Thermal Transport in Graphene and other Two-Dimensional Systems

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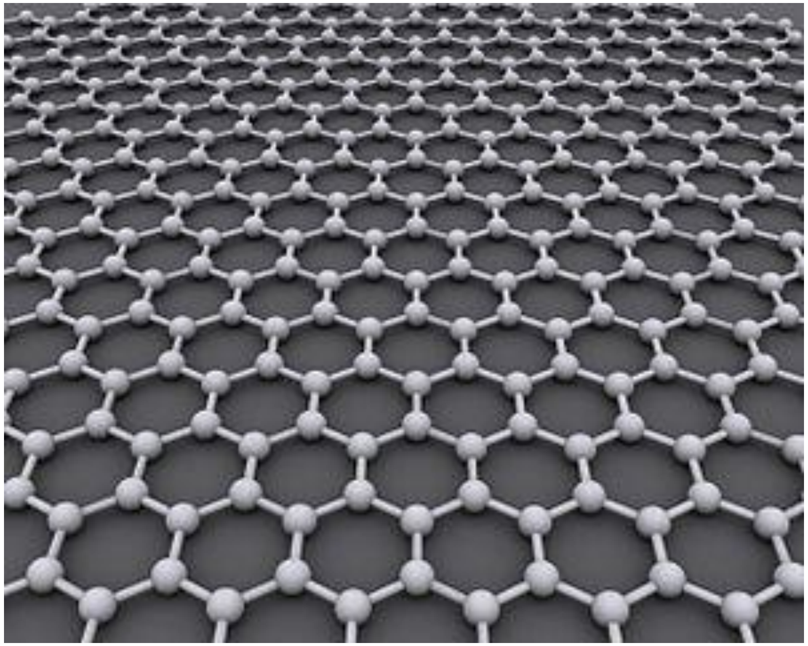
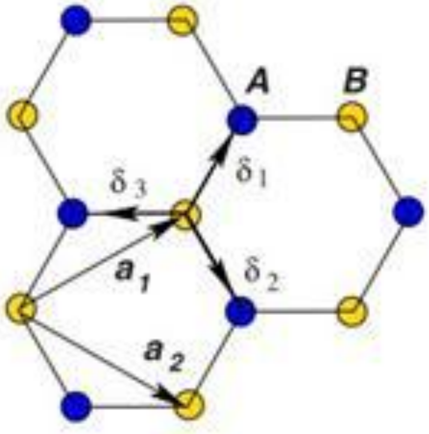
AT AUSTIN

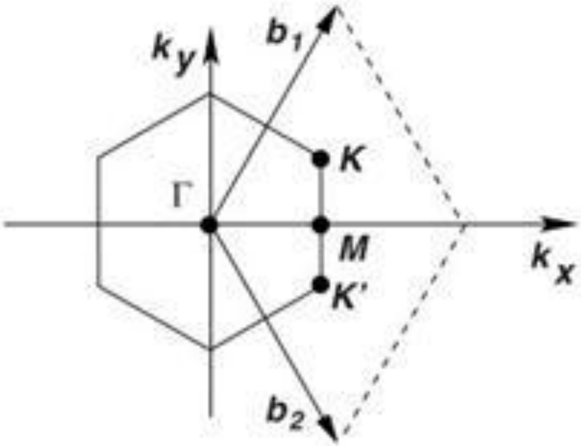
Outline

- Thermal Transport Theories and Simulations of Graphene
- Raman Measurements of Thermal Transport in Graphene
- Thermal Conductance Measurements of Graphene with Micro-devices
- Thermal Interface Conductance of Graphene
- Thermal Transport in Graphene Foam and Ultrathin Graphite Foam
- Thermal Transport in Few-Layer Hexagonal Boron Nitride

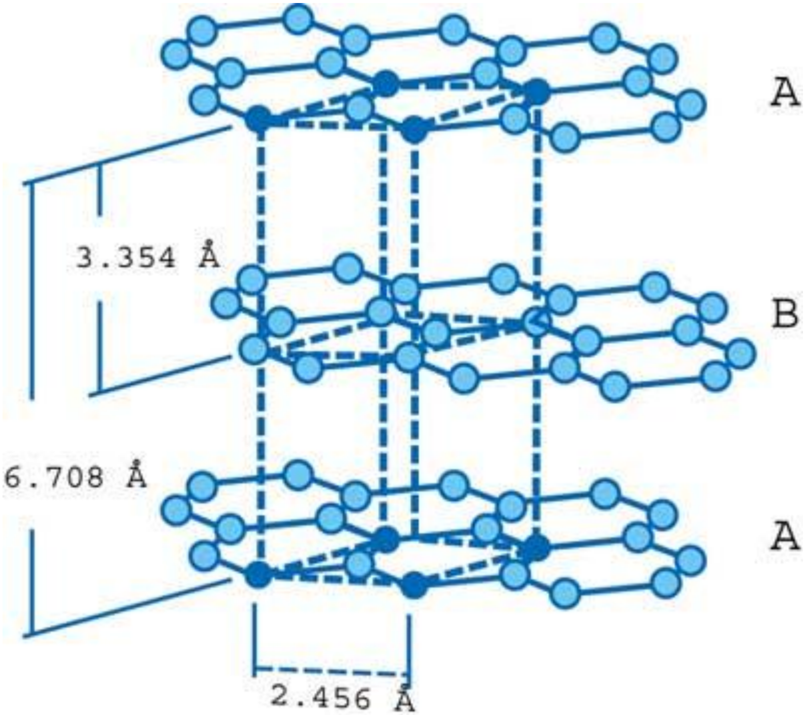
Graphene

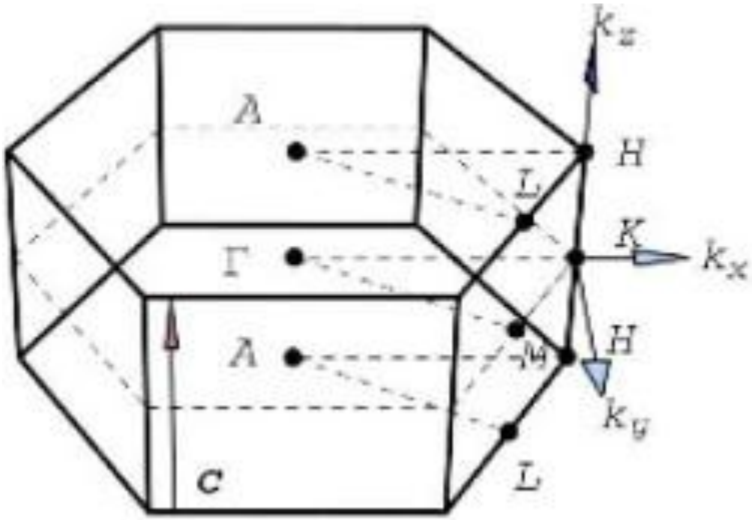




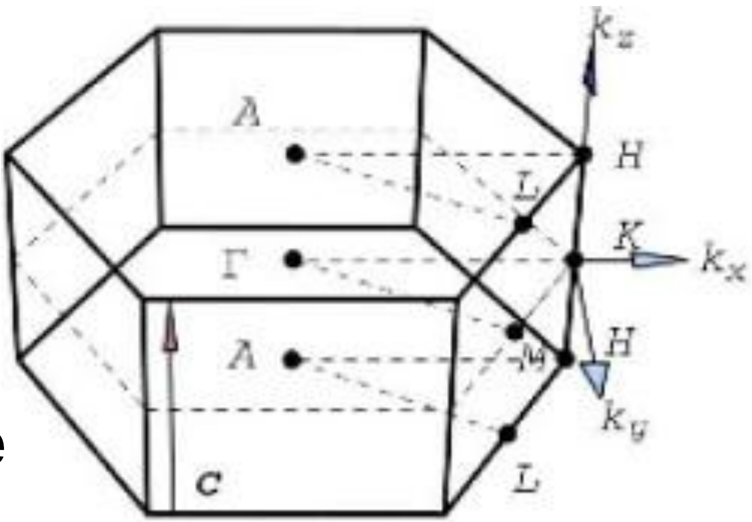


Graphite

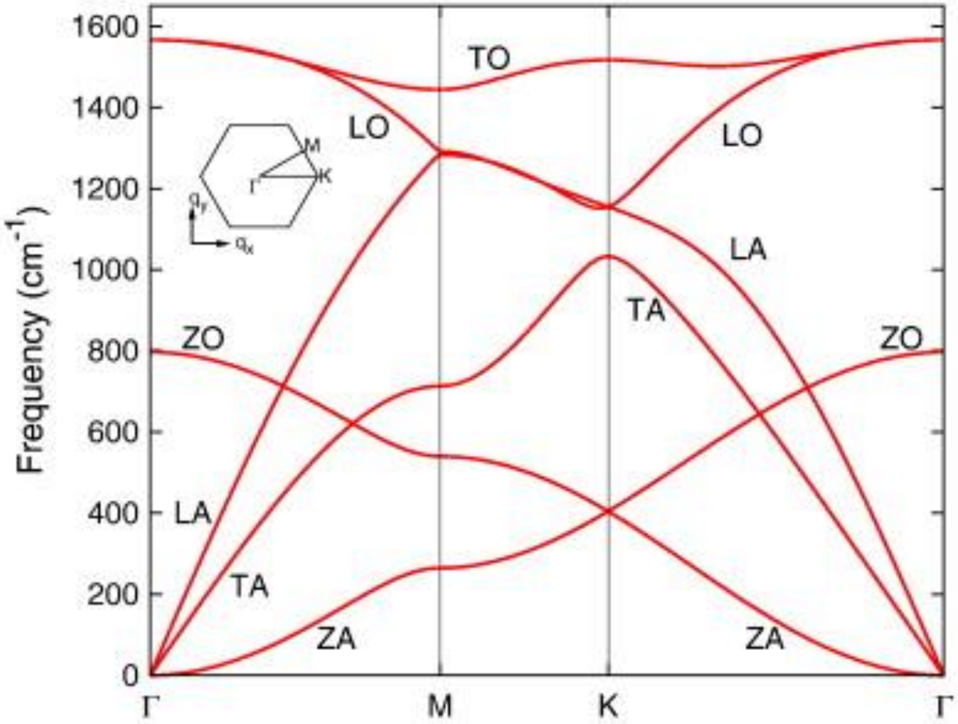




Phonon Dispersion



Graphene



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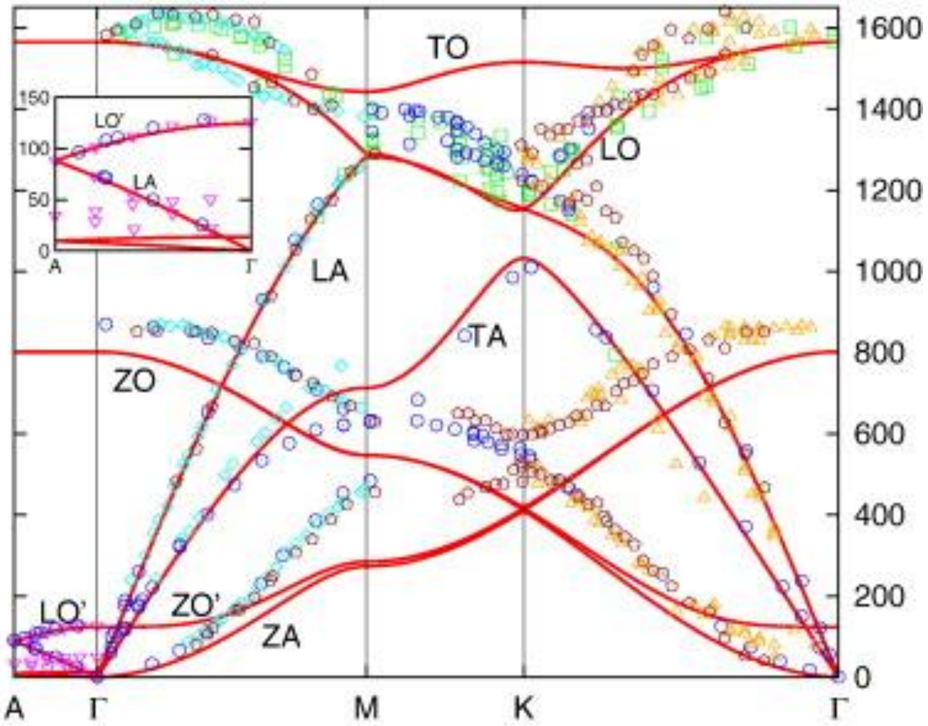
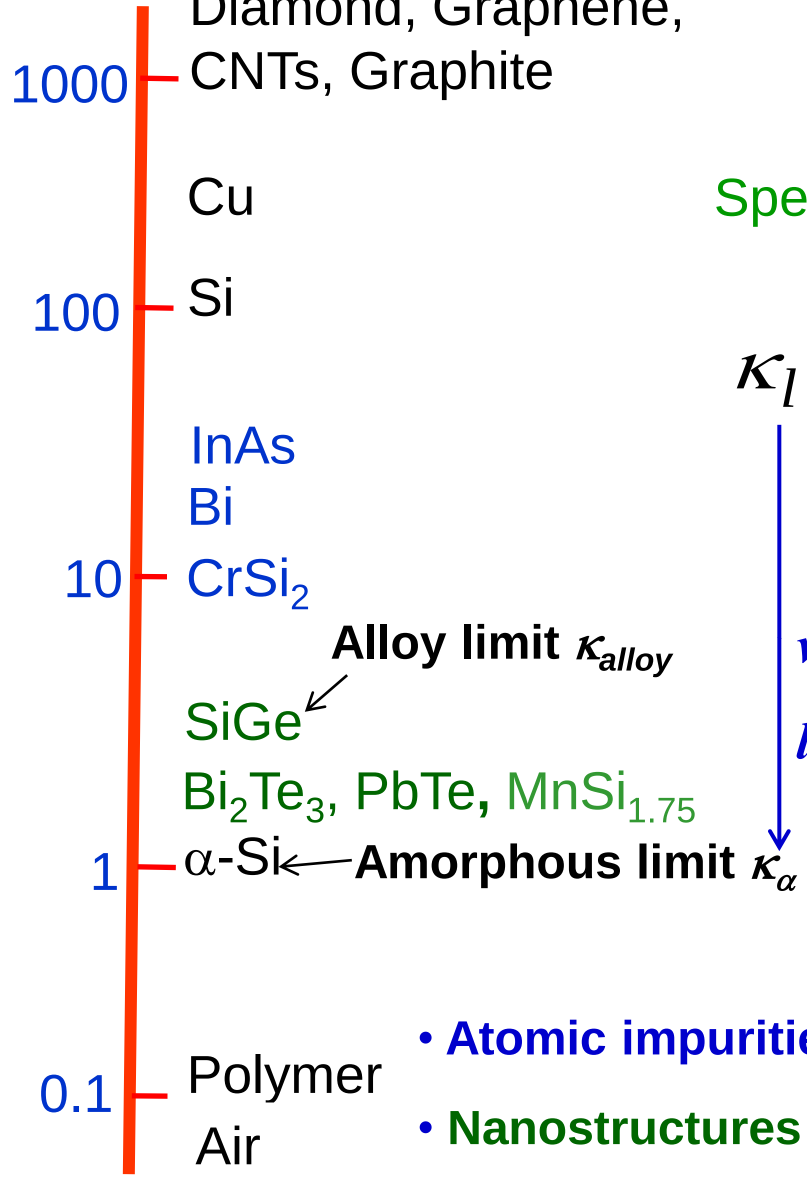


Karssemeijer and Fasolino, Surface Science 605, 1611 (2011)

Thermal Conductivity

κ (W/m-K) @ 300 K



$$\kappa = \kappa_l + \kappa_e$$

Lattice or Phonons

Electronic

Spectral specific heat

Wavelength

$$\kappa_l = \sum_i \int_{\lambda_{\min,i}}^{\lambda_{\max,i}} C_i(\lambda) v_{z,i}(\lambda) l_i(\lambda) d\lambda$$

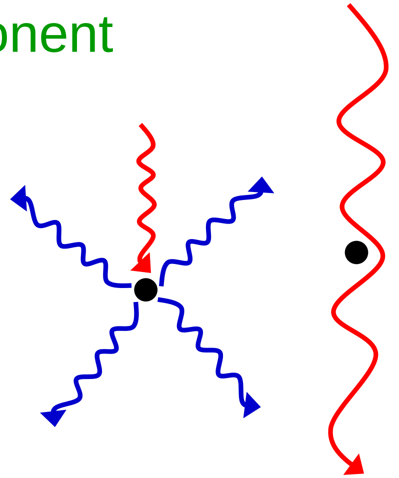
Polarizations

Group velocity component

M.F.P.

$v_{x,i}(\lambda)$ = speed of sound

$l_i(\lambda) = \lambda/2$

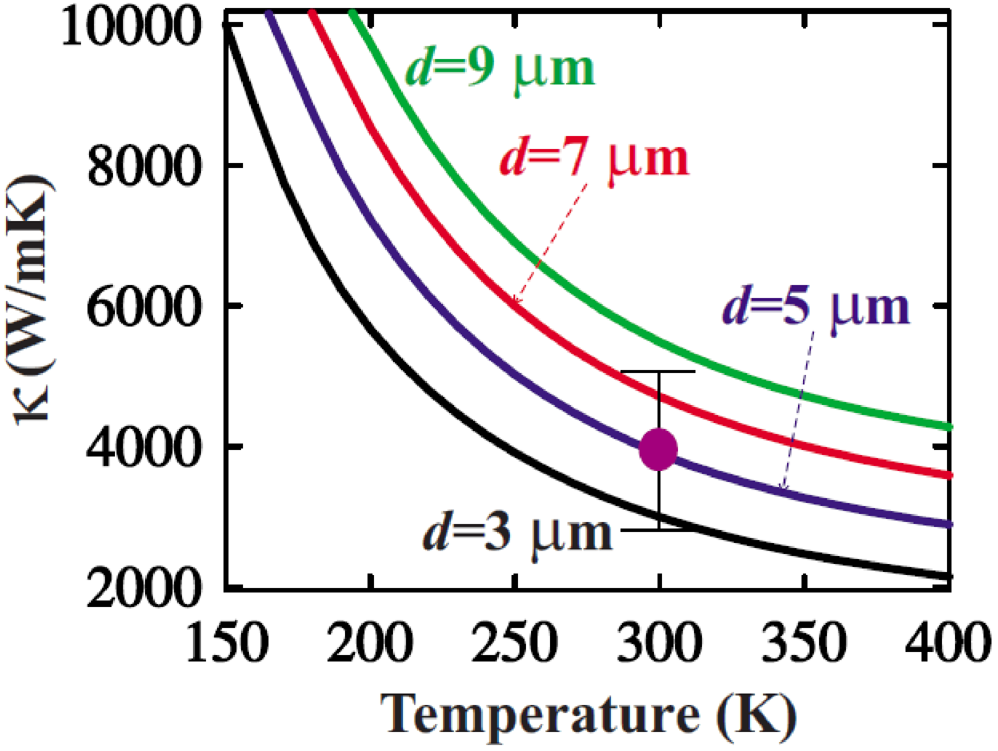


- **Atomic impurities scatter only short-λ phonons.**
- **Nanostructures scatter long-λ wave.**

PHYSICAL REVIEW B **79**, 155413 (2009)

Phonon thermal conduction in graphene: Role of Umklapp and edge roughness scattering

D. L. Nika,[1,2] E. P. Pokatilov,[1,2] A. S. Askerov,[2] and A. A. Balandin[1,3,*]

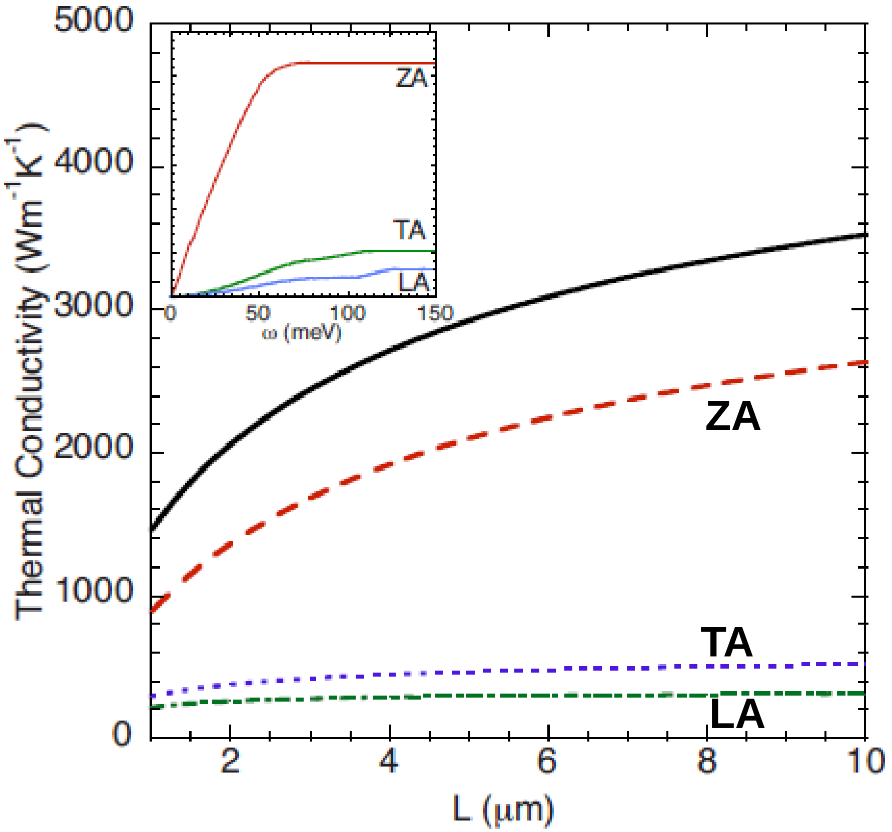


- Intrinsic thermal conductivity of 2D graphene increases with length.
- The contribution of the flexural (ZA) modes is negligible.

PHYSICAL REVIEW B **82**, 115427 (2010)

Flexural phonons and thermal transport in graphene

L. Lindsay,[1,2] D. A. Broido,[1] and Natalio Mingo[3,4]

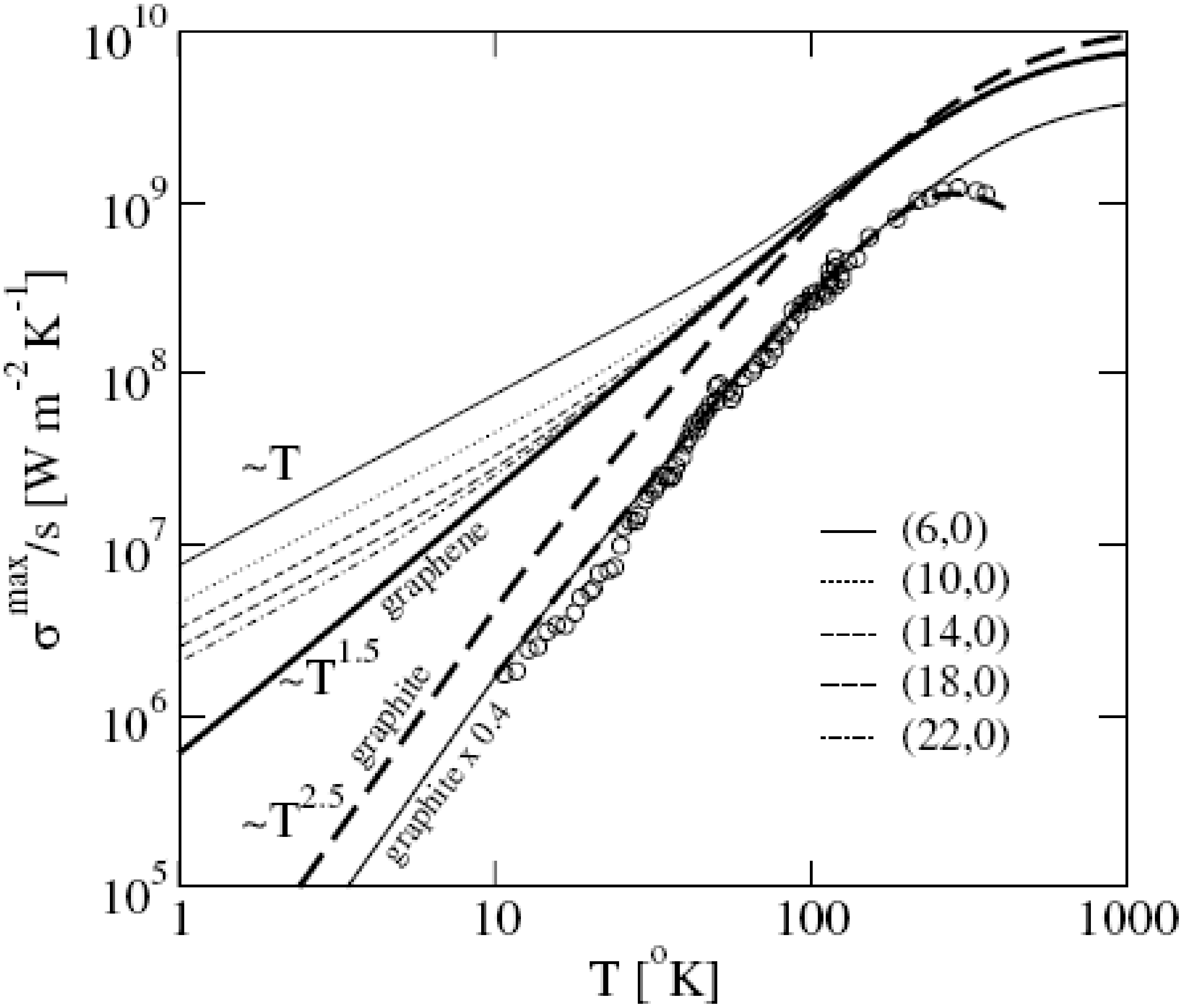


- The phase space for phonon-phonon scattering involving the ZA modes is restricted so that the ZA modes actually make the dominant contribution to the thermal conductivity of suspended graphene.

PRL **95,** 096105 (2005) PHYSICAL REVIEW LETTERS

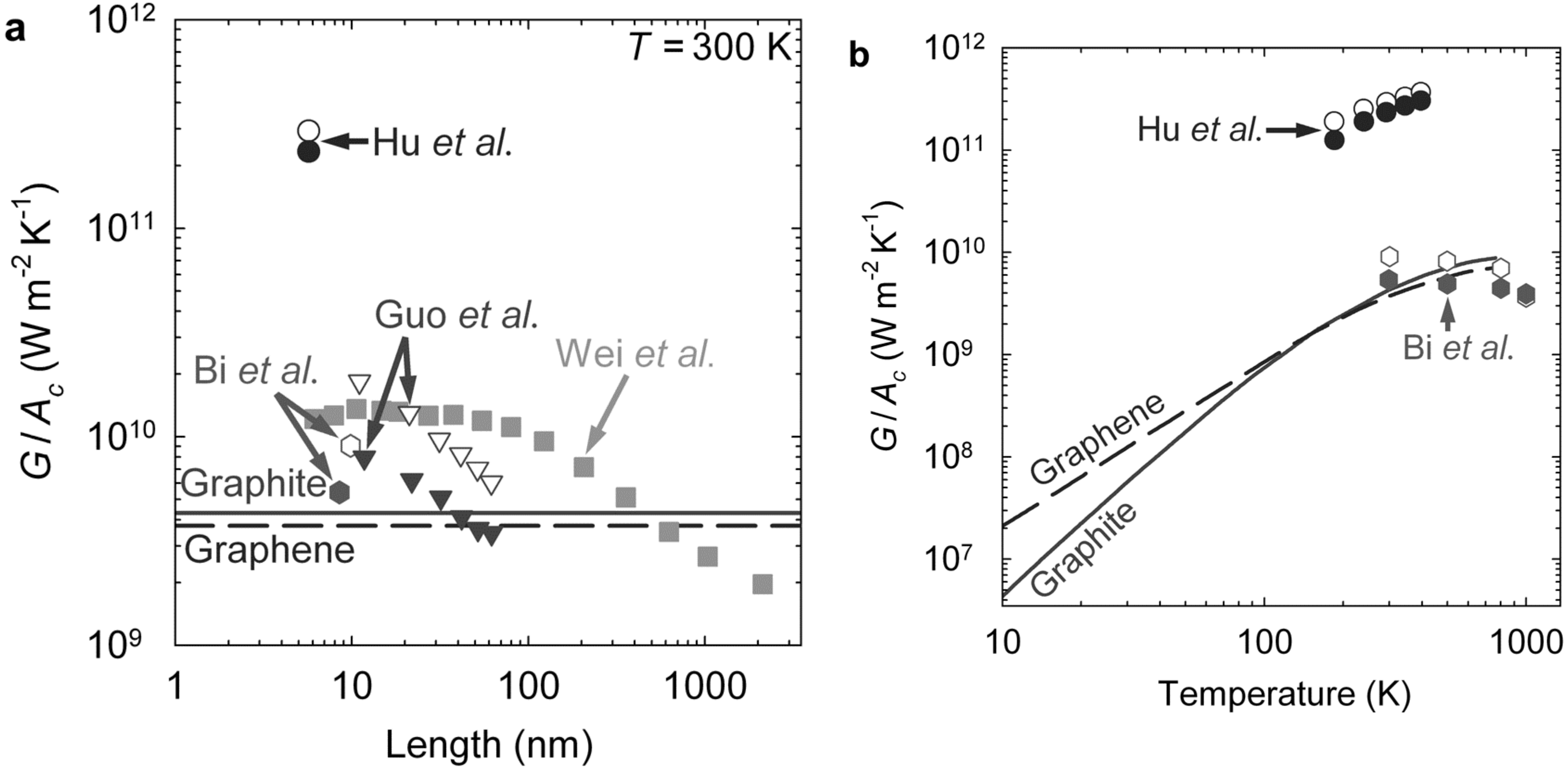
Carbon Nanotube Ballistic Thermal Conductance and Its Limits

N. Mingo[1] and D. A. Broido[2]



"This means that all the results in Refs. [8,9] for nanotubes shorter than 10^3 Å violate the quantum upper bounds. We attribute this to the fact that those are results from a classical molecular dynamics simulation, in which the quantum limits play no role."

Many MD simulation results exceed the ballistic thermal conductance limit of graphene.



M. M. Sadeghi, M. T. Pettes, L. Shi, Solid State Communications, DOI: 10.1016/j.ssc.2012.04.022 (2012)

Outline

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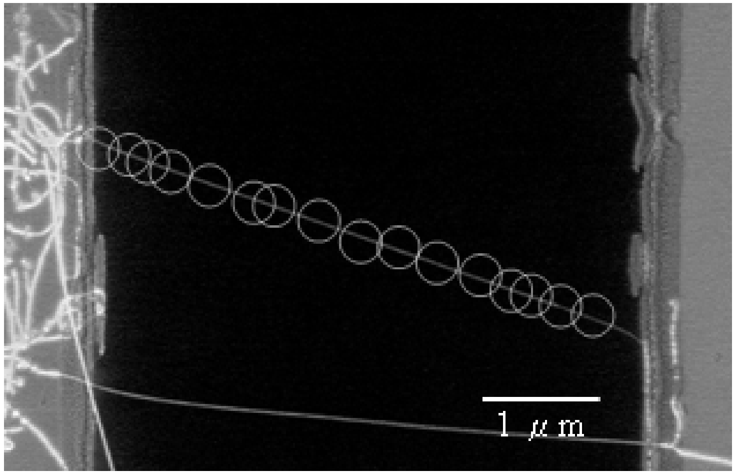
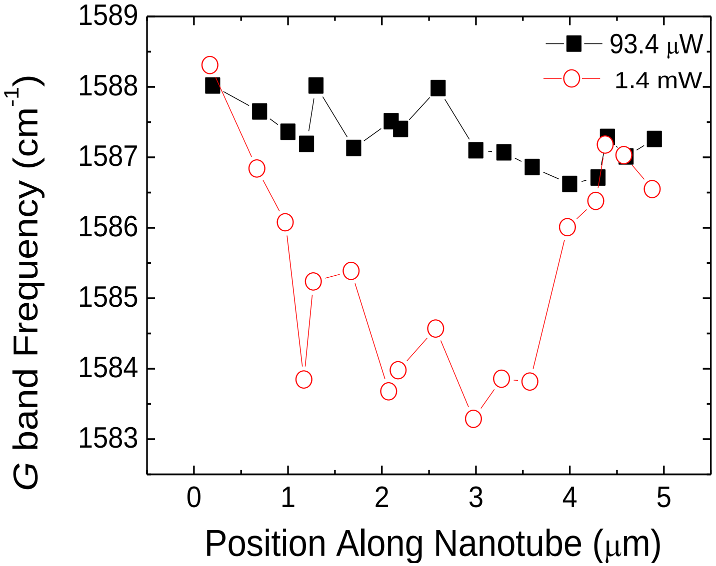
- **Raman Measurements of Thermal Transport in Graphene**
- **Thermal Conductance Measurements of Graphene with Micro-devices**
- **Thermal Interface Conductance of Graphene**
- **Thermal Transport in Graphene Foam and Ultrathin Graphite Foam**
- **Thermal Transport in Few-Layer Hexagonal Boron Nitride**

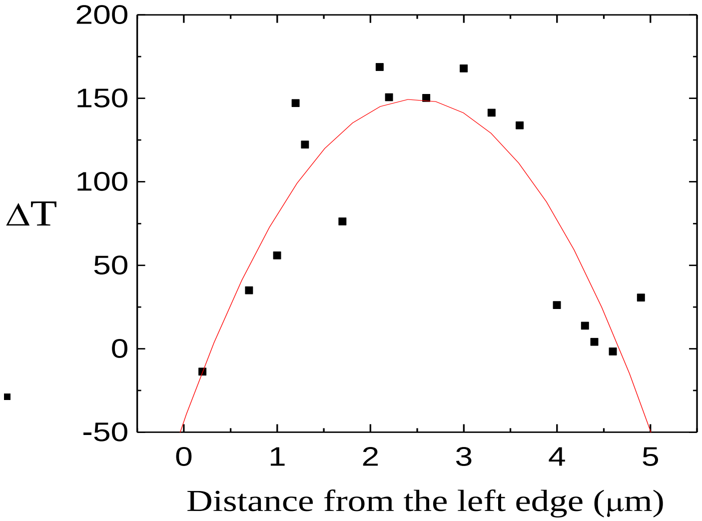
Raman Measurement of Thermal Transport in Carbon Nanotubes





- **Each circle corresponds to the position of the laser spot when spectra were taken at two different laser powers.**

- **Unknown optical absorbance**



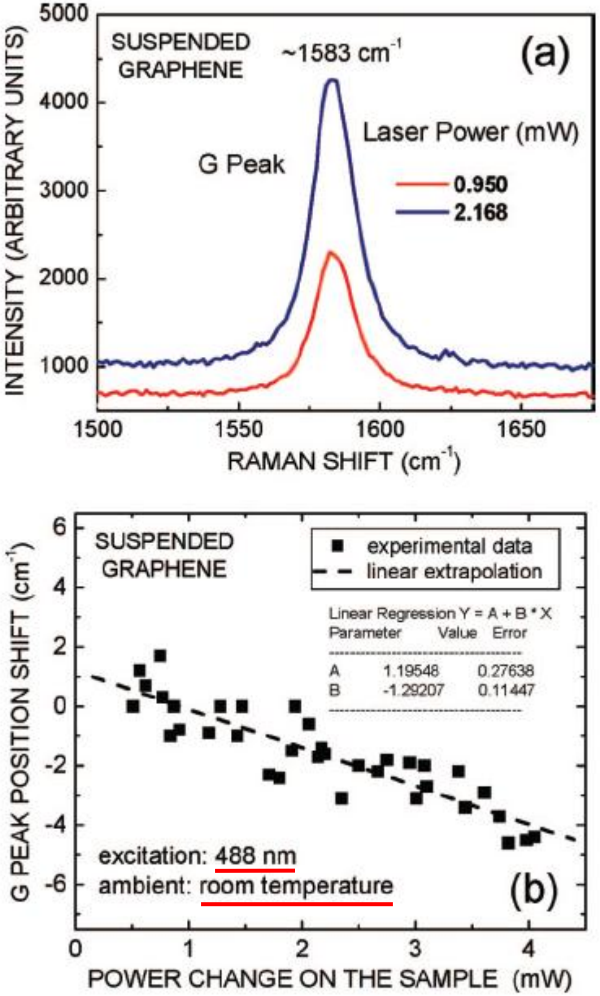
I-K. Hsu, R. Kumar, A. Bushmaker, S. B. Cronin, M. T. Pettes, L. Shi, T. Brintlinger, M. S. Fuhrer, J. Cumings, Appl. Phys. Lett. 92, 063119 (2008)

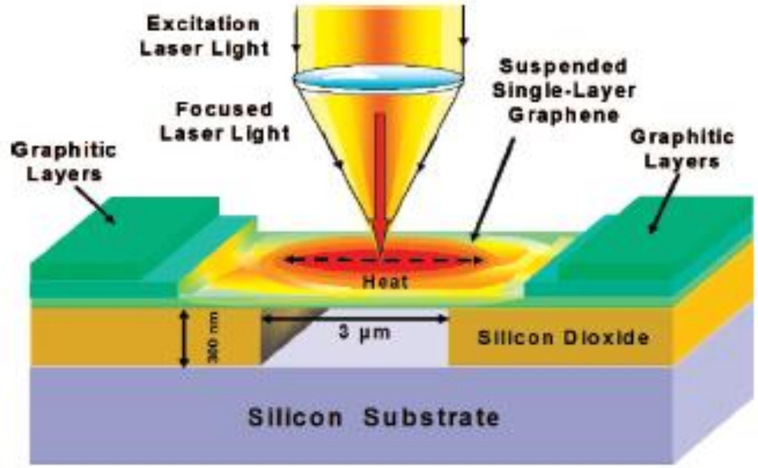
Superior Thermal Conductivity of Single-Layer Graphene

NANO LETTERS
2008
Vol. 8, No. 3
902-907

Alexander A. Balandin,[*,†,‡] Suchismita Ghosh,[†] Wenzhong Bao,[§] Irene Calizo,[†] Desalegne Teweldebrhan,[†] Feng Miao,[§] and Chun Ning Lau[§]

Received December 5, 2007; Revised Manuscript Received January 15, 2008





Thermal conductivity:

4840-5300 W/mK

Measurements:

- Raman G peak shift → temperature rise in graphene (>200 K)
- Raman G band intensity → Optical absorbance ≈ 9% per laser pass

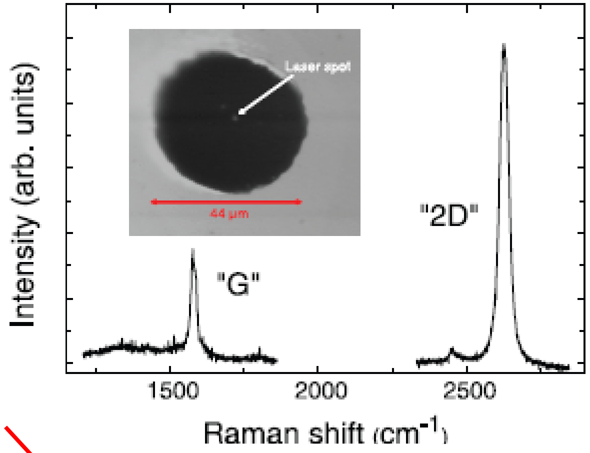
Assumptions:

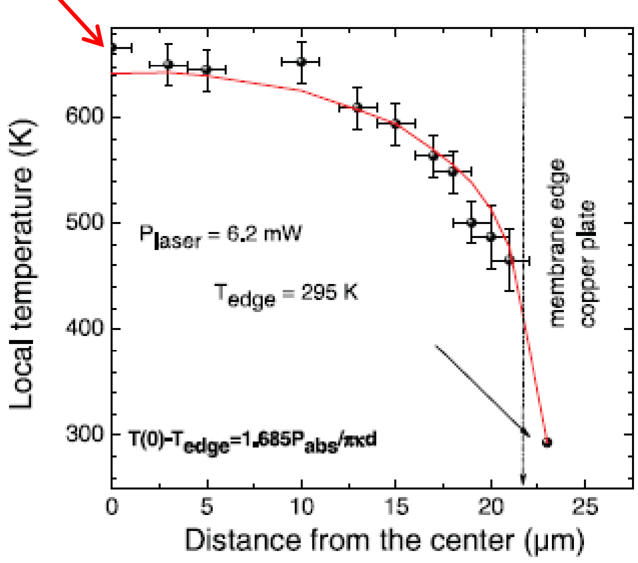
- Negligible heat transfer between graphene and the SiO_2 support
- Graphite layers ≈ perfect heat sinks
- Same thermal conductivity for suspended and supported graphene

VOL. 4 ▪ NO. 4 ▪ 1889–1892 ▪ 2010 ACSNANO

Thermal Conductivity of Graphene in Corbino Membrane Geometry

Clement Faugeras,[†,*] Blaise Faugeras,[‡] Milan Orlita,[†,⊥] M. Potemski,[†] Rahul R. Nair,[§] and A. K. Geim[§]



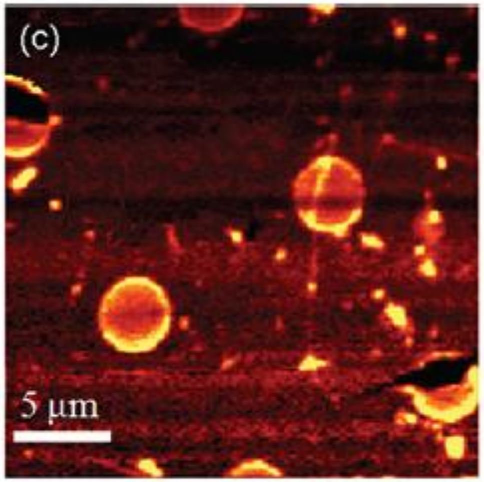


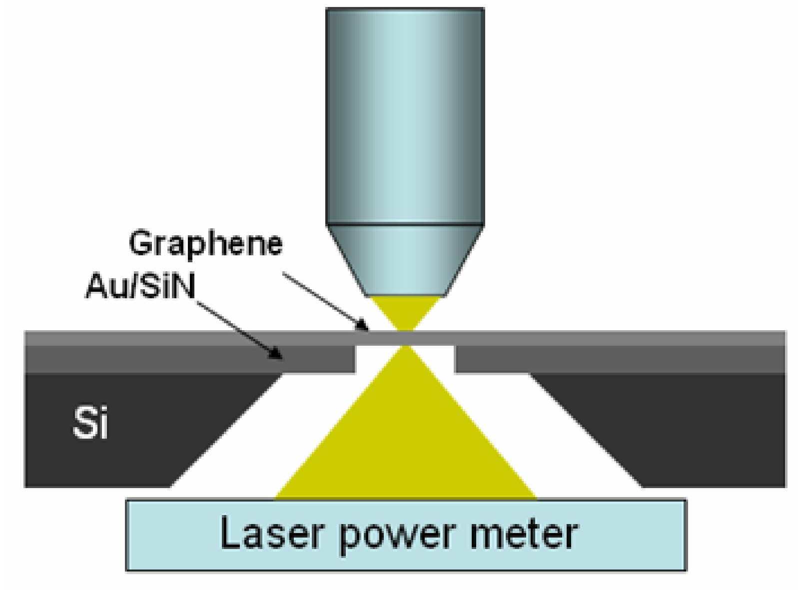
To conclude, we have used micro-Raman scattering experiments to study the room temperature heat conductivity of a large graphene membrane. We have deduced that graphene is a thermal conductor as good as graphite. The 3D equivalent thermal coefficient of graphene is $\kappa \approx 630$ W/(m · K), that is, somewhat smaller than the values previously reported.[3] The difference between the present and previous estimations of κ is mainly due to different assumptions regarding the efficiency of the graphene's optical absorbance.

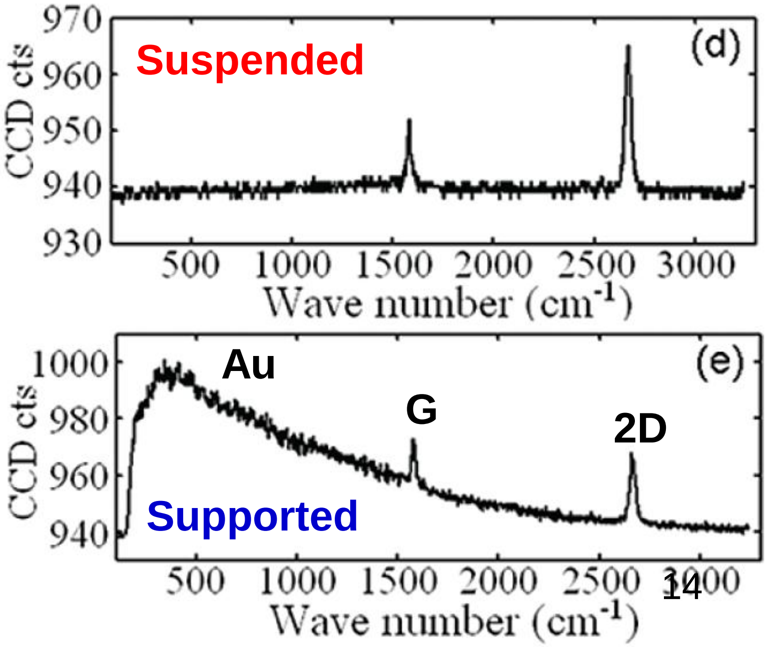
Nano Lett. **2010,** *10,* 1645–1651

Thermal Transport in Suspended and Supported Monolayer Graphene Grown by Chemical Vapor Deposition

Weiwei Cai,† Arden L. Moore,† Yanwu Zhu, Xuesong Li, Shanshan Chen, Li Shi,* and Rodney S. Ruoff*







Optical absorption:

~9% at 488 nm (Balandin, *Nano Lett.* 2008, 8, 902)

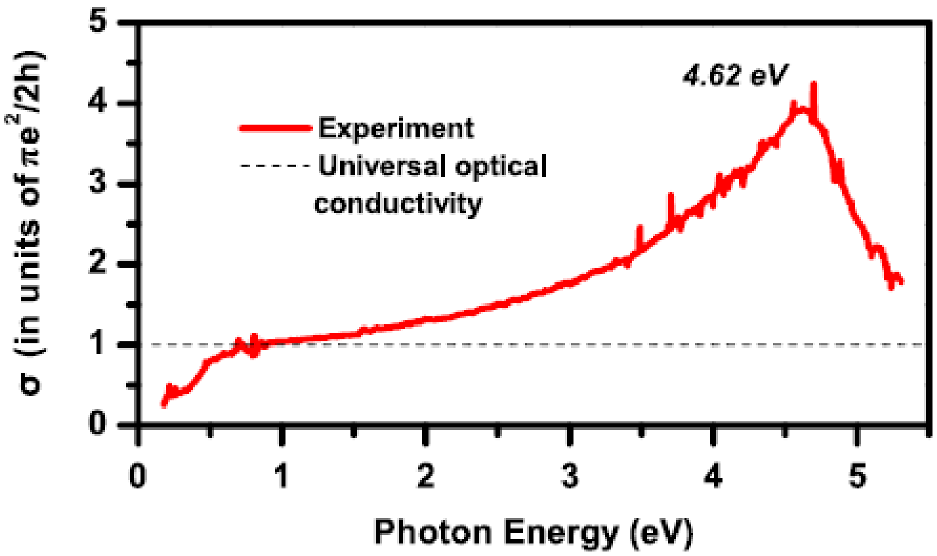
(2.3 ±0.1)% at 550 nm (Nair, *Science* 2008, 320, 1308)

(3.3±1.1)% at 532 nm (*this work*)

PRL **106,** 046401 (2011)

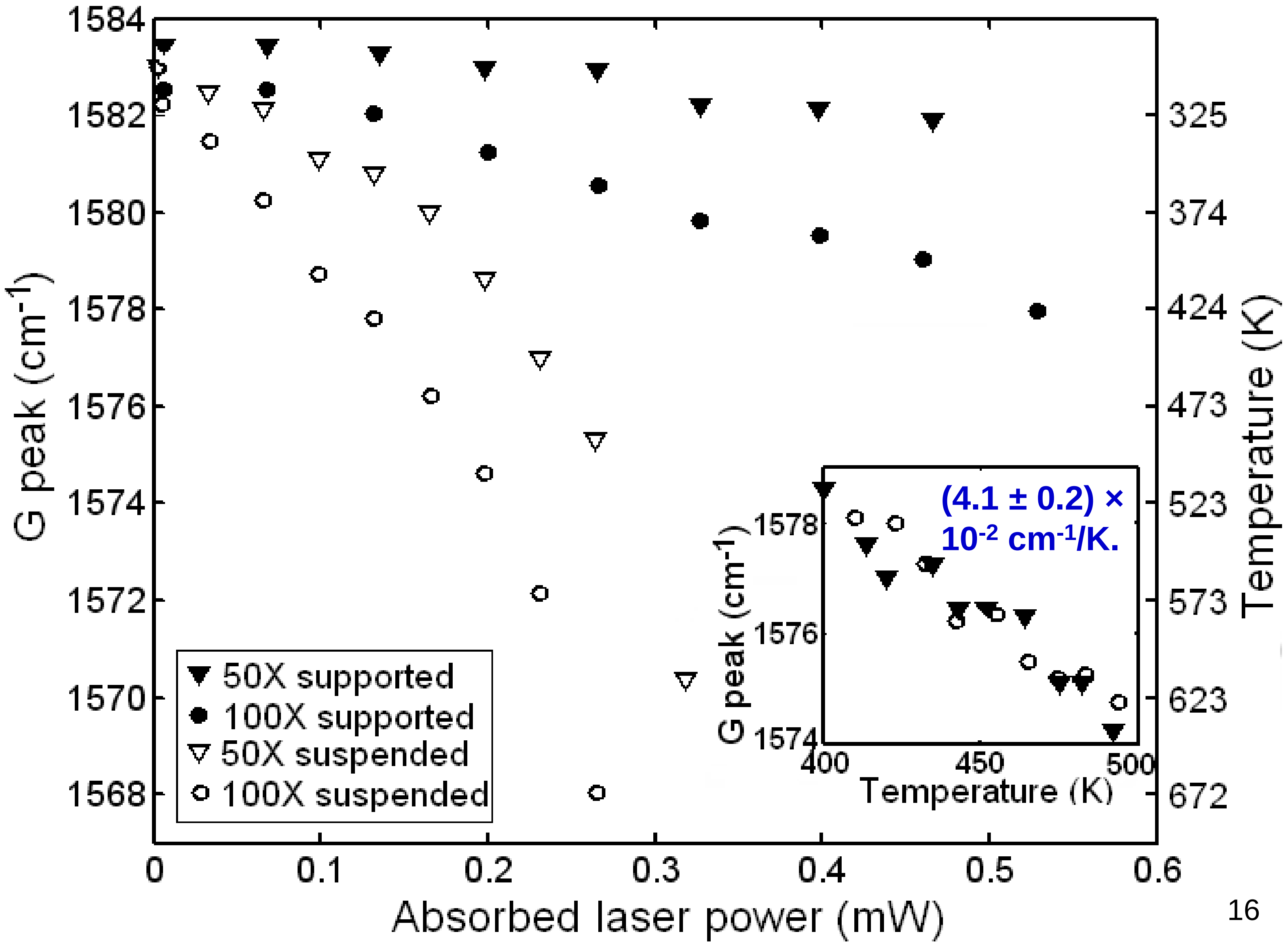
Seeing Many-Body Effects in Single- and Few-Layer Graphene: Observation of Two-Dimensional Saddle-Point Excitons

Kin Fai Mak,[1] Jie Shan,[2] and Tony F. Heinz[1,*]



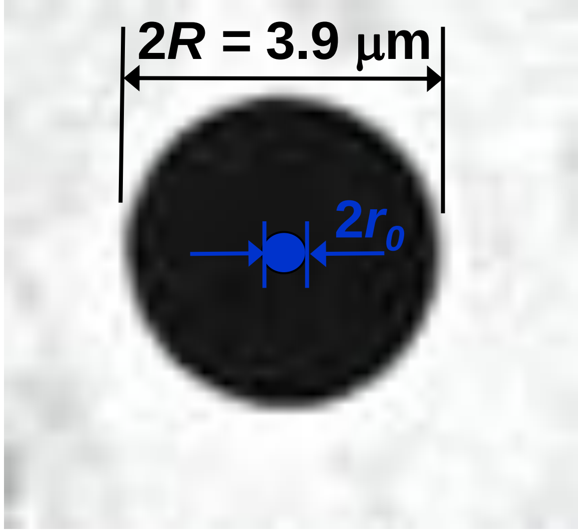
- The optical absorbance is proportional to the optical conductivity (σ), and may increase from 2.3% at 1eV (~1240 nm) to ~3.4% at ~2.54 eV (~488 nm).

Raman Peak Shift

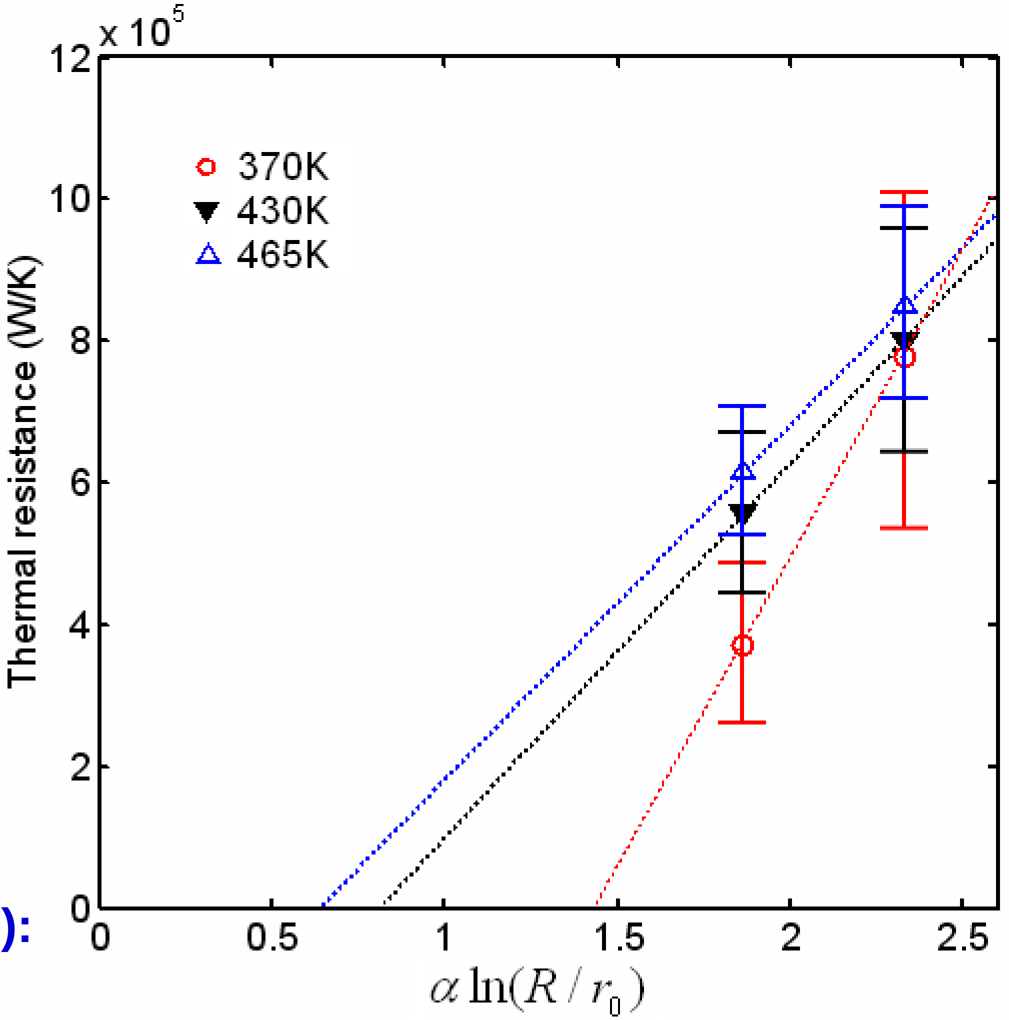


(4.1 ± 0.2) × 10^{-2} cm^{-1}/K.

Raman Measurement of Suspended CVD Graphene



- Laser spot radius r_0 was measured to be 0.17 and 0.28 µm for the 100 x and 50 x objective lens, respectively.

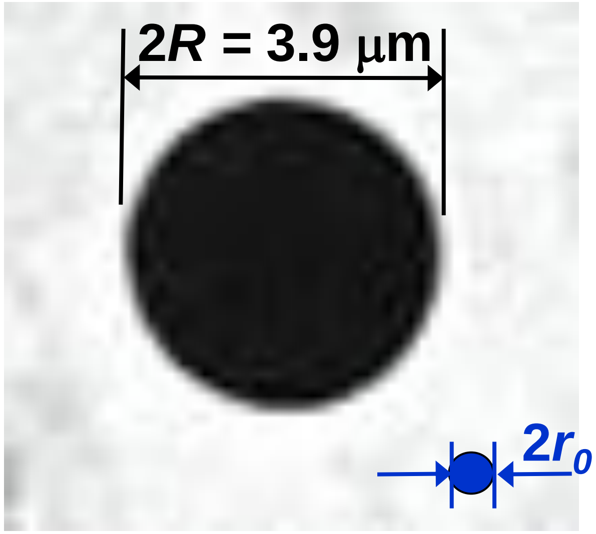


Measured Thermal Resistance (R_m):

$$R_m \equiv \frac{\Delta T_m}{Q} = \alpha \frac{\ln(R/r_0)}{2\pi \kappa t} + \text{Contact resistance} + \text{Ballistic resistance}$$

- Long wavelength phonons with m.f.p. > r_0 are not thermalized within the laser spot, giving rise to the ballistic resistance that increases with decreasing r_0.

Raman Measurement of Supported CVD Graphene



- With the laser spot on the supported graphene,

$$R_m = f(g, \kappa_s, r_0),$$

where

g = the graphene-Au thermal interface conductance,

κ_s = thermal conductivity of the supported graphene.

- Two R_m values at two different r_0 were used to obtain

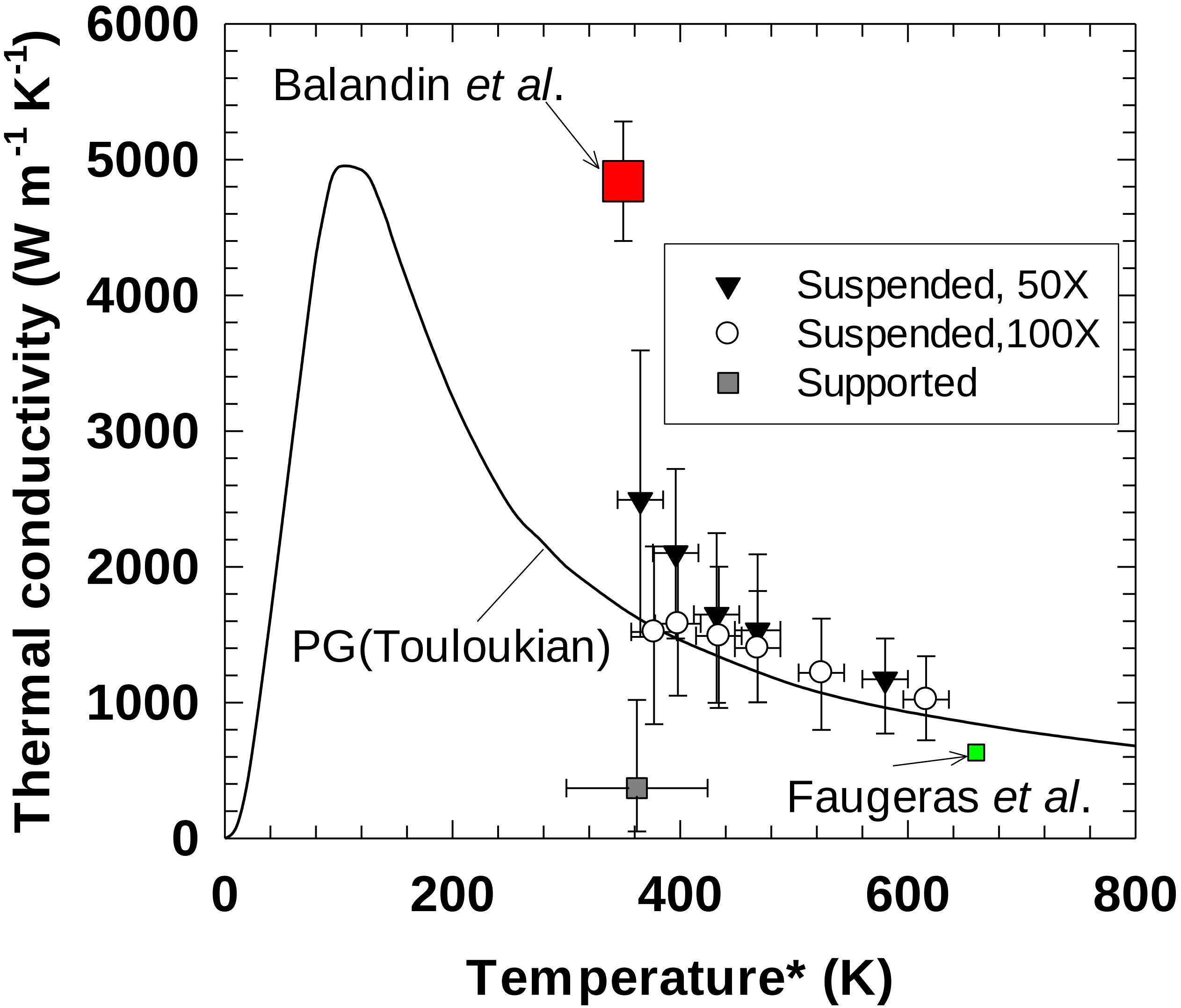
g = (28 + 16/-9.2) MW/m^2 K,

κ_s = (370 + 650/-320) W/m K, at *near room temperature*

- Thermal contact resistance

$$R_c = f(g, \kappa_s, R) = (4.4 + 8.4/-2.0) \times 10^4 \text{ K/W} << R_m$$

Thermal Conductivity Comparison

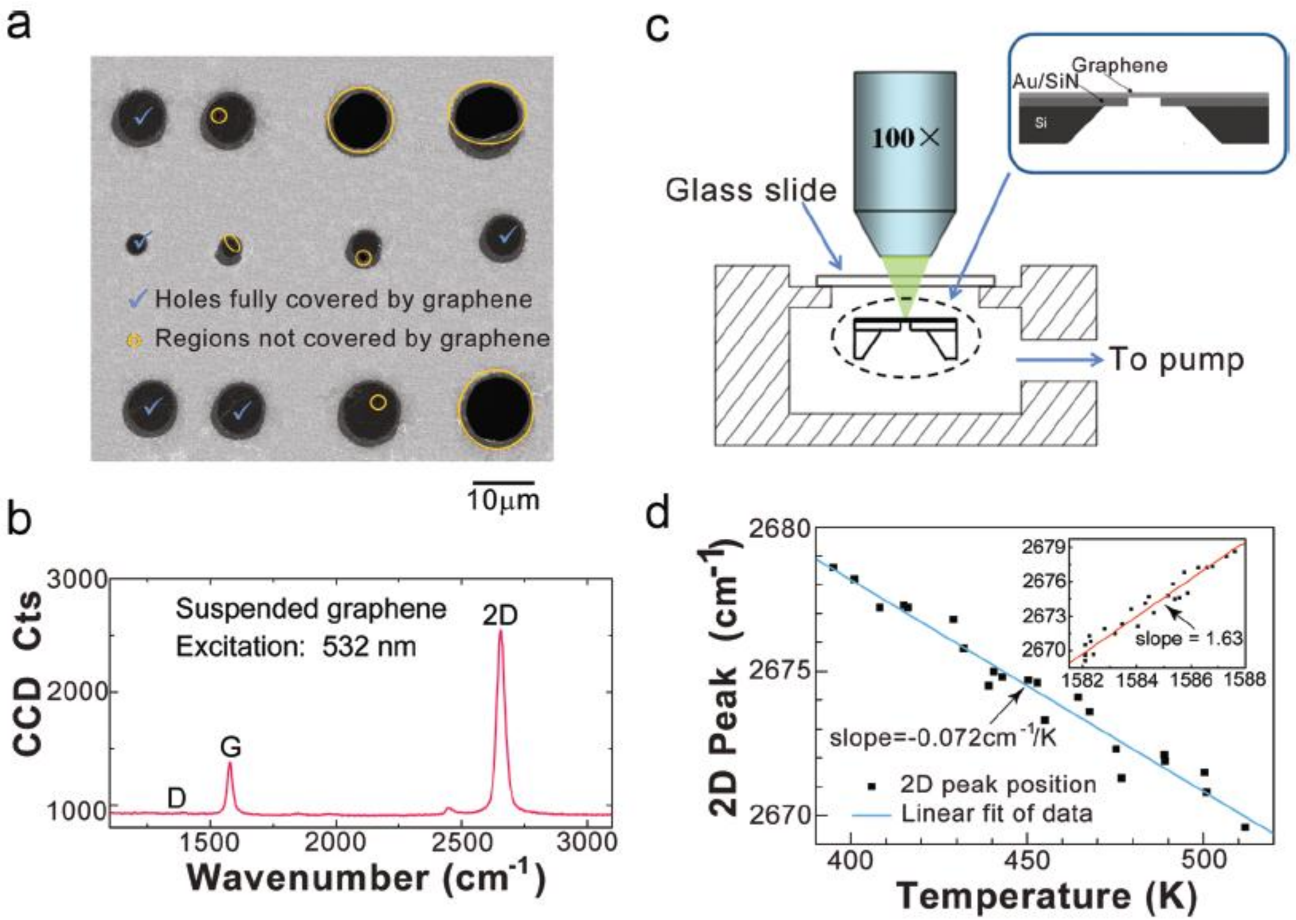


- *** For Raman measurements, the temperature is the graphene temperature measured by the Raman laser beam, whereas the substrate temperature is at room temperature.**

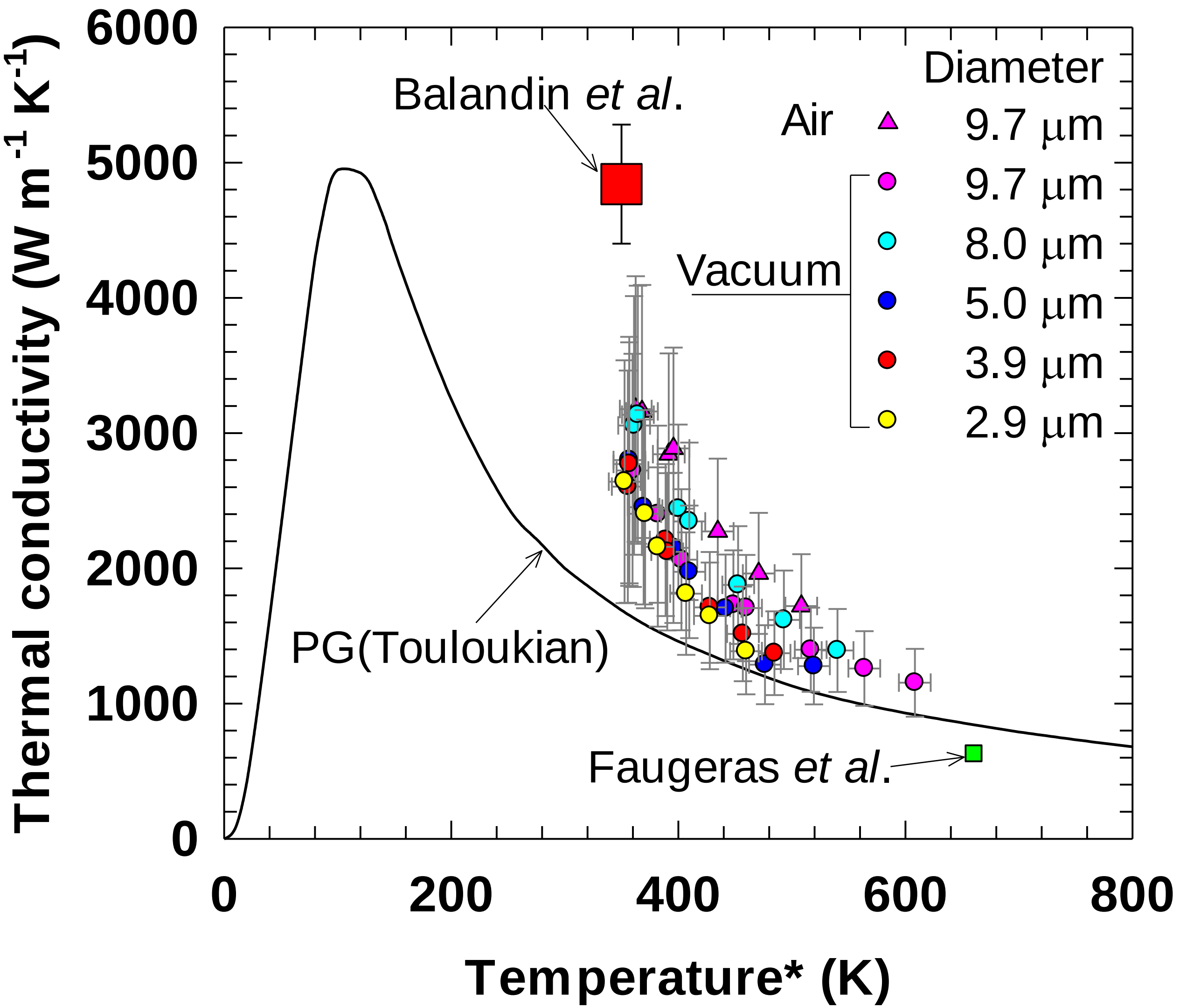
VOL. 5 ▪ NO. 1 ▪ 321–328 ▪ 2011 ACSNANO

Raman Measurements of Thermal Transport in Suspended Monolayer Graphene of Variable Sizes in Vacuum and Gaseous Environments

Shanshan Chen,[†,‡] Arden L. Moore,[†] Weiwei Cai,[†,‡] Ji Won Suk,[†] Jinho An,[†] Columbia Mishra,[†]
Charles Amos,[†] Carl W. Magnuson,[†] Junyong Kang,[‡] Li Shi,[†,*] and Rodney S. Ruoff[†,*]



Thermal Conductivity vs. Suspended Graphene Size



- The thermal conductivity value measured in air is higher than that measured in vacuum.
- The size dependence is masked by the large measurement uncertainty.

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Alternative Thermal Measurement Methods

Journal of Heat Transfer

OCTOBER 2003, Vol. 125 / 881

Measuring Thermal and Thermoelectric Properties of One-Dimensional Nanostructures Using a Microfabricated Device

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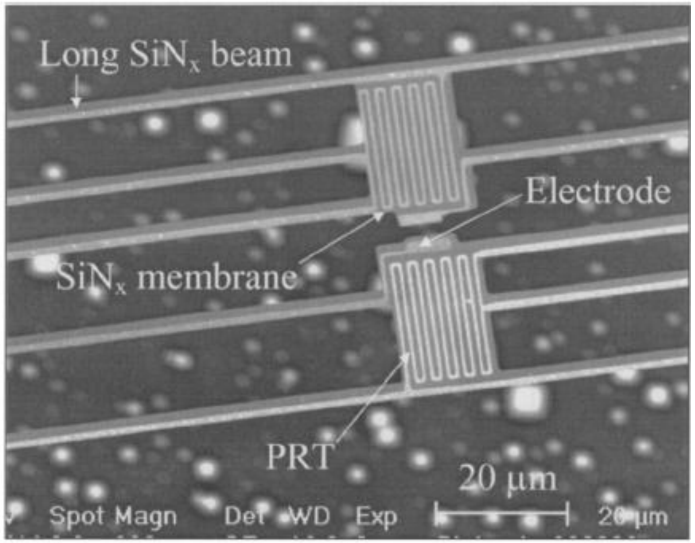
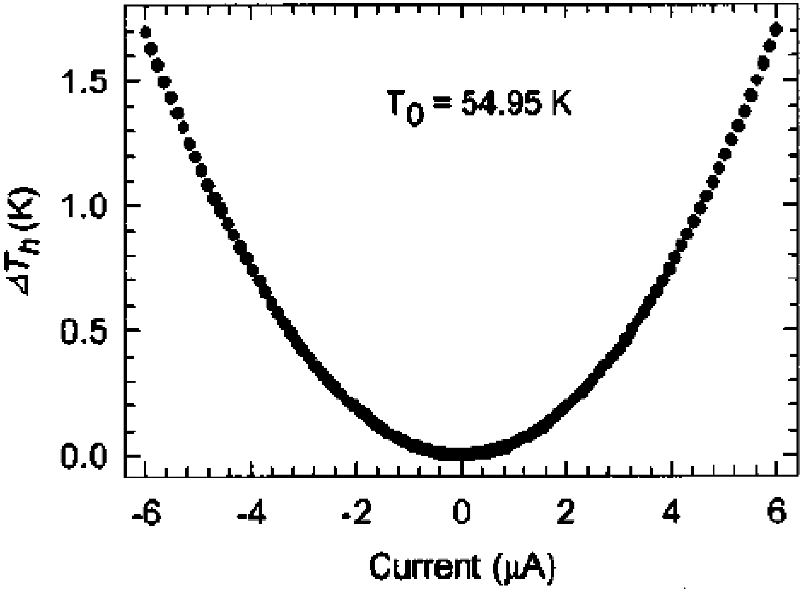
Philip Kim
Department of Physics,
Columbia University, New York

Arunava Majumdar
Materials Science Division,
Lawrence Berkeley National Laboratory,
Department of Mechanical Engineering,
University of California, Berkeley, CA 94720





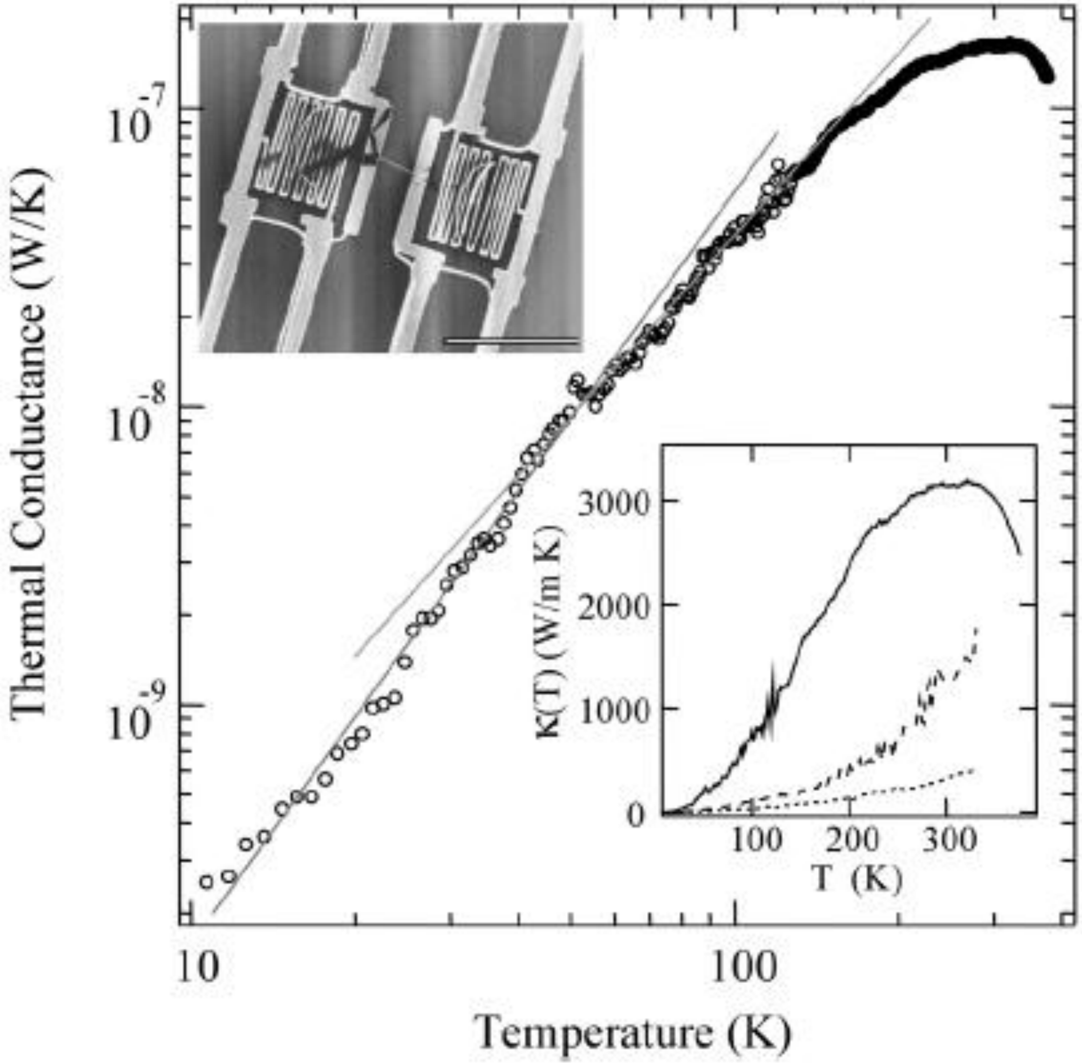
<u>Temperature sensitivity</u>:

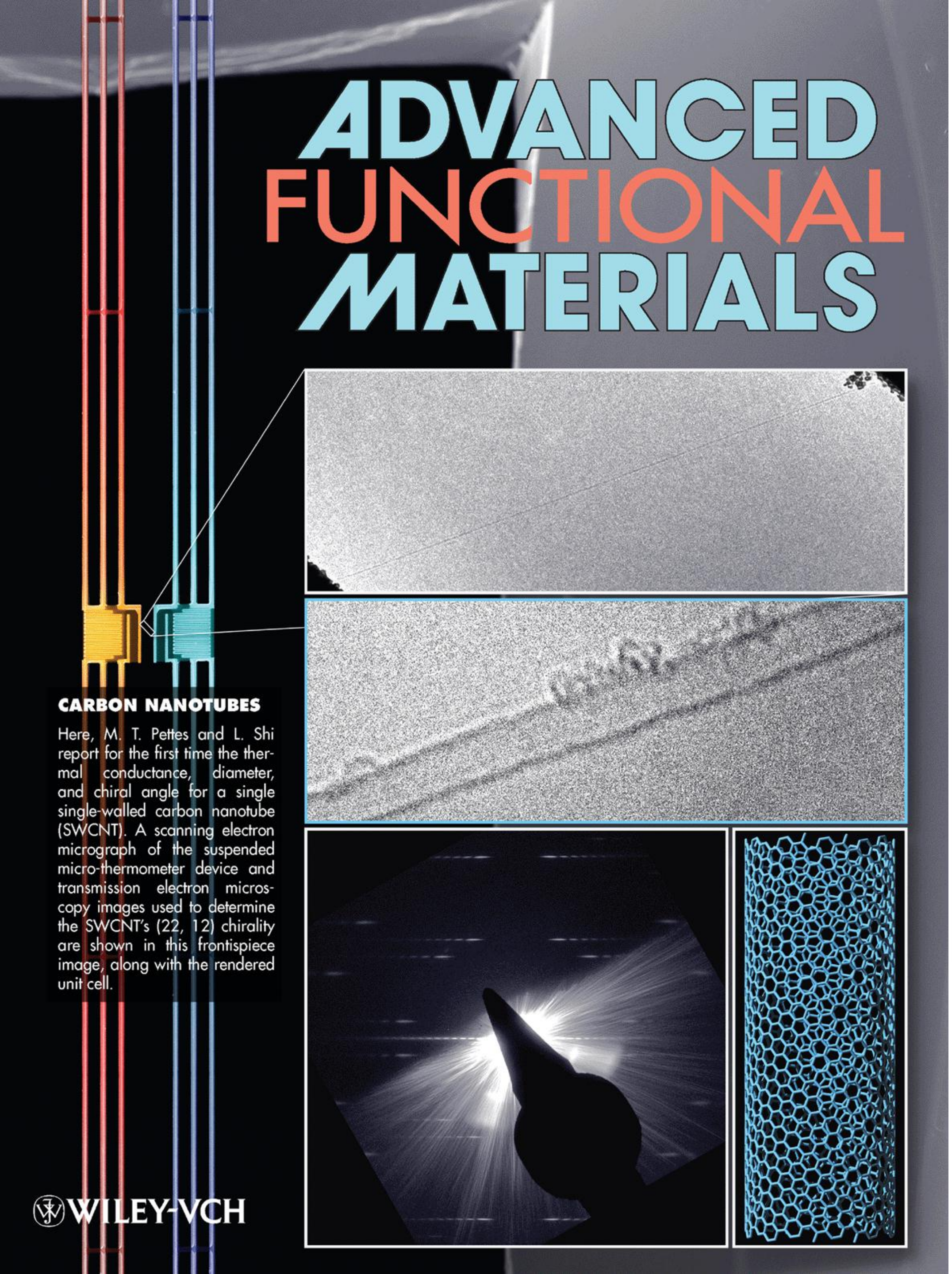
- Raman spectroscopy: ~40 K
- Resistance thermometry: ~40 x 10^{-3} K

VOLUME 87, NUMBER 21 PHYSICAL REVIEW LETTERS 19 NOVEMBER 2001

Thermal Transport Measurements of Individual Multiwalled Nanotubes

P. Kim,[1] L. Shi,[2] A. Majumdar,[2] and P. L. McEuen[1,3,*]




ADVANCED FUNCTIONAL MATERIALS

CARBON NANOTUBES

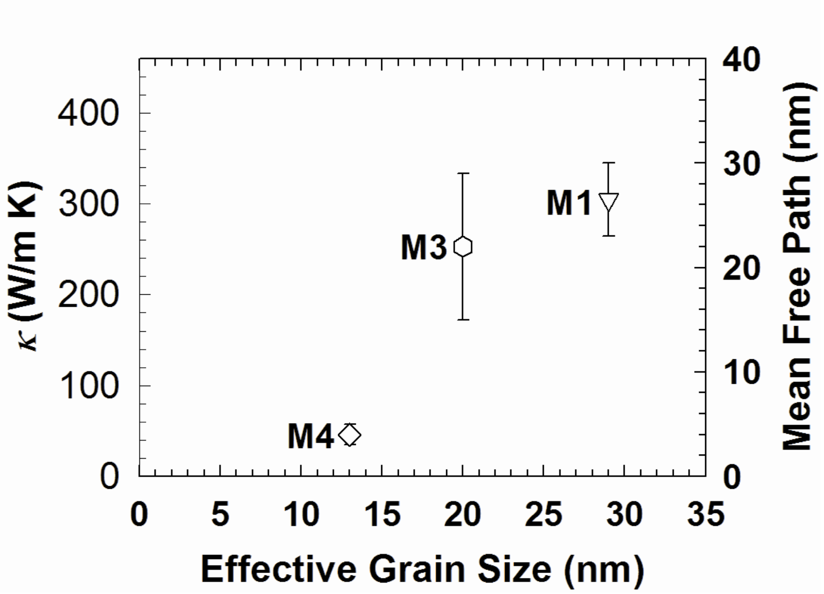
Here, M. T. Pettes and L. Shi report for the first time the thermal conductance, diameter, and chiral angle for a single single-walled carbon nanotube (SWCNT). A scanning electron micrograph of the suspended micro-thermometer device and transmission electron microscopy images used to determine the SWCNT's (22, 12) chirality are shown in this frontispiece image, along with the rendered unit cell.

WILEY-VCH

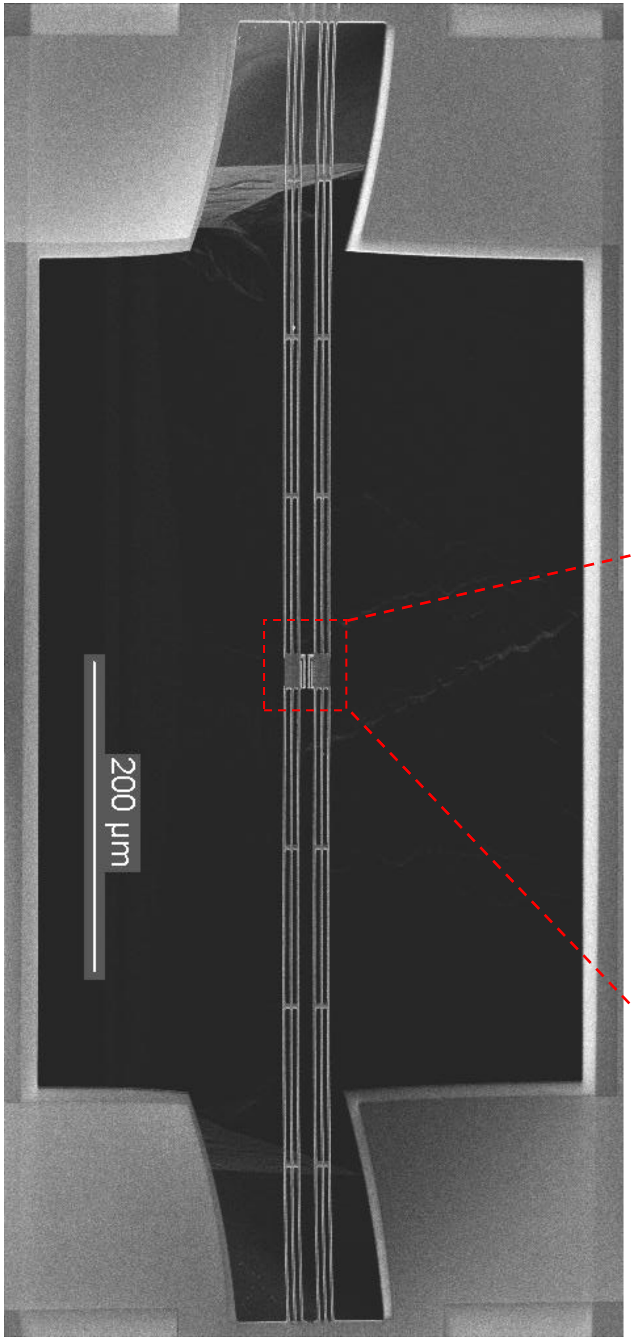
Adv. Funct. Mater. **2009**, *19*, 3918–3925

Thermal and Structural Characterizations of Individual Single-, Double-, and Multi-Walled Carbon Nanotubes

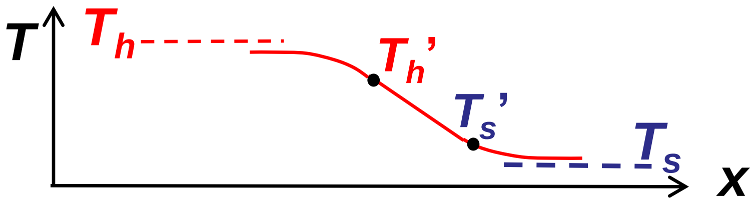
By *Michael T. Pettes* and *Li Shi**

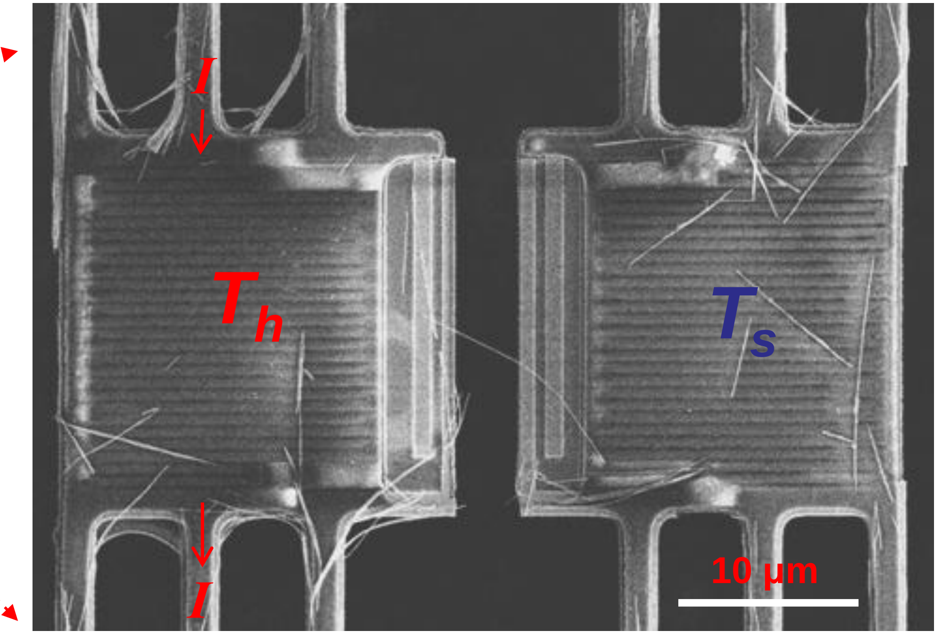


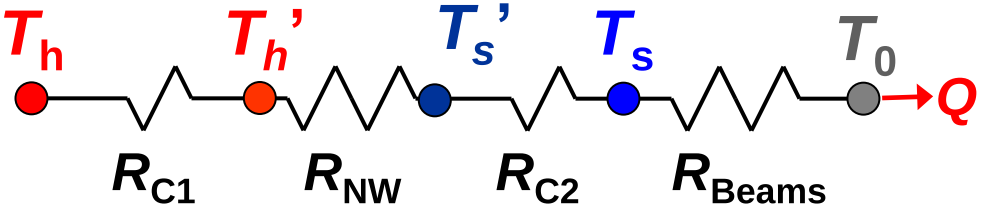
Thermal Measurement of Individual Nanowires



L. Shi, D. Li, C. Yu, W. Jang, D. Kim, Z. Yao, P. Kim, A. Majumdar, J. Heat Transfer 125, 881 (2003)

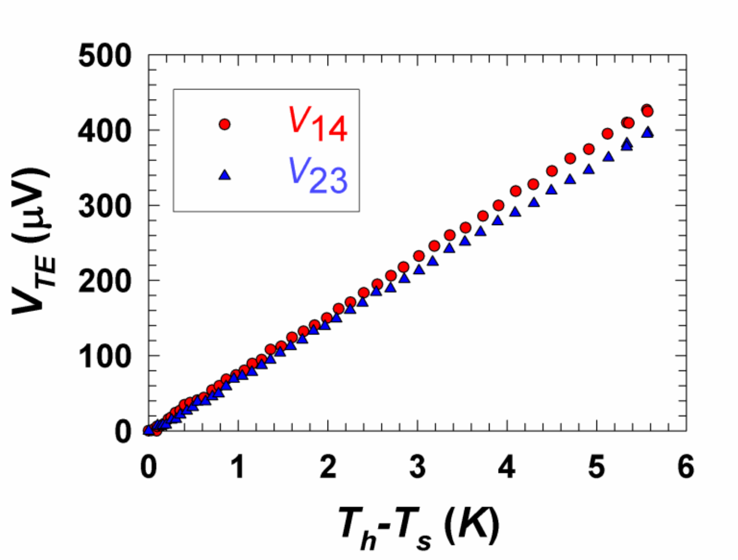


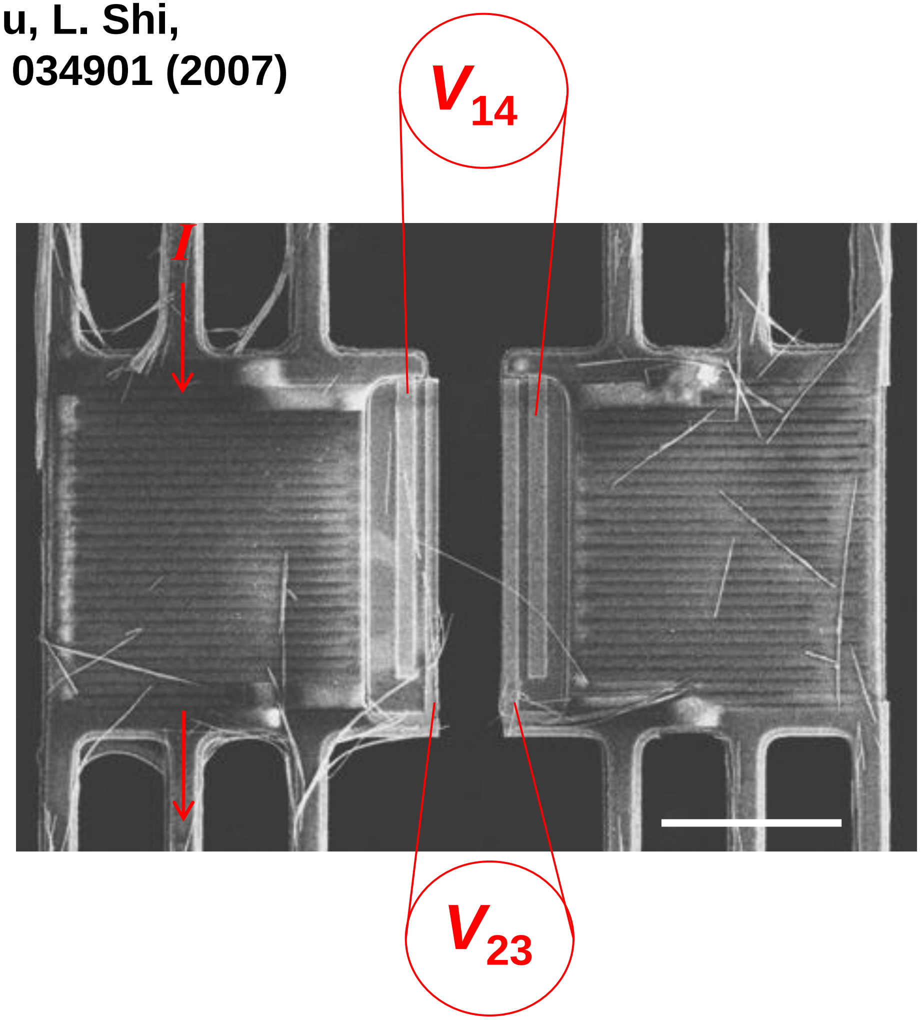




Four-Probe Thermoelectric Measurements of Individual Nanowires

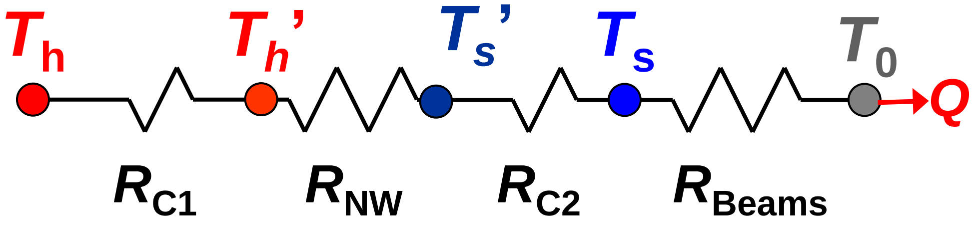
- **A. Mavrokefalos, M. T. Pettes, F. Zhou, L. Shi, Review of Scientific Instruments 78, 034901 (2007)**





$$V_{23} / V_{14} \rightarrow (T_h'-T_s')/(T_h-T_s)$$

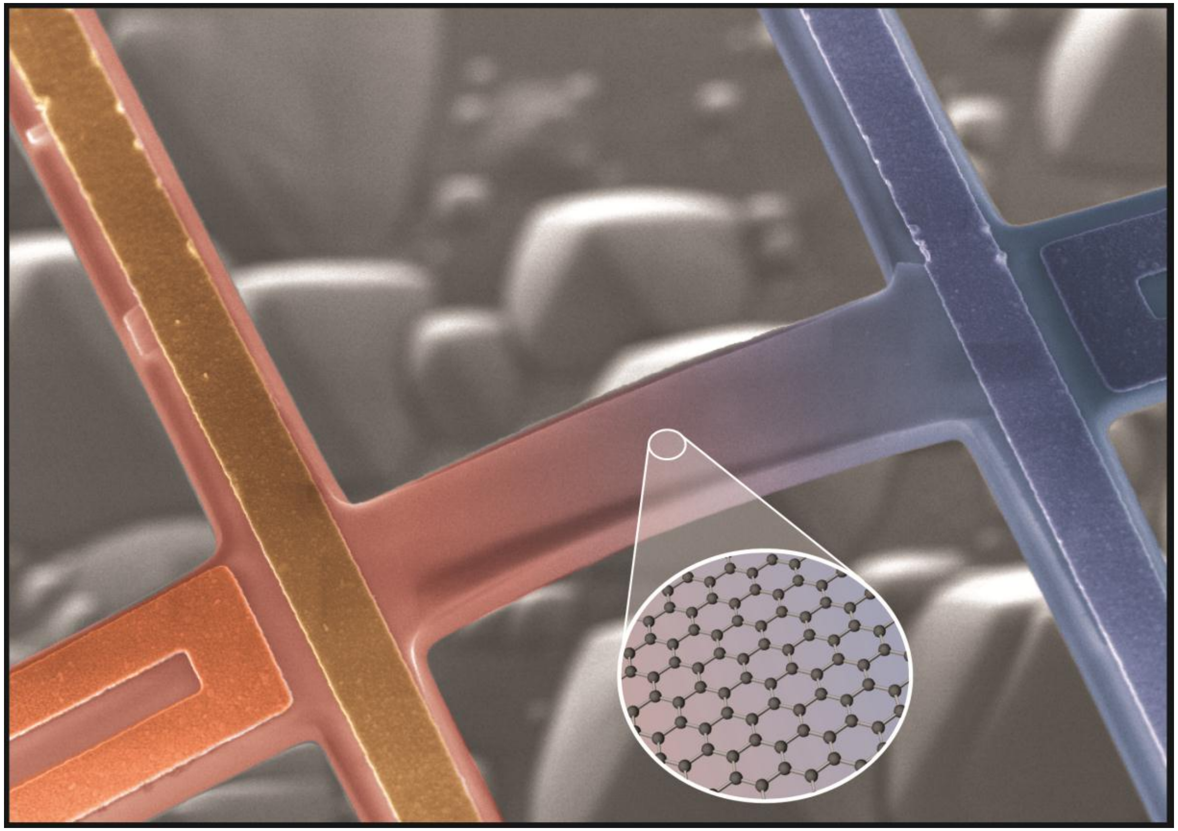
$$S \approx V_{14}/(T_h-T_s)$$



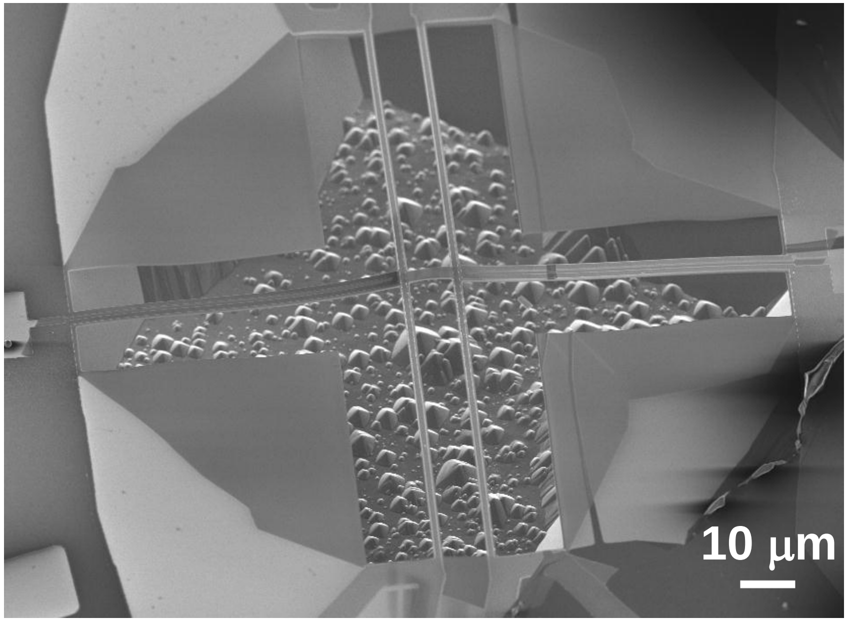
SCIENCE VOL 328 9 APRIL 2010

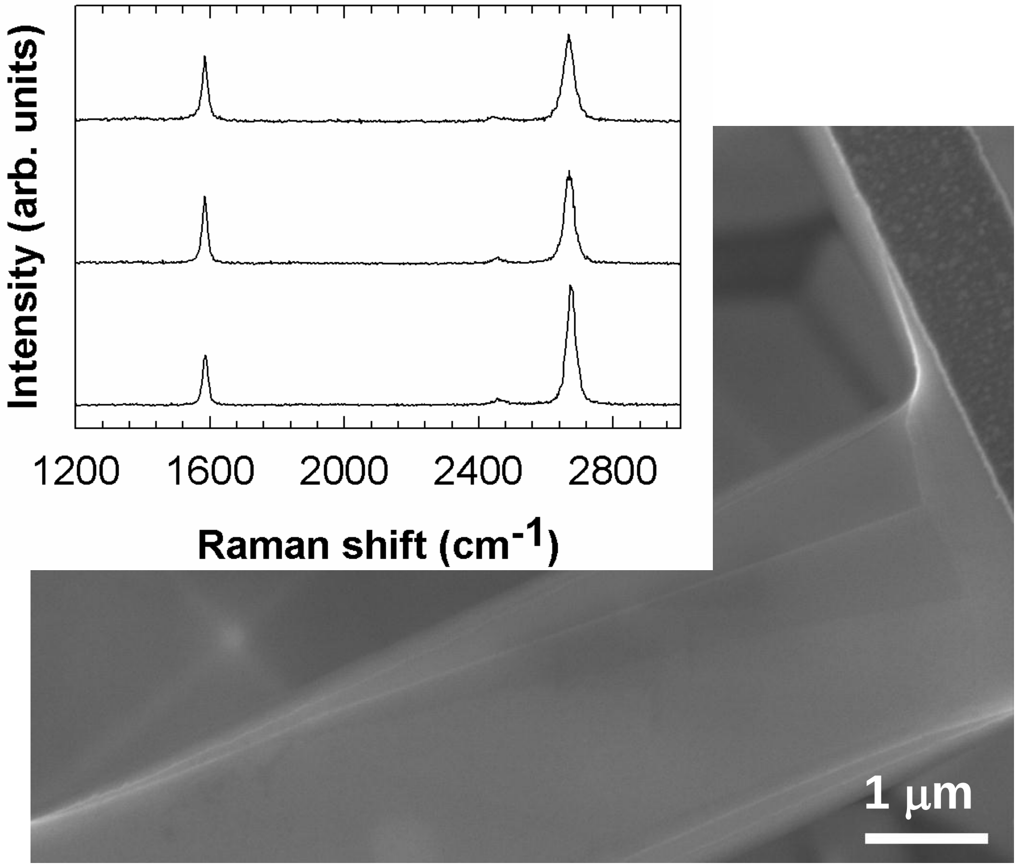
Two-Dimensional Phonon Transport in Supported Graphene

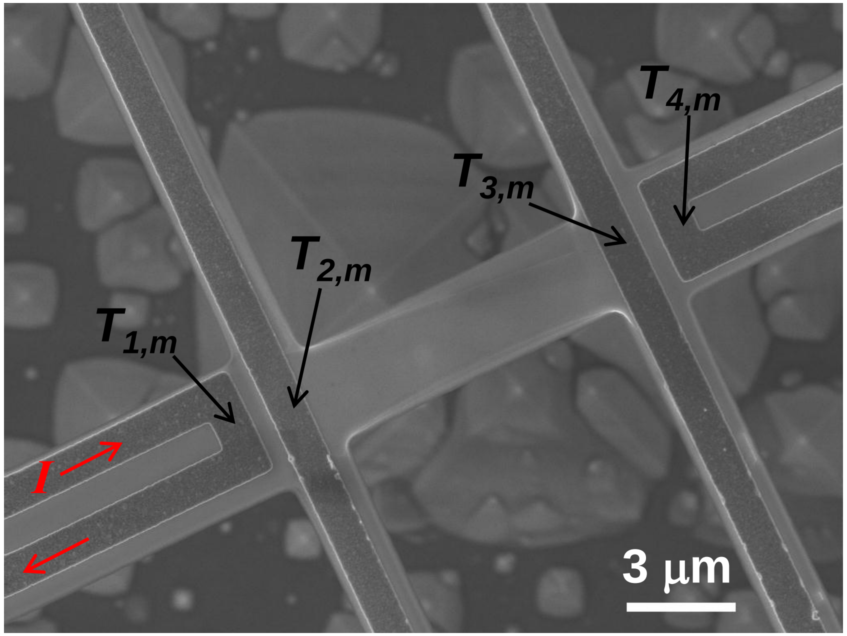
Jae Hun Seol,[1] Insun Jo,[2] Arden L. Moore,[1] Lucas Lindsay,[3,4] Zachary H. Aitken,[5] Michael T. Pettes,[1] Xuesong Li,[1,6] Zhen Yao,[2] Rui Huang,[5] David Broido,[3] Natalio Mingo,[7] Rodney S. Ruoff,[1,6] Li Shi[1,6]*

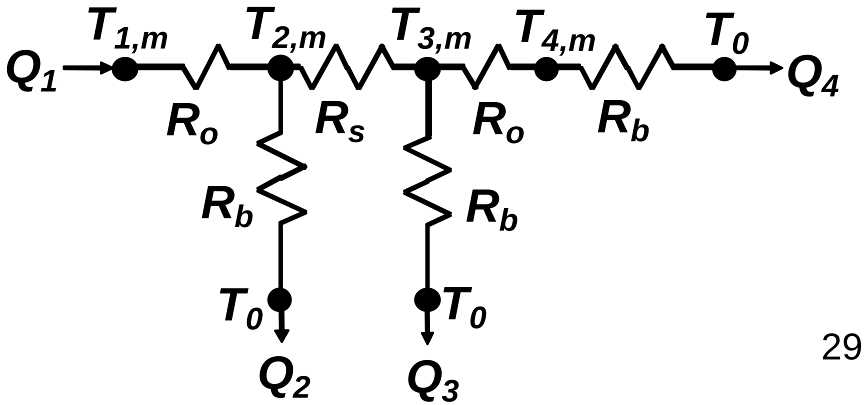


Thermal Measurement of Supported Graphene

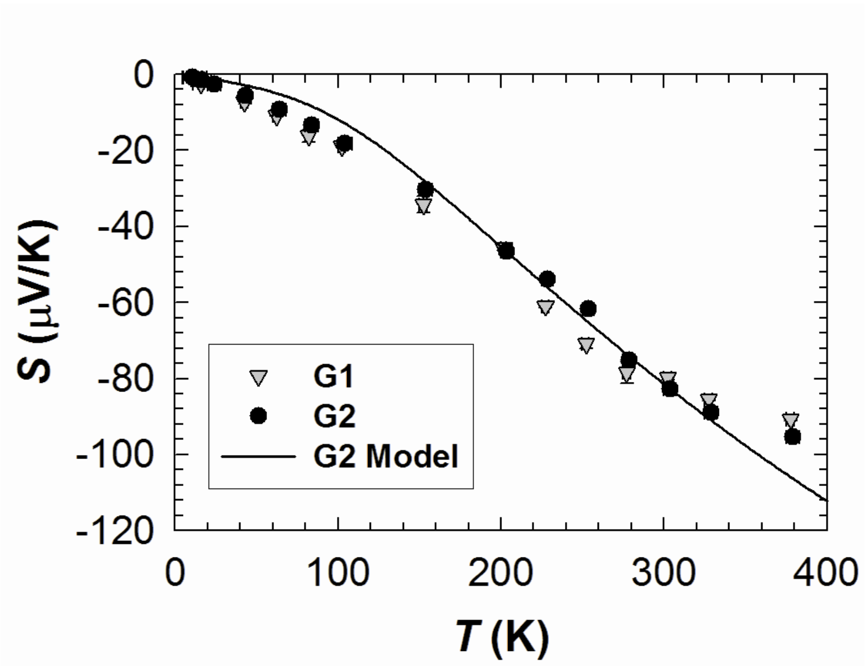


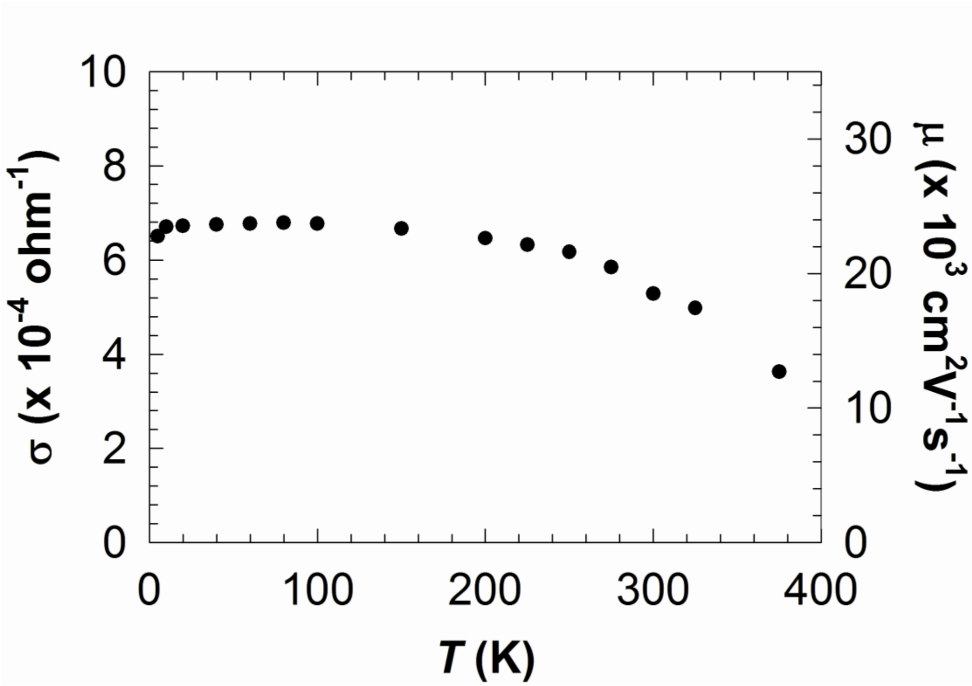






Seebeck Coefficient (*S*) & Electrical Conductivity (σ)

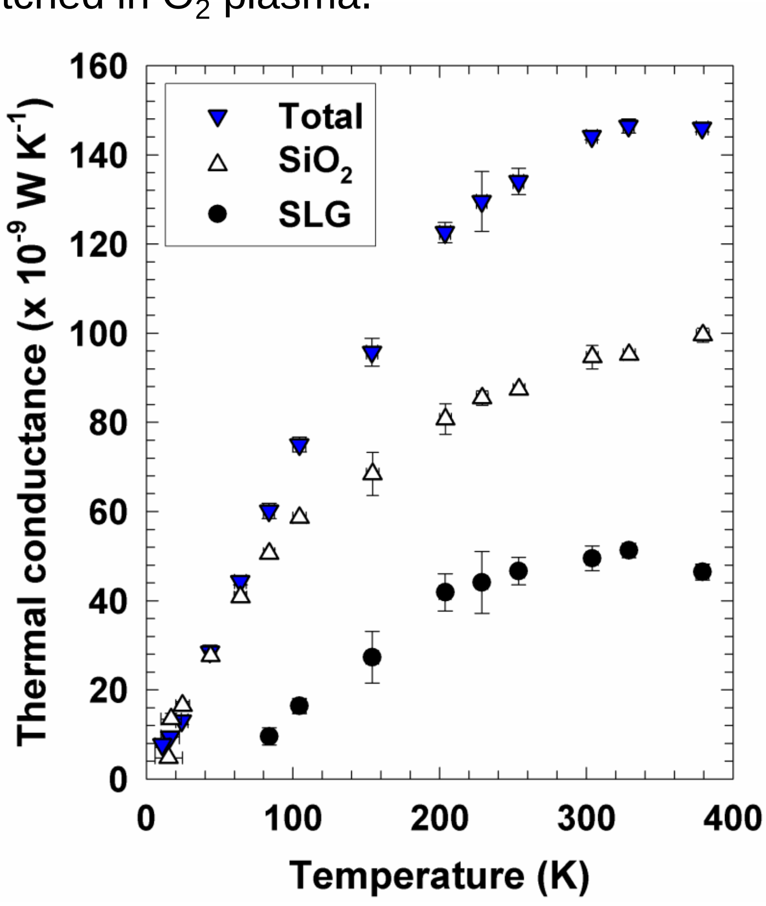




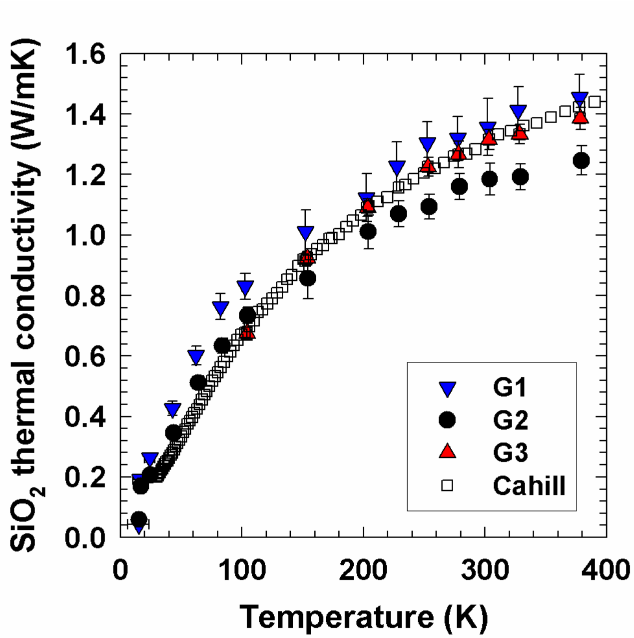
- $S = f(E_F)$ can be fitted with $E_F = 0.049$ eV.
- Electron concentration $n = (E_F/\hbar v_F)^2/\pi = 1.7 \times 10^{11}$ cm^{-2} .
- Electron mobility ($\mu = \sigma/ne$) is comparable to the highest values reported for supported graphene.

Thermal Conductance ($G \equiv 1/R_s$)

- *G* of the graphene/SiO_2 central beam was measured before and after the graphene was etched in O_2 plasma.



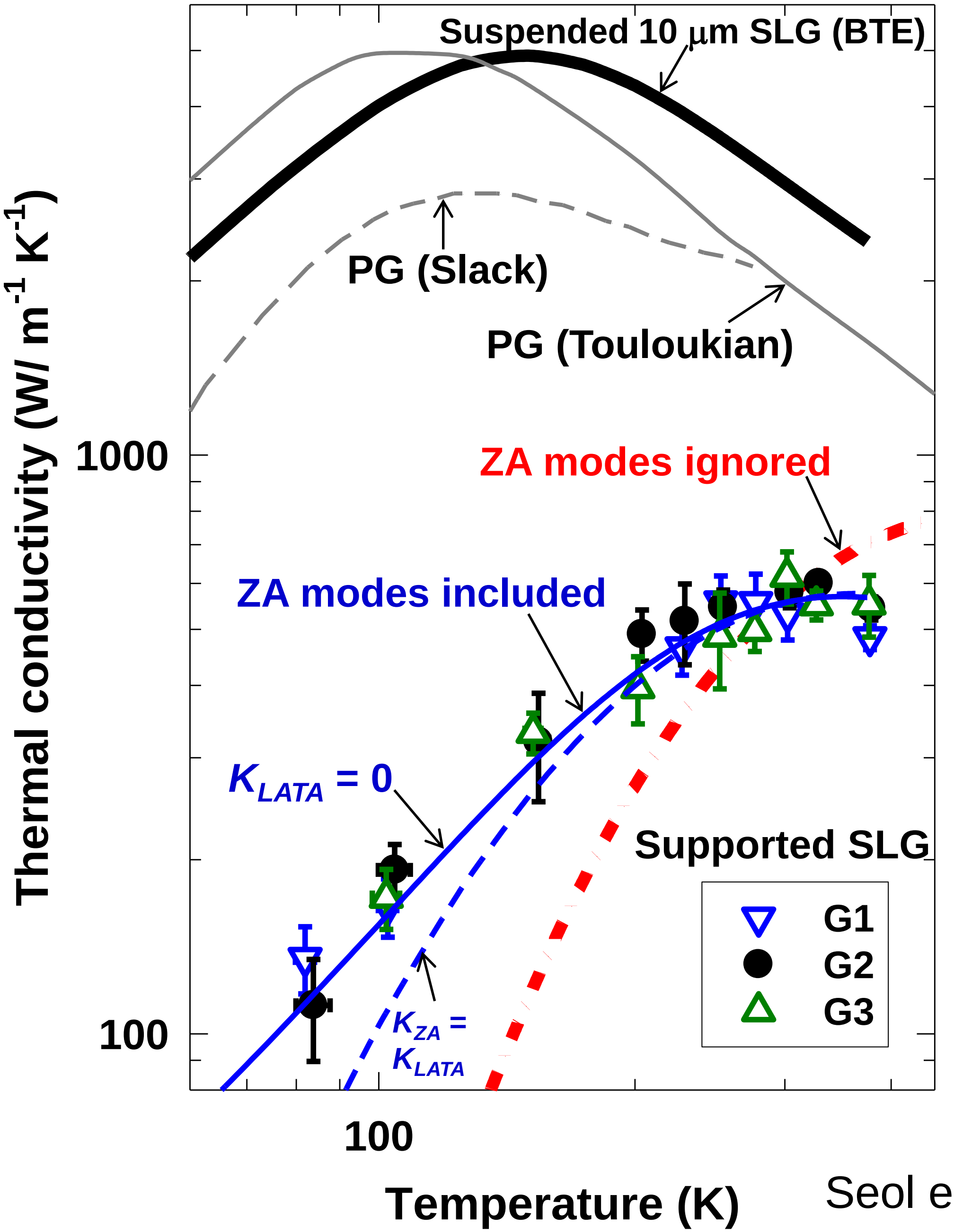
- The obtained SiO_2 thermal conductivity is in good agreement with literature values.



“If the substrate is itself a thin film of low thermal conductivity, the additional conductance of the graphene sheet may be just observable.”

P. G. Klemens, Int. J. Thermophysics 22 (2001)

Thermal Conductivity Suppression in Supported Graphene



- **Phonon leakage across the interface:**

$$\tau_{substrate,j} \propto \omega^2 DOS(\omega) / K_j^2$$

j = ZA, LA, or TA

Interface force constant:

$K_{ZA} \approx 0.4$ N/m

$K_{LATA} < K_{ZA}$

- **Roughness scattering:**
  - **Rayleigh scattering:** $\tau \sim \omega^{-4}$
  - **Geometric scattering:** $l \sim \omega^0$

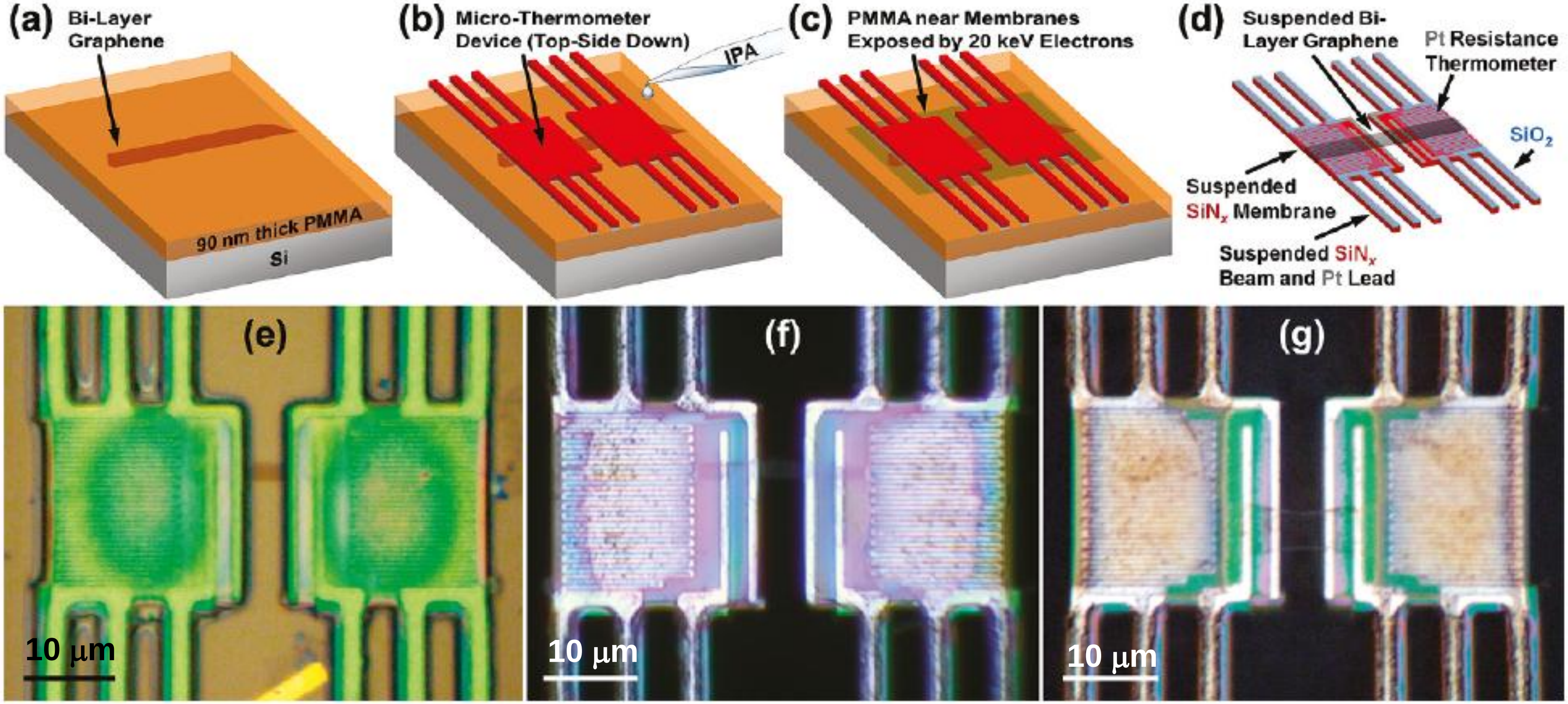
- In 2D and at low *T:*

Relaxation time $\tau \sim \omega^{\alpha}$

→ $\kappa \sim T^{2+\alpha}$

Seol et al., Science 328, 213 (2010)

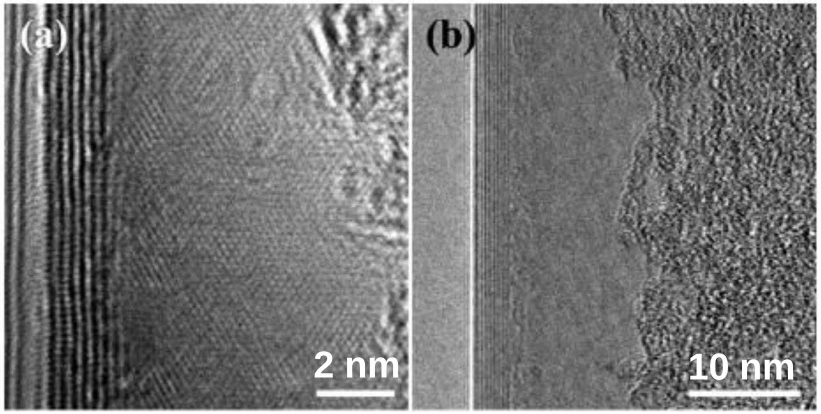
Suspended Graphene between Micro-Thermometers

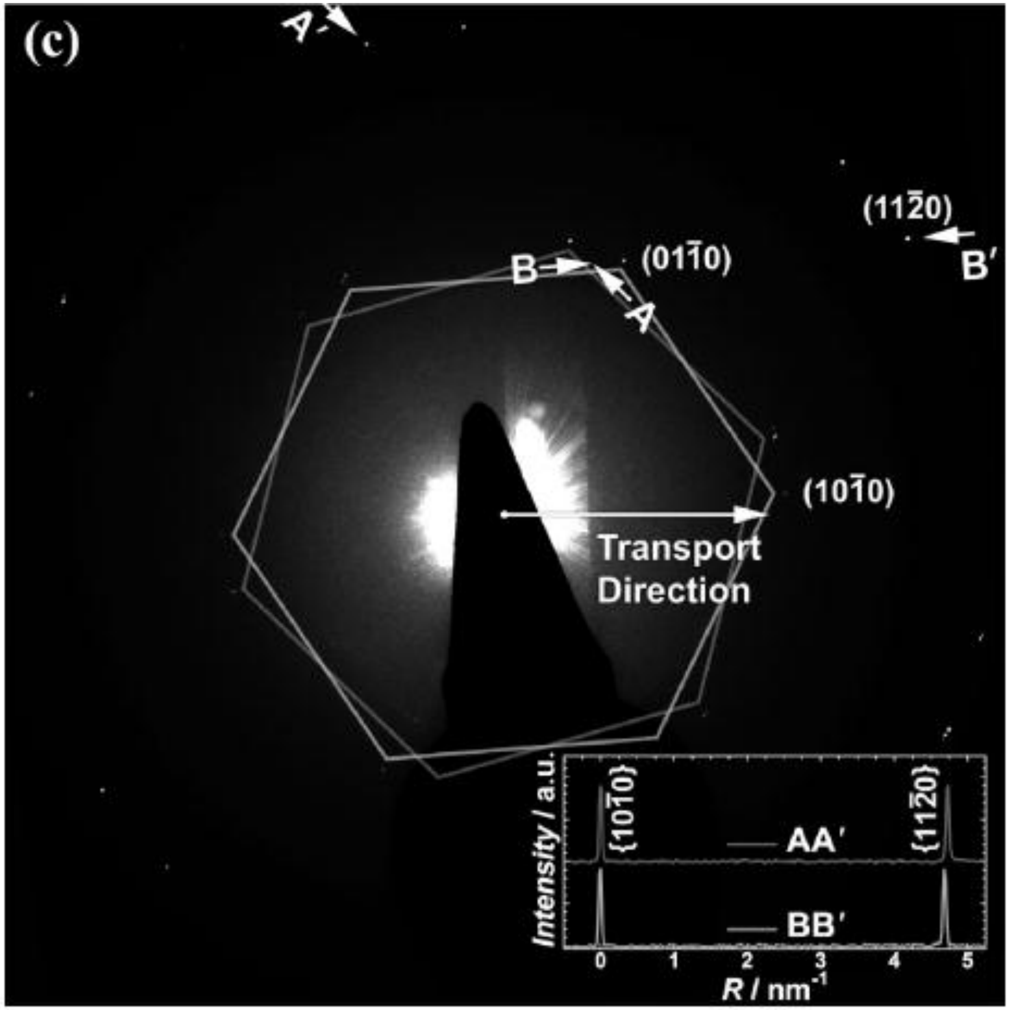


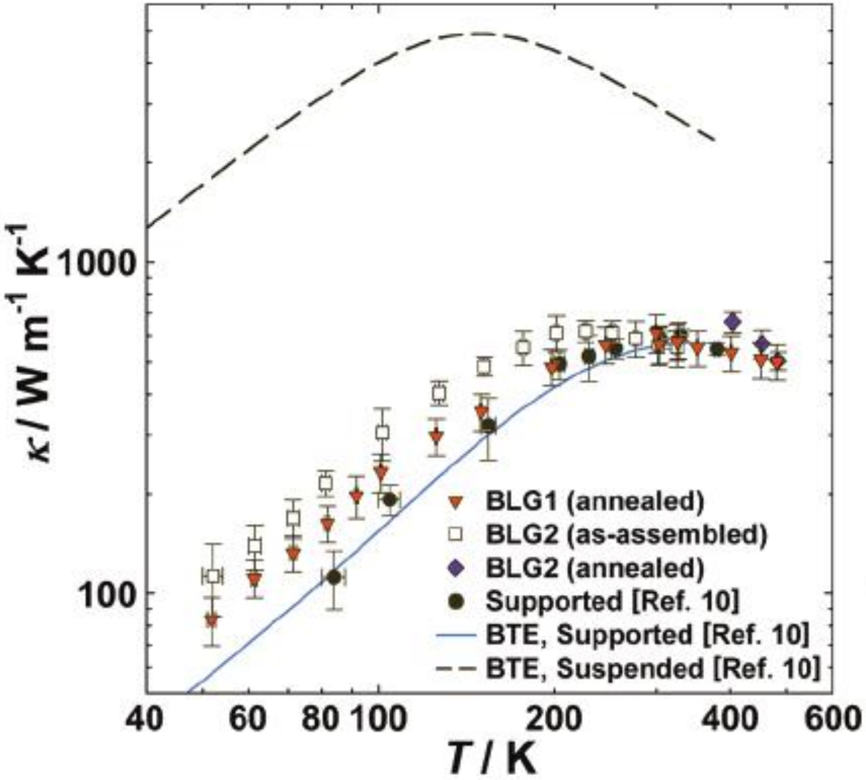
Influence of Polymeric Residue on the Thermal Conductivity of Suspended Bilayer Graphene

Nano Lett. 2011, 11, 1195–1200

Michael Thompson Pettes,[†,‖] Insun Jo,[‡,‖] Zhen Yao,[‡,§] and Li Shi*[,†,§]



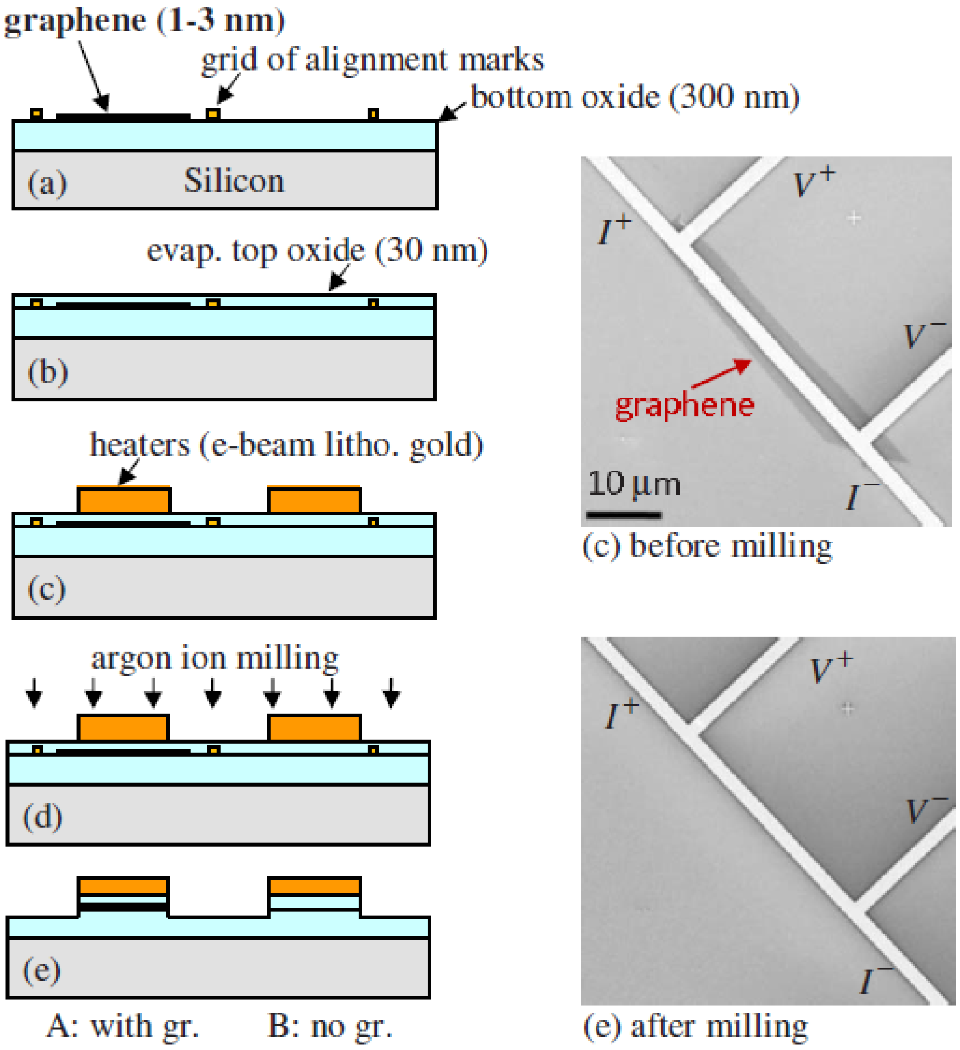




Outline

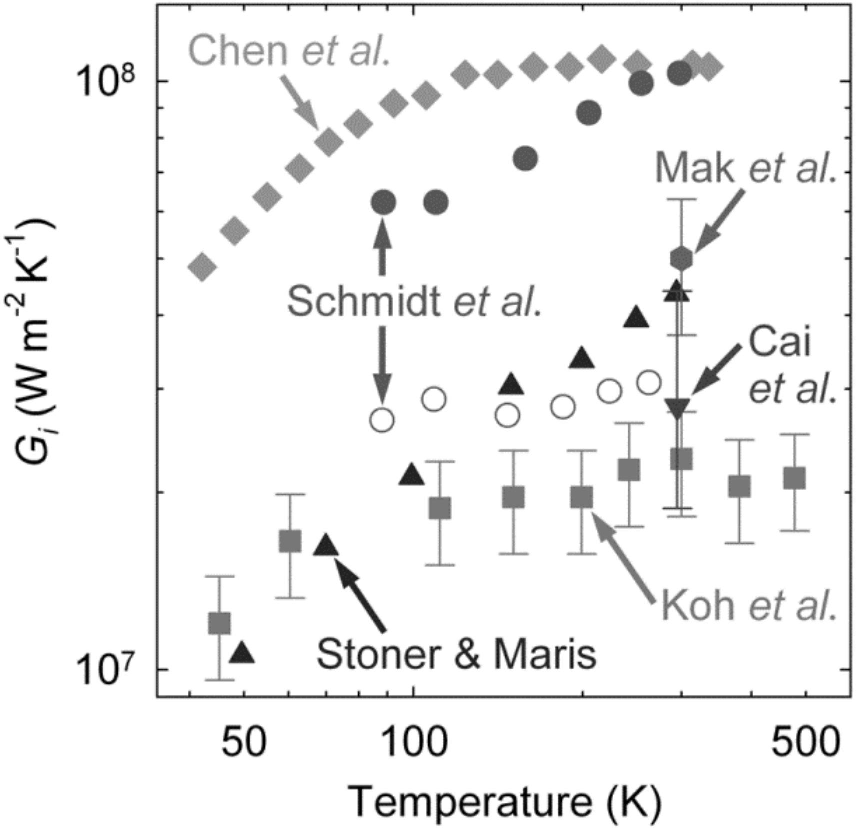
- **Thermal Transport Theories and Simulations of Graphene**
- **Raman Measurements of Thermal Transport in Graphene**
- **Thermal Conductance Measurements of Graphene with Micro-devices**
- ➢ **Thermal Interface Conductance of Graphene**
- **Thermal Transport in Graphene Foams and Ultrathin Graphite Foams**
- **Thermal Transport in Few-Layer Hexagonal Boron Nitride**

Thermal Interface Conductance of Graphene



(c) before milling

(e) after milling



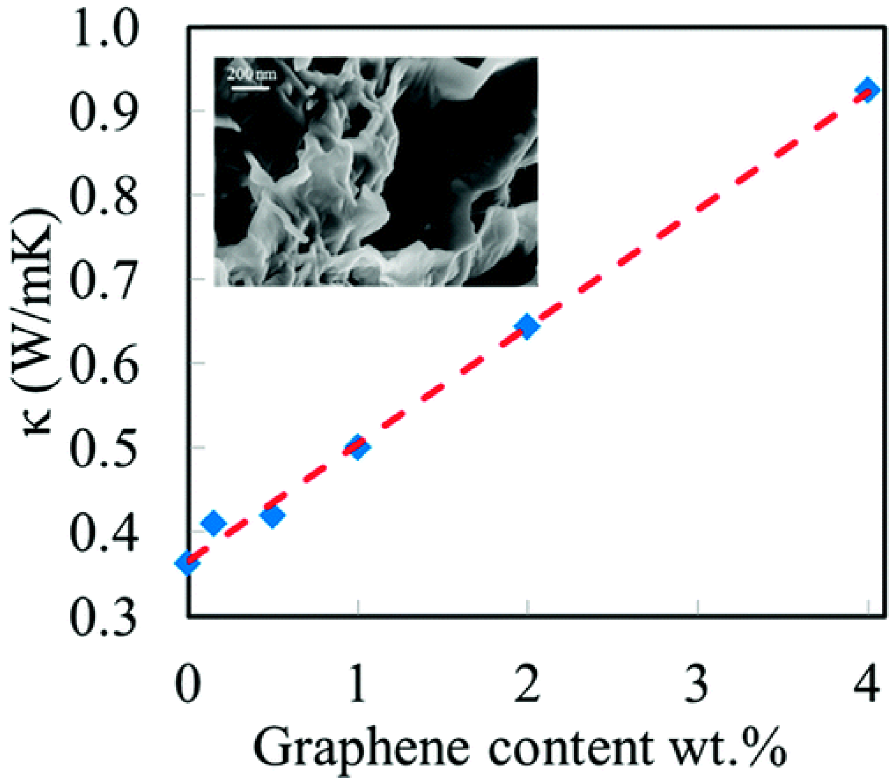
M. M. Sadeghi, M. T. Pettes, L. Shi, Solid State Communications, DOI: 10.1016/j.ssc.2012.04.022 (2012)

Chen, Jang, Bao, Lau, Dames, Appl. Phys. Lett.2009, 95, 161910

Enhanced Thermal Conductivity in a Nanostructured Phase Change Composite due to Low Concentration Graphene Additives

Fazel Yavari,[‖,†] Hafez Raeisi Fard,[‖,†] Kamyar Pashayi,[†] Mohammad A. Rafiee,[†] Amir Zamiri,[†,*]
Zhongzhen Yu,[§] Rahmi Ozisik,[‡] Theodorian Borca-Tasciuc,[†,*] and Nikhil Koratkar[†,*]

J. Phys. Chem. C 2011, 115, 8753–8758



- The thermal conductivity enhancement with the addition of graphene is superior to the effects of silver nanowires or CNTs.
- The performance is still limited by the large interface thermal resistance.

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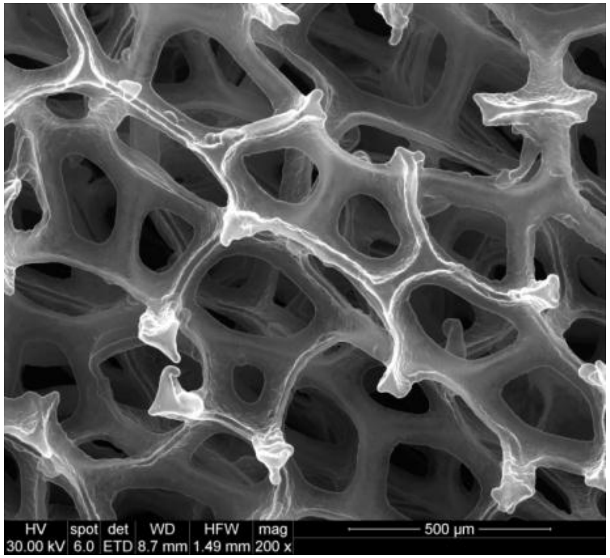
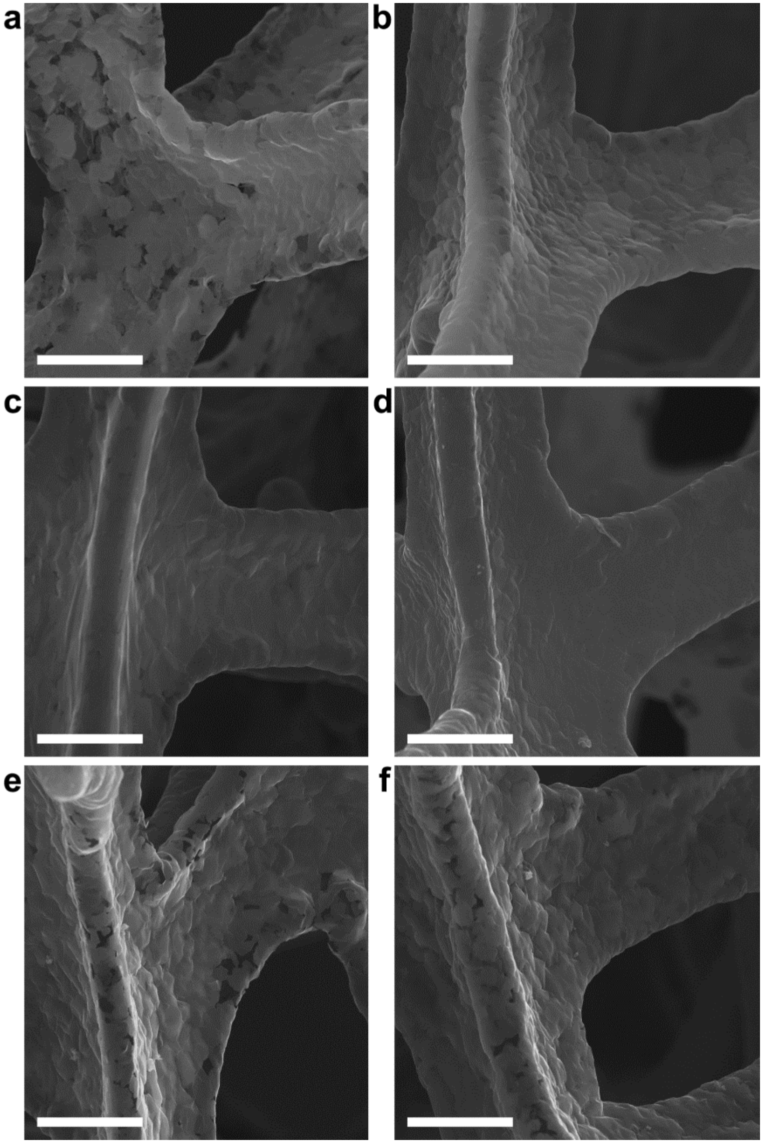
Graphene Foam and Ultrathin Graphite Foam

- **Methane CVD growth at 1050°C on sacrificial Ni foam**



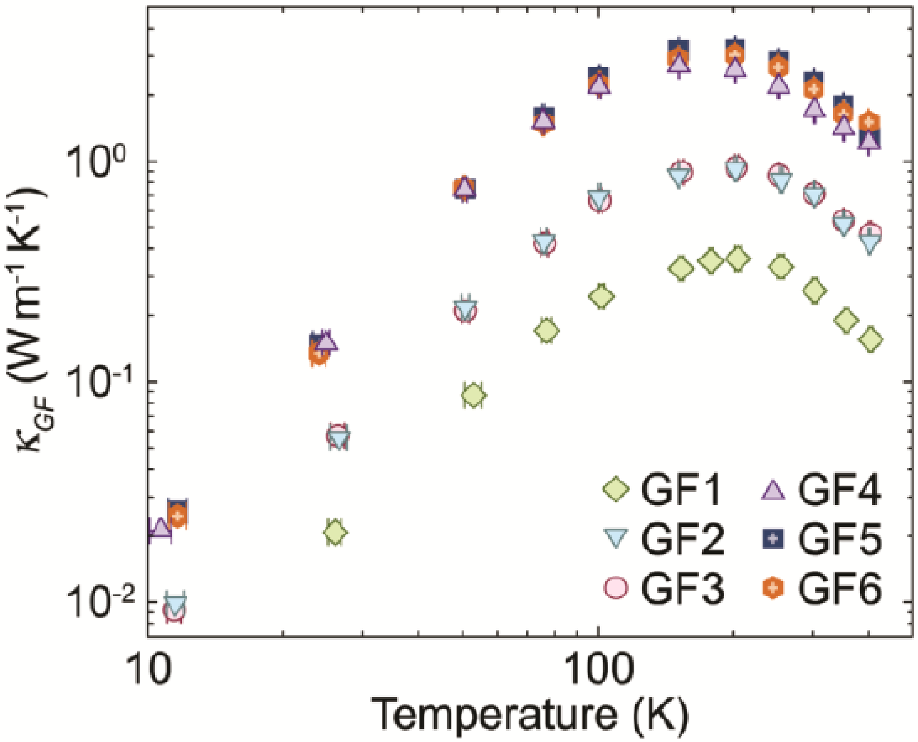
Sample	Ni foam	Growth time (hr)	Ni etchant	$\rho_{m,GF}$ (10^{-3} g cm^{-3})
GF1	as-purchased	1	HCl	10.0 ± 2.1
GF2	as-purchased	1	$Fe(NO_3)_3$	9.6 ± 1.8
GF3	annealed	1	$Fe(NO_3)_3$	9.9 ± 1.9
GF4	annealed	1	$(NH_4)_2S_2O_8$	11.6 ± 1.9
GF5	annealed	3	HCl	32.0 ± 2.7
GF6	annealed	3	$(NH_4)_2S_2O_8$	31.7 ± 2.7



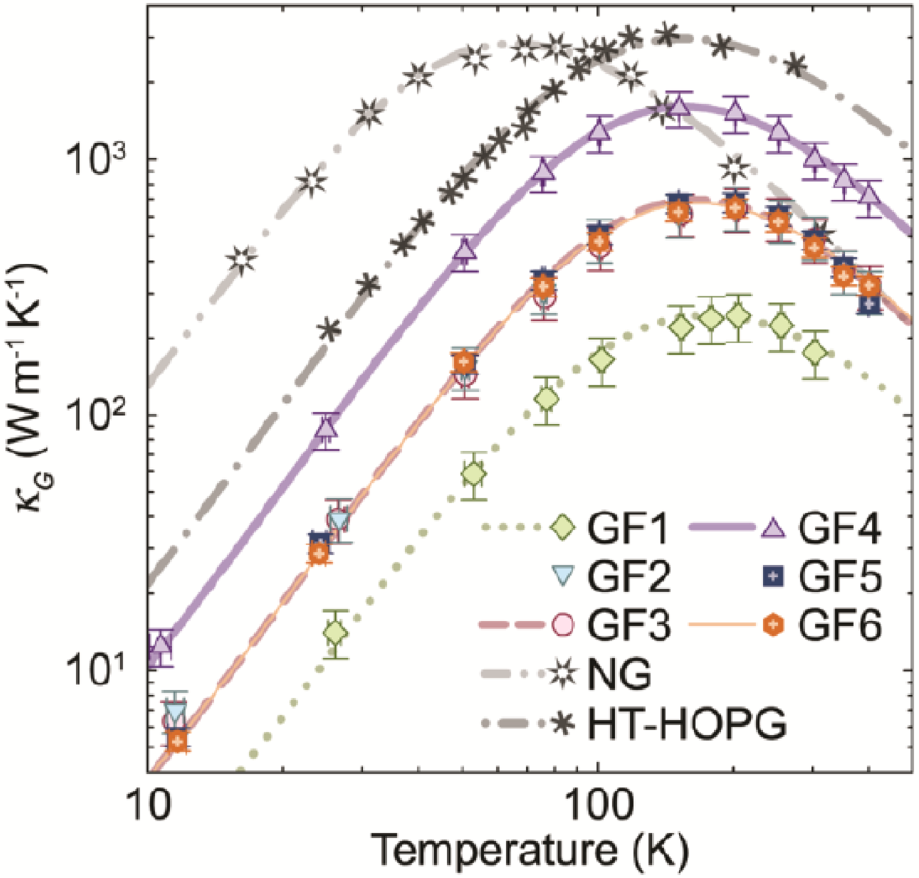
Scale bars: 50 μm

Graphene Foam and Ultrathin Graphite Foam

- **Effective thermal conductivity**



- **Solid thermal conductivity**



- **Solid concentration (ϕ):**

  ~0.45 vol % for GF1-4

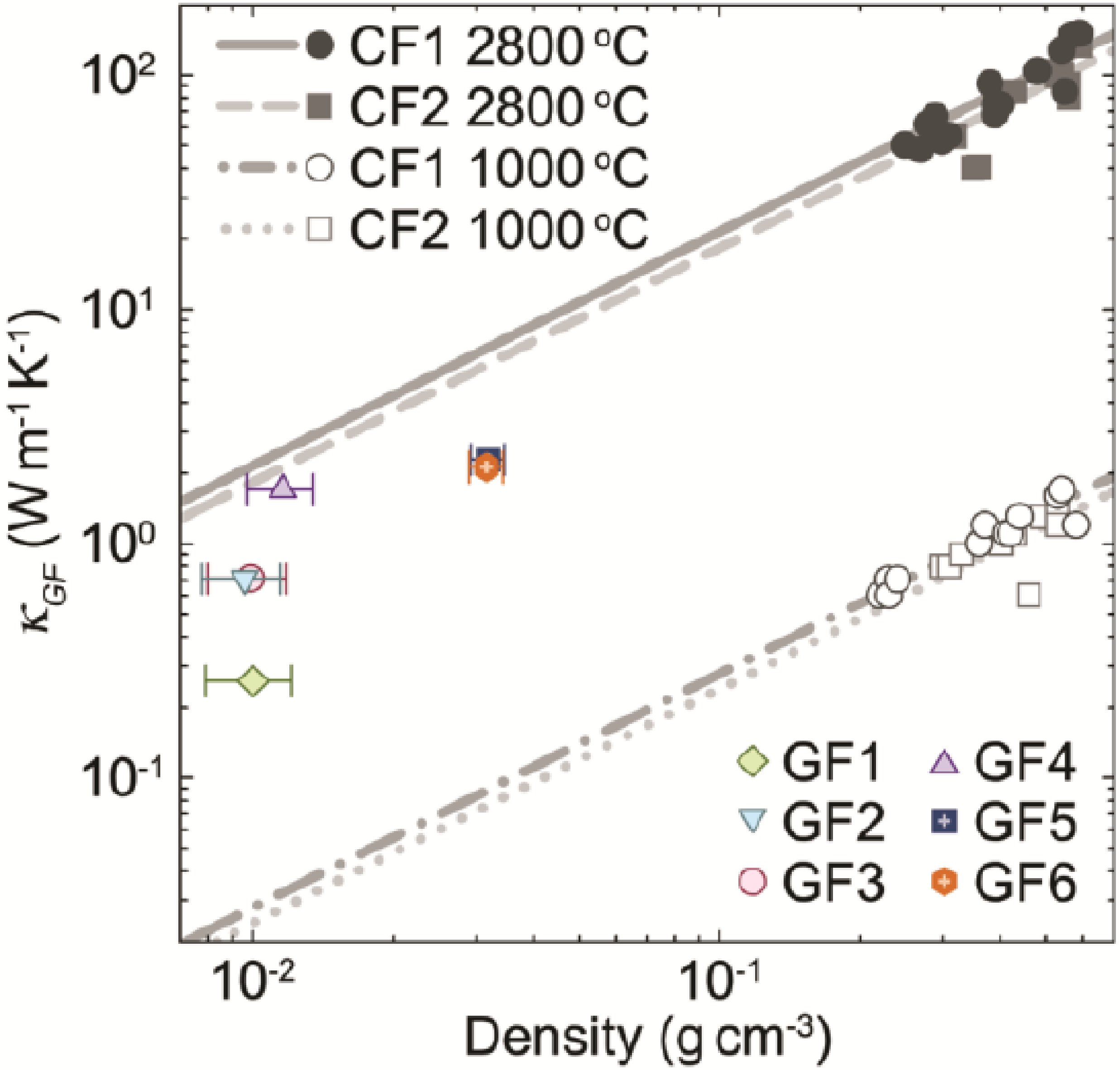
  ~1.4 vol % for GF5-6

- **Metal foam theory:**

$$\kappa_G = 3\kappa_{GF} / \phi$$

- **Lemlich *J. Colloid Interface Sci. 64*, 107–110 (1978)**
- **Schuetz & Glicksman, *J. Cellular Plastics 20*, 114–121 (1984)**

Comparison with Graphitized Carbon Foams



Pettes, Ji, Ruoff, Shi, Nano Letters (2012)

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Summary

- The absence of interlayer phonon scattering in suspended monolayer graphene may result in higher intrinsic basal plane thermal conductivity than that of graphite.

- Contact of graphene with an amorphous solid or organic matrix can suppress phonon transport in graphene.

- The solid thermal conductivity of graphene foam is comparable to HOPG, and the effective thermal conductivity is not limited by internal thermal contact resistance.

Acknowledgement

- Collaboration:

David Broido, Weiwei Cai, Shanshan Chen, Insun Jo, Lucas Lindsey, Hengxing Ji, Anastassios Mavrokefalos, Natalio Mingo, Arden Moore, Michael Pettes, Rod Ruoff, Mir Mohammad Sadeghi, Jaehun Seol, Annie Weathers, Zhen Yao, Feng Zhou

- Support:

NSF

ONR

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