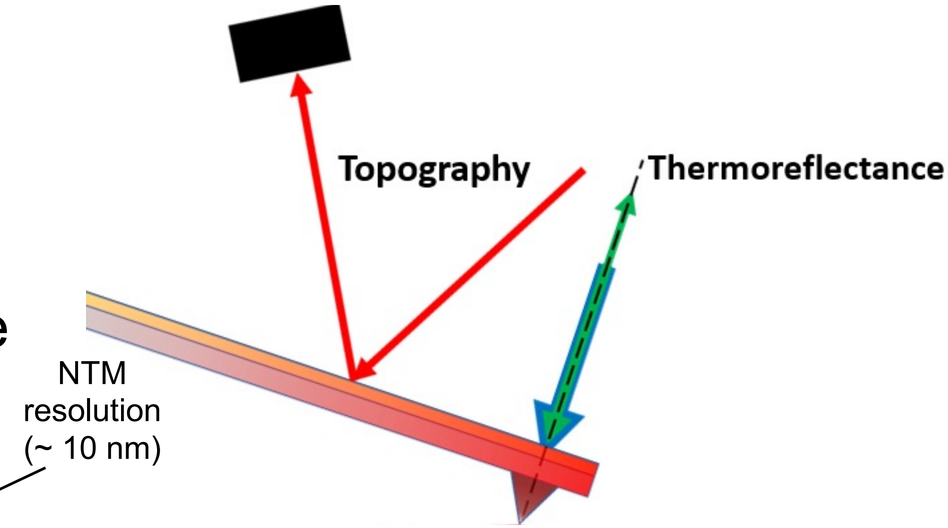
Nanoscale thermal microscope ("NTM")
"Beta version" in lab at UVA

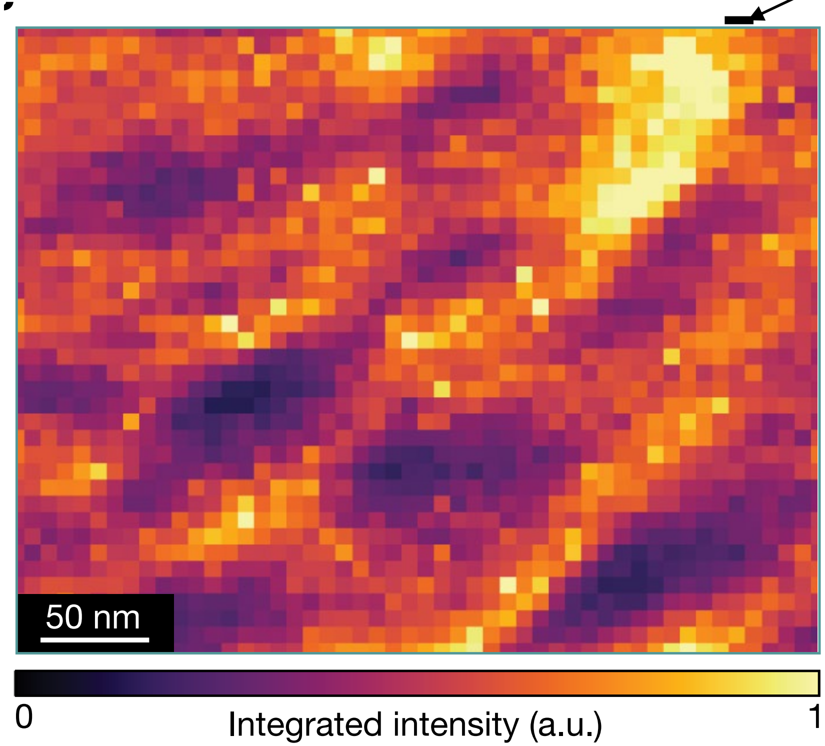


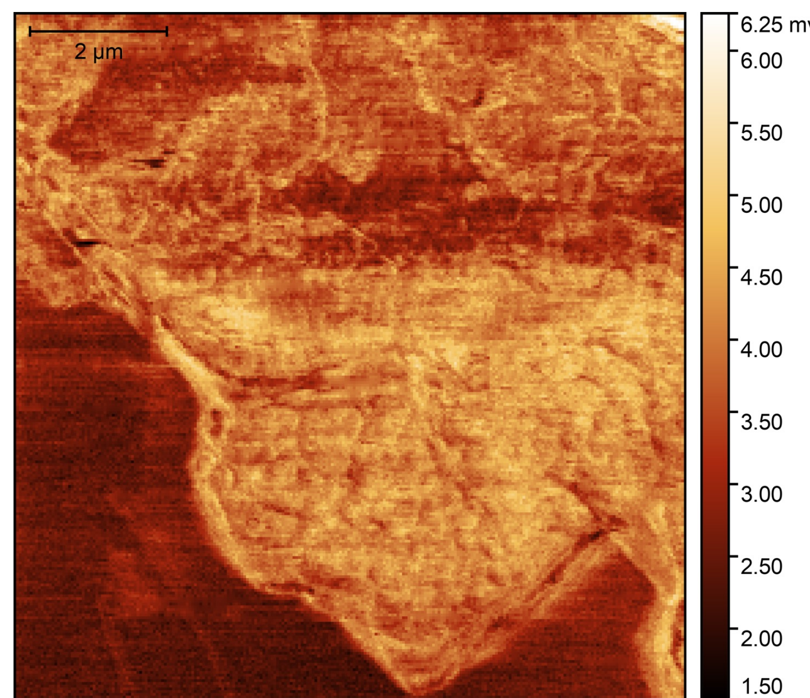
Disclosure: Hopkins co-Founder of LT, Inc.

Nanoscale thermal resistance changes in graphullerene

- NTM enables thermal conductivity map with ~10 nm resolution
- Resolving spatial changes in thermal resistance changes due to twisting of graphullerene “sheets” observed in nano-PL

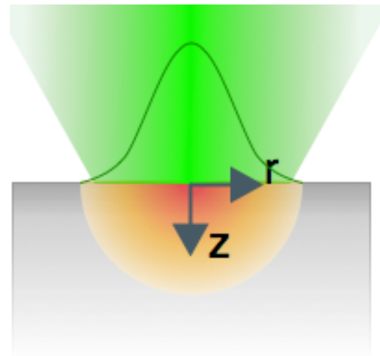


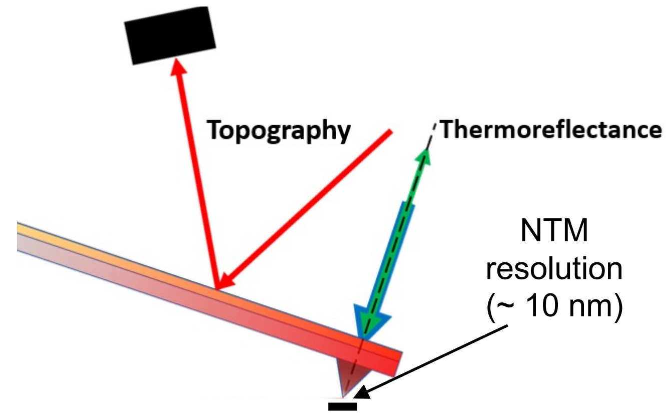




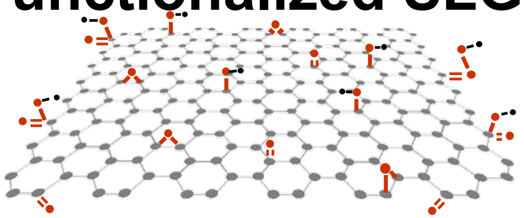
Bonding in graphene and low-D carbon leads to enhanced thermal properties

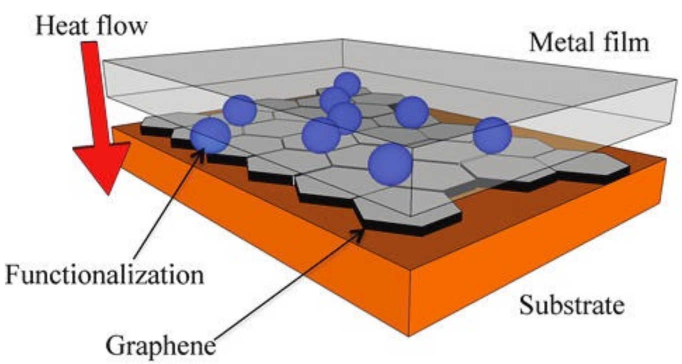
ONR support under Dr. Mark Spector



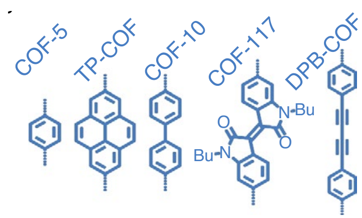


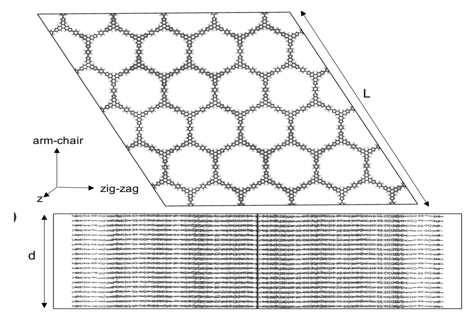
Functionalized SLG



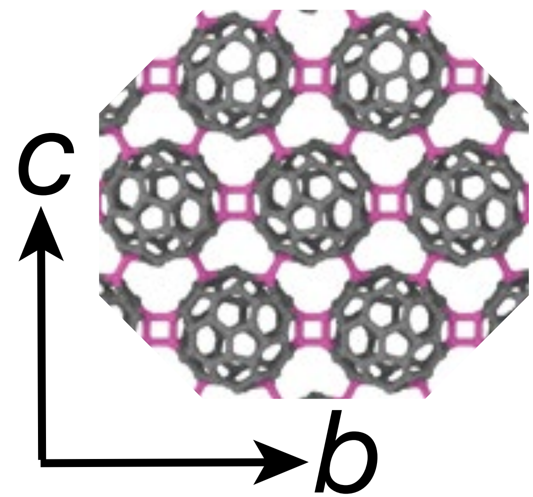


COFs





Graphullerene



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