Thermal Management and Electromagnetic Interference Shielding with Graphene and Low-Dimensional Van der Waals Materials

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2D-Tech Webinar
March 2021

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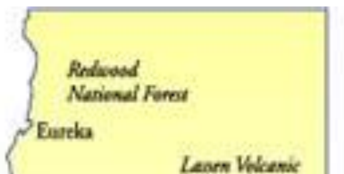

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Outline

Topic: 2D and 1D van der Waals Materials

- *Part I: 2D Materials – Graphene*
  - *Thermal conductivity fundamentals*
  - *Physics of heat conduction in 2D*
  - *Thermal conductivity of graphene*
- *Part II: Practical Applications of Graphene*
  - *Thermal interface materials*
  - *Electromagnetic interference shielding*
- *Part III: 1D Materials – $TaSe_3$*
  - *Current carrying capabilities*
  - *Composites with 1D materials*
- *Outlook*

Fundamentals of Heat Conduction in Graphene and Few-Layer Graphene

Definitions and Basic Theory

Fourier's law:

$$\frac{\dot{Q}}{S} = -K\nabla T$$

Phonon vs. electron conduction:

$$\frac{K_e}{\sigma} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T$$

Heat current carried by phonons :

$$Q = \sum_{q,j} N_{\mathbf{q},i}(\mathbf{q})\hbar\omega_i(\mathbf{q})\frac{\partial\omega}{\partial\mathbf{q}},$$

RT thermal conductivity of important materials:

Silicon (Si): 145 W/mK

SiO_2: 0.5 – 1.4 W/mK

Copper: 385 - 400 W/mK

RT thermal conductivity for carbon materials:

Diamond: 1000 – 2200 W/mK

Graphite: 20 – 2000 W/mK (orientation)

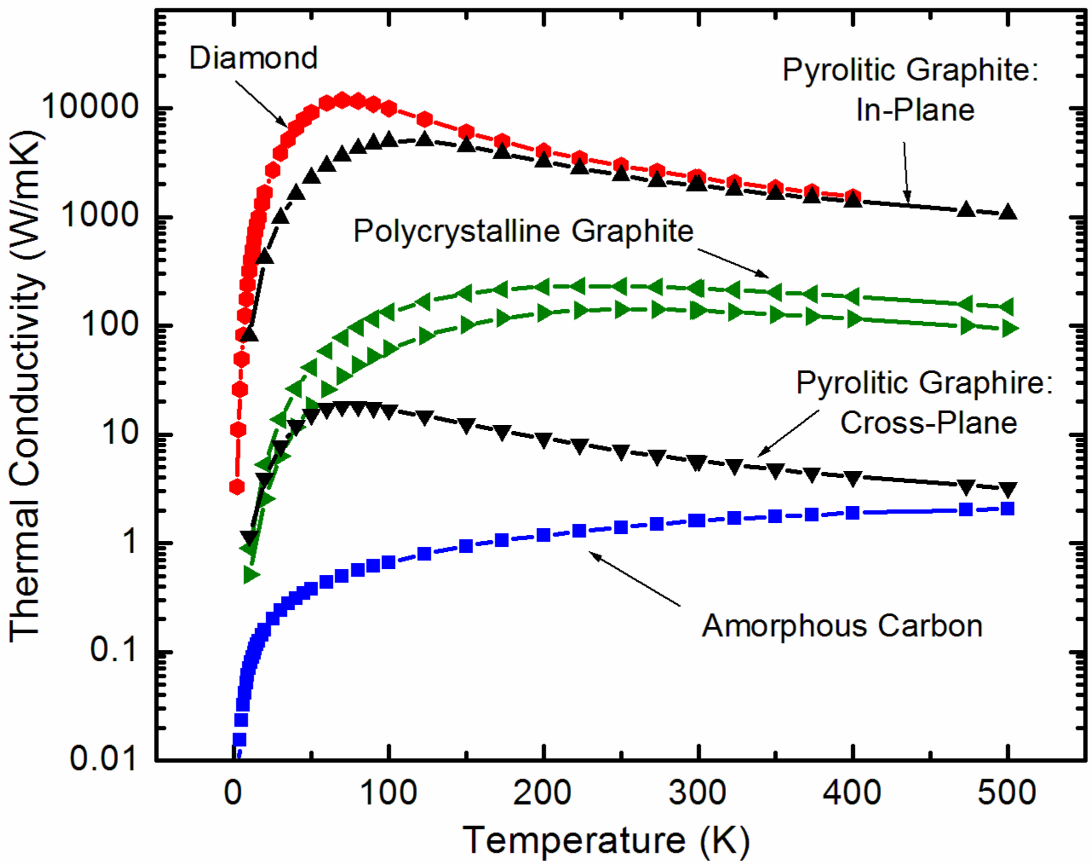
DLC: 0.1 – 10 W/mK

CNT: ~3000 – 3500 W/mK

CNT: ~1758 – 5800 W/mK

According to J. Hone, M. Whitney, C. Piskoti, A. Zettl, A. Phys. Rev. B 1999, R2514 (1999)

Thermal Conductivity of Bulk Carbon Materials



← Bulk graphite: 2000 W/mK at RT

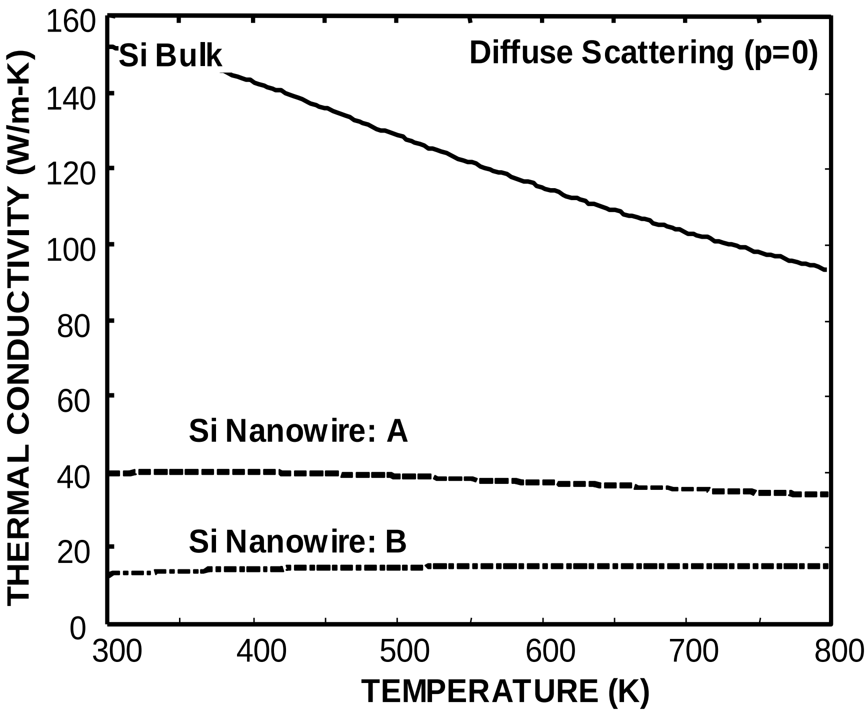
← Order of magnitude difference in high-quality graphite depending on the method and polycrystallinity

A.A. Balandin, "Thermal properties of graphene and nanostructured carbon materials," Nature Materials, 10, 569 - 581 (2011).

What happens with thermal conductivity of 3D crystal if we thin it down to 2D crystal?

Thermal Conductivity at Nanoscale: Extrinsic Phonon Transport Regime

Thermal conductivity usually decreases as one goes from bulk material to nanostructure or thin film



J. Zou and A.A. Balandin, *J. Appl. Phys.*, **89**, 2932 (2001).

←Thermal conductivity of bulk Si at room temperature: K= 148 W/m-K

← Thermal conductivity of Si nanowire with cross section of 20 nm x 20 nm: K=13 W/mK

→ Phonon thermal conductivity:

$$K_p = (1/3)C_p \upsilon \Lambda$$

→ Boundary-limited MFP ($\Lambda = v\tau$):

$$\frac{1}{\tau_B} = \frac{\upsilon}{D}\frac{1-p}{1+p}$$

$$K_p \sim C_p \upsilon \Lambda \sim C_p \upsilon^2 \tau_B \sim C_p \upsilon D$$

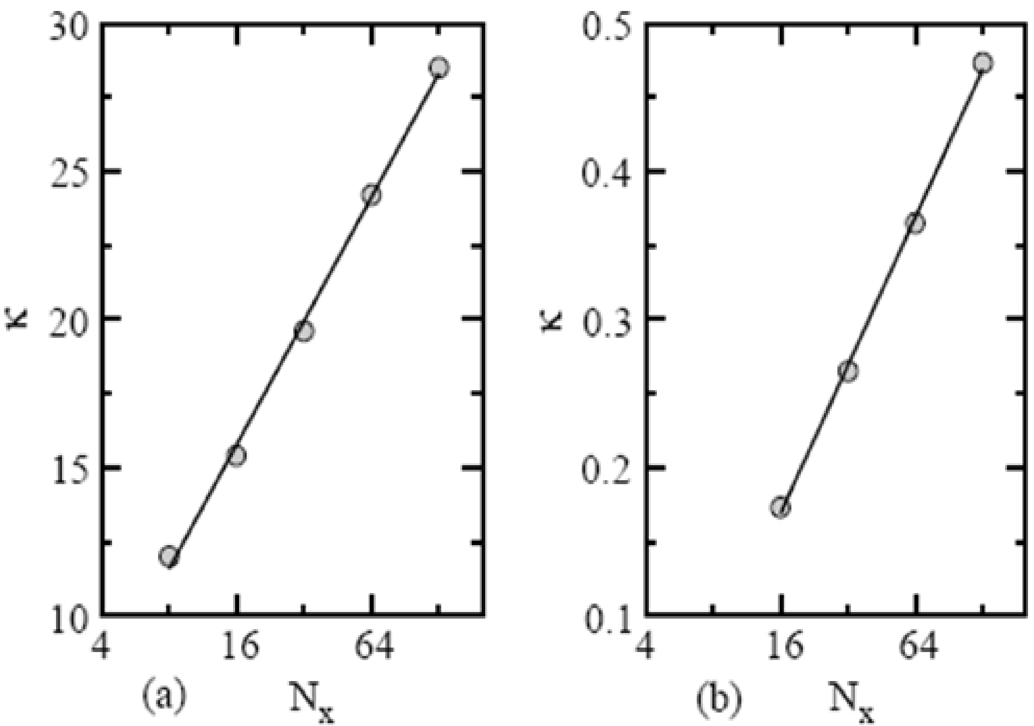
What happens in strictly 2D system?

Thermal Conductivity of 2D Crystals in Intrinsic Phonon Transport Regime: *Infinity*

- → The momentum conservation in 1D and 2D systems with inharmonicity leads to the divergence of the intrinsic thermal conductivity *K* with the system size
- → Thermal conductivity remains finite and does not depend on the system size in 3D

Divergence of the Lattice Thermal Conductivity in 2D and 1D Crystal Lattices

The intrinsic thermal conductivity of 2-D or 1-D inharmonic crystals is anomalous.



Thermal conductivity in 2D lattice vs. N_x.
Data is after S. Lepri et al. Phys. Rep., 377, 1 (2003).

K ~ log(N) in 2D

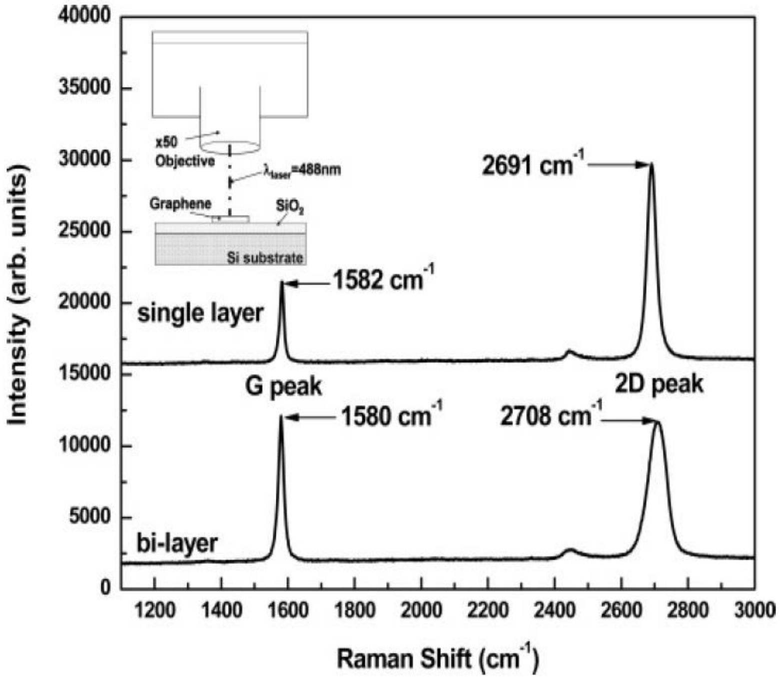
K ~ N^{α} in 1D, $\alpha \neq 1$

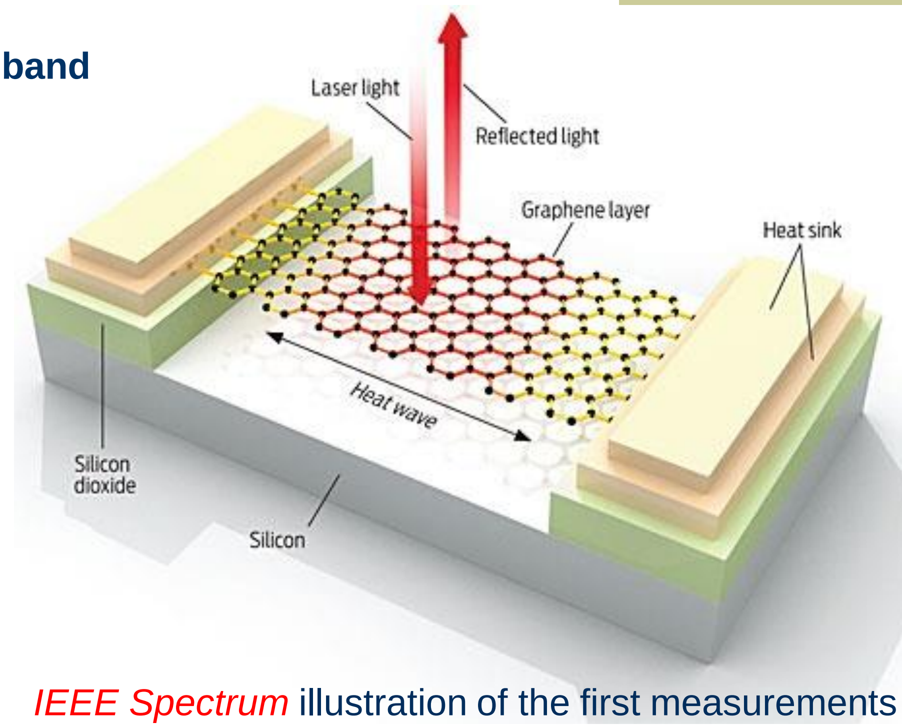
N – system size

[1] K. Saito, et al., *Phys. Rev. Lett.* (2010).
[2] A. Dhar. *Advances in Physics* (2008).
[3] G. Basile et al. *Eur. Phys. J.* (2007).
[4] L. Yang et al. *Phys. Rev. E* (2006).
[5] L. Delfini et al. *Phys, Rev. E* (2006).
[6] S. Lepri et al. *Chaos* (2005).
[7] J. Wang et al., *Phys. Rev. Lett*. (2004).
[8] S. Lepri et al. *Phys. Rep.* (2003).
[9] R. Livi and S. Lepri. *Nature* (2003).
[10] O. Narayan et al., *Phys. Rev. Lett*. (2002).
[11] A. Dhar. *Phys. Rev. Lett*. (2001).
[12] A. Lepri and R. Livi, *J. Stat. Phys*. (2000).
[13] T. Pozen et al., Phys. Rev. Lett. (2000).
[14] S. Lepri et. al. *Europhys. Lett*. (1998).

Converting Raman Spectrometer to Thermometer – The Plan of the Experiment

D band: A_{1g} (~1350 cm^{-1}); ***G peak:*** E_{2g}; ***2D* band**



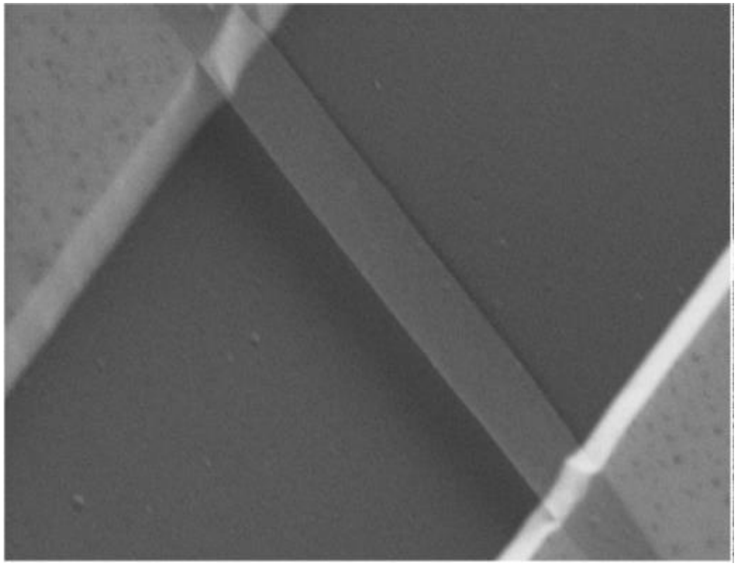


IEEE Spectrum illustration of the first measurements of thermal conductivity of graphene carried out at UC Riverside.

A.A. Balandin, MRS Medal Plenary Talk at MRS Fall Meeting, Boston November 2013.

Details: A.A. Balandin et al., *Nano Letters*, 8, 902 (2008); A.A. Balandin, *Nature Mat.*, 10, 569 (2011).

Optothermal Measurement of Graphene Thermal Conductivity



Bilayer graphene ribbon bridging 3-μm trench in Si/SiO_2 wafer

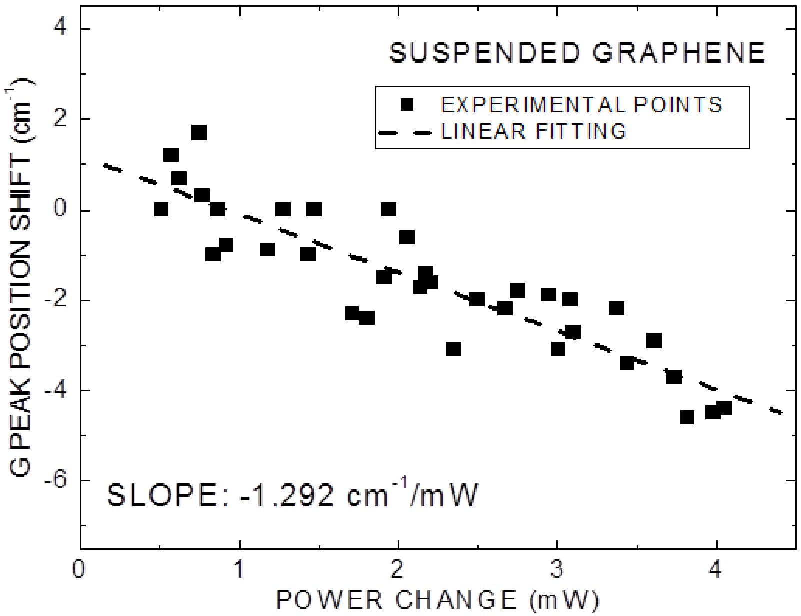
$$K = (L/2a_G W)\chi_G(\Delta\omega/\Delta P_G)^{-1}.$$

Connect ΔP_D ← → ΔP_G through calibration

→ Laser acts as a heater: ΔP_G

→ Raman "thermometer": $\Delta T_G = \Delta\omega/\chi_G$

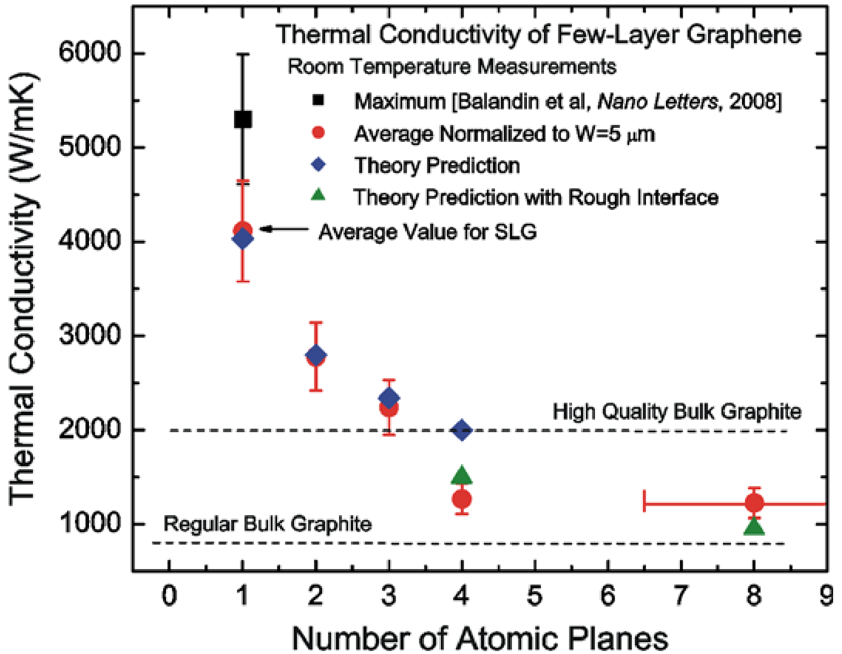
→ Thermal conductivity: $K=(L/2a_G W)(\Delta P_G/\Delta T_G)$



A.A. Balandin, et al., *Nano Letters*, **8**, 902 (2008) – cited 12,400 as of March 2021

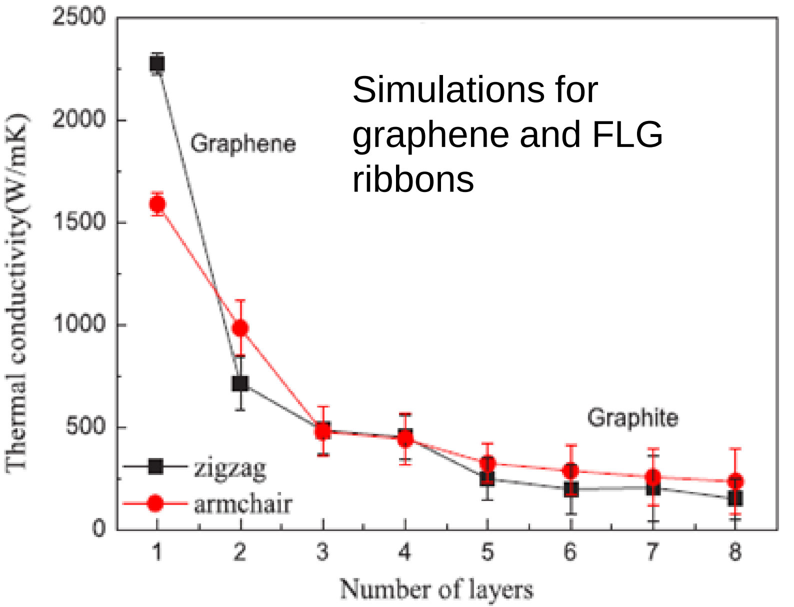
Evolution of the Intrinsic Thermal Conductivity in Low-Dimensional Systems

Experiment and Umklapp Scattering Theory



S. Ghosh, W. Bao, D.L. Nika, S. Subrina, E.P. Pokatilov, C.N. Lau and A.A. Balandin, "Dimensional crossover of thermal transport in few-layer graphene," *Nature Materials*, **9**, 555 (2010).

Molecular Dynamics Simulations



W.-R. Zhong et al., *Appl. Phys. Lett*., **98**, 113107 (2011).

Consistent with the prediction:

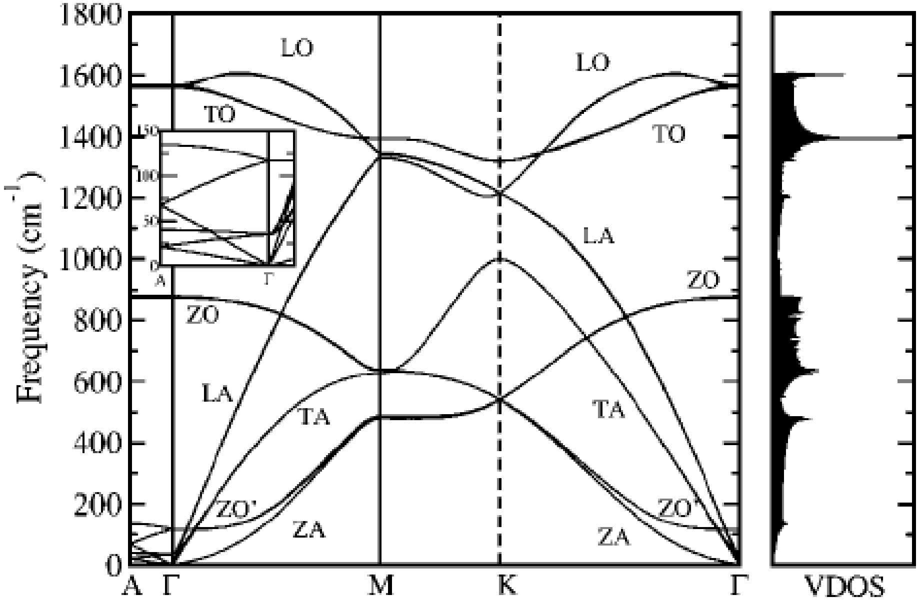
S. Berber,Y.-K. Kwon, and D. Tomanek, *Phys. Rev. Lett*., **84**, 4613 (2000).

Klemens Model of Heat Conduction: Bulk Graphite vs. Graphene

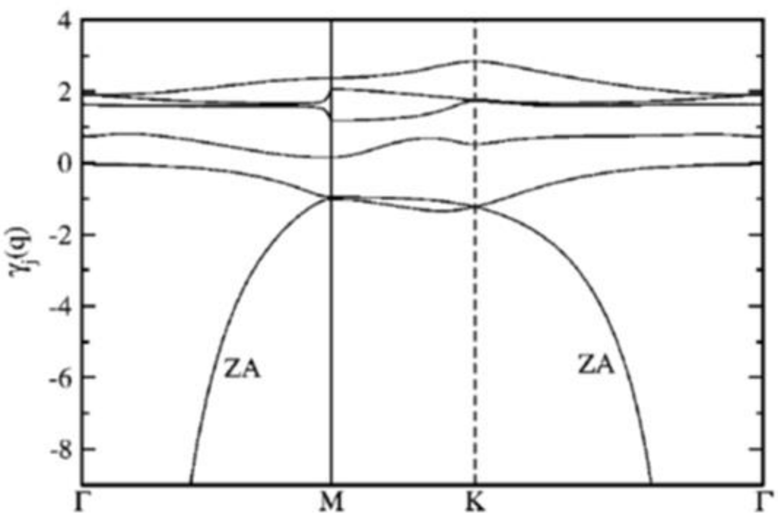
Phonon Thermal Conductivity:

$$K_p = (1/3) C_p \upsilon \, \Lambda$$

$$K_p = \Sigma_j \int C_j(\omega) \upsilon_j^2(\omega) \tau_j(\omega) d\omega$$



P.G. Klemens, *J. Wide Bandgap Materials*, **7**, 332 (2000).



Umklapp life-time, which defines MFP:

$$\tau_{U,s} = \frac{1}{\gamma_s^2} \frac{M \upsilon_s^2}{k_B T} \frac{\omega_{s,\max}}{\omega^2}$$

2D: C(ω) ~ ω → K ~T^{-1}ω^{-1}

3D: C(ω) ~ ω^2

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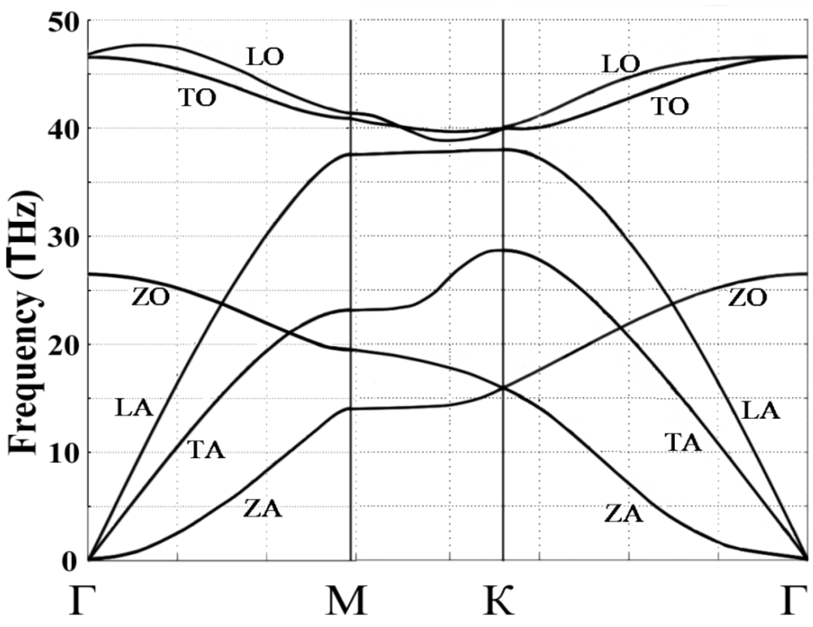
The Role of the Long-Wavelength Phonons in Heat Transport in Graphene

Thermal conductivity in graphene:

$$K \propto \frac{1}{\omega_m} \int_{\omega_C}^{\omega_m} \frac{d\omega}{\omega} \propto \frac{1}{\omega_m} \ln\left(\frac{\omega_m}{\omega_C}\right).$$

Graphene:



MFP = *L* – physical size of the system

→ Limitation on MFL: $L = \tau v_s$

$$\tau_{U,s} = \frac{1}{\gamma_s^2} \frac{M \upsilon_s^2}{k_B T} \frac{\omega_{s,\max}}{\omega^2}$$

→ Limiting low-bound frequency:

$$\omega_{s,\min} = \frac{\upsilon_s}{\gamma_s} \sqrt{\frac{M \upsilon_s}{k_B T} \frac{\omega_{s,\max}}{L}}$$

$$\boxed{\begin{aligned} K &= (2\pi\gamma^2)^{-1} \rho(\upsilon^4 / f_m T) \ln(f_m / f_B), \\ f_B &= \left(M\upsilon^3 f_m / 4\pi\gamma^2 k_B T L\right)^{1/2} \end{aligned}}$$

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Theories of Heat Conduction in Graphene

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PERSPECTIVE

Phononics of Graphene and Related Materials

Alexander A. Balandin

Cite This: *ACS Nano* 2020, 14, 5170−5178

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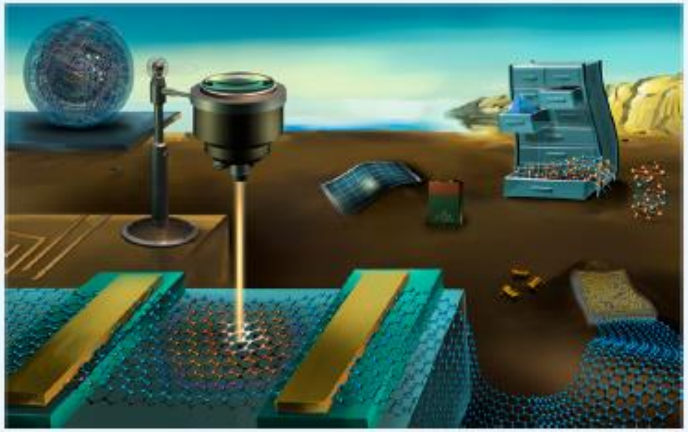
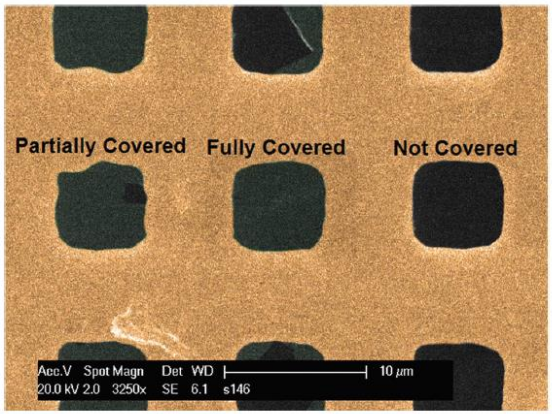
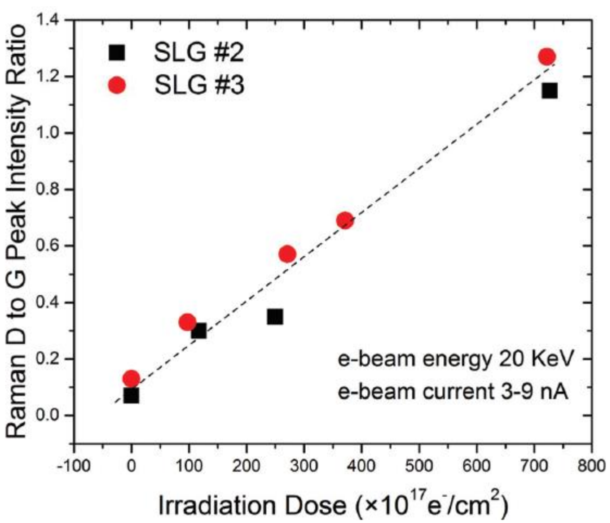
ABSTRACT: In this Perspective, I present a concise account concerning the emergence of the research field investigating the phononic and thermal properties of graphene and related materials, covering the refinement of our understanding of phonon transport in two-dimensional material systems. The initial interest in graphene originated from its unique linear energy dispersion for electrons, revealed in exceptionally high electron mobility, and other exotic electronic and optical properties. Electrons are not the only elemental excitations influenced by a reduction in dimensionality. Phonons—quanta of crystal lattice vibrations—also demonstrate an extreme sensitivity to the number of atomic planes in the few-layer graphene, resulting in unusual heat conduction properties. I outline recent theoretical and experimental developments in the field and discuss how the prospects for the mainstream

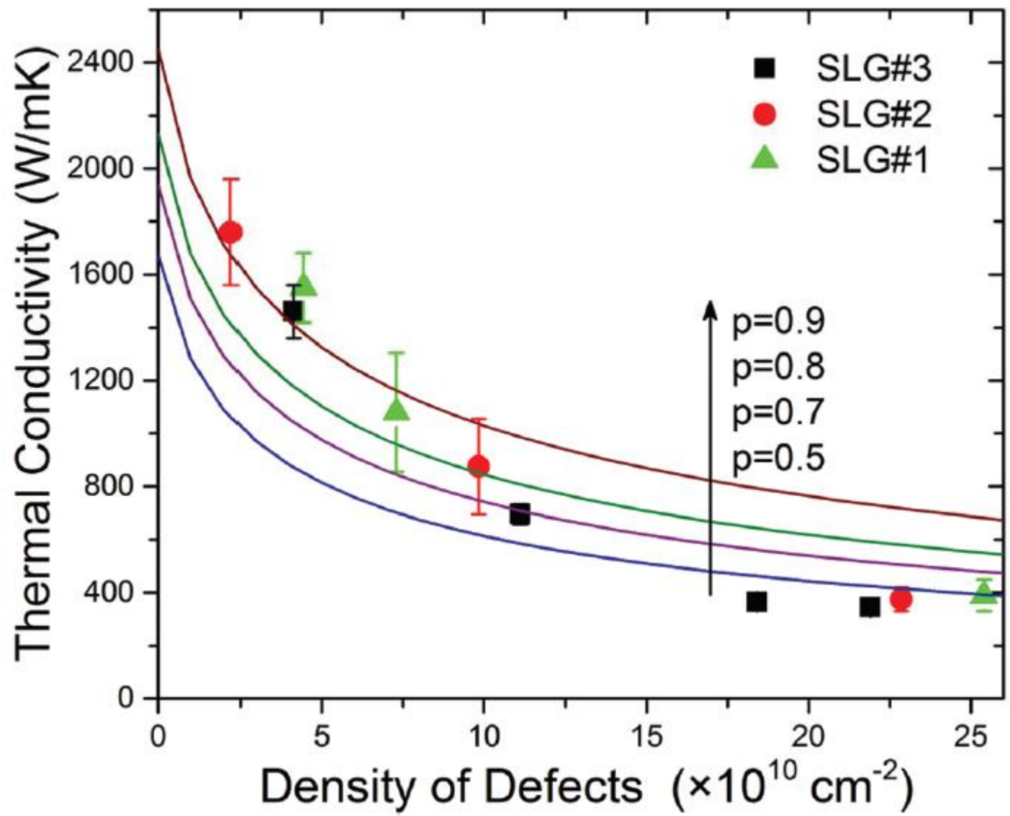


electronic application of graphene, enabled by its high electron mobility, gradually gave way to emerging real-life products based on few-layer graphene, which utilize its unique heat conduction rather than its electrical conduction properties.

Effects of the Defects Introduced by Electron Beam Irradiation







H. Malekpour, et al, Nanoscale, 8, 14608 (2016).

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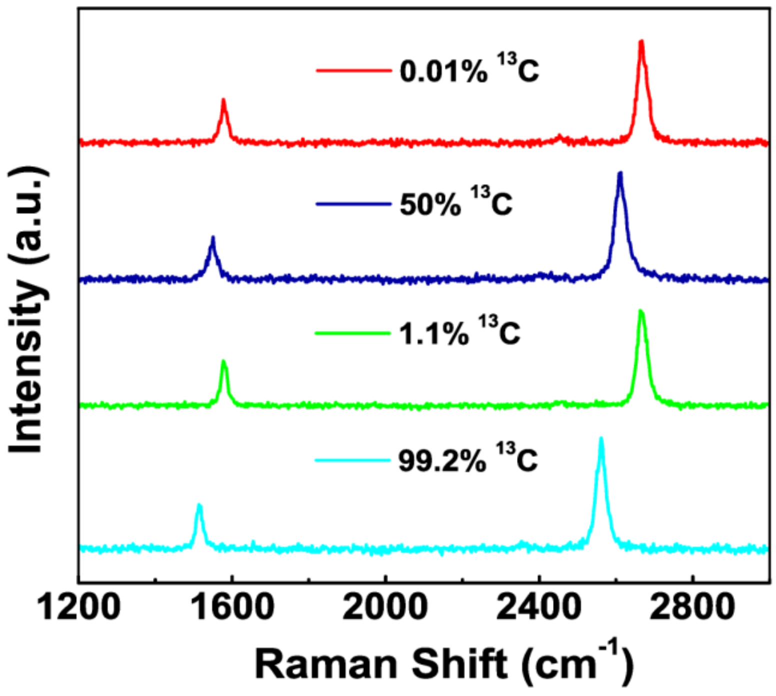
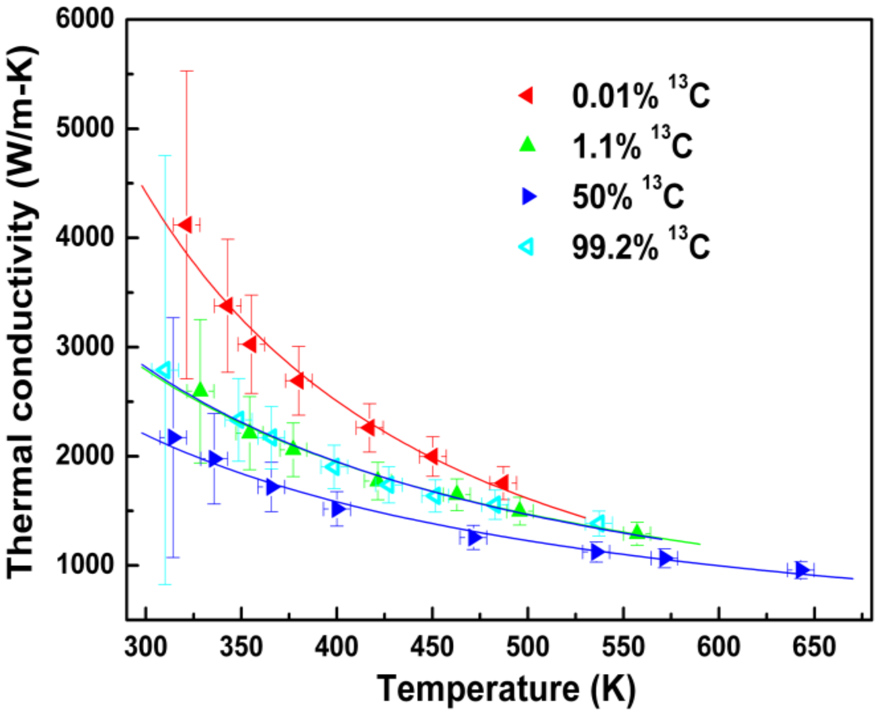
Phonon Transport in Isotopically Engineered Graphene





^{13}C and ^{12}C difference:
~ 64 cm^{-1}

$$\omega \propto M^{-1/2}$$

S. Chen, Q. Wu, C. Mishra, J. Kang, H. Zhang, K. Cho, W. Cai, A.A. Balandin and R.S. Ruoff, "Thermal conductivity of isotopically modified graphene," *Nature Materials*, 11, 203 (2012).

Thermal Management with Graphene

Source: the composite image consists of photos available on Internet

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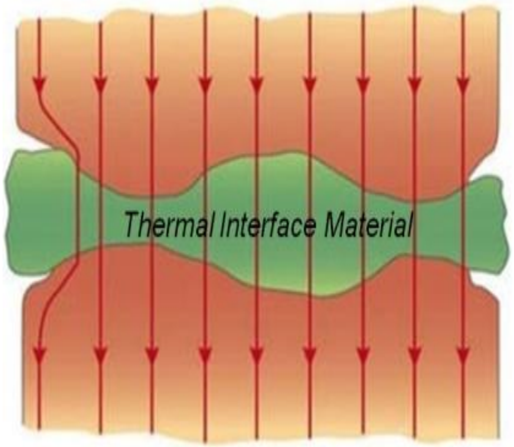
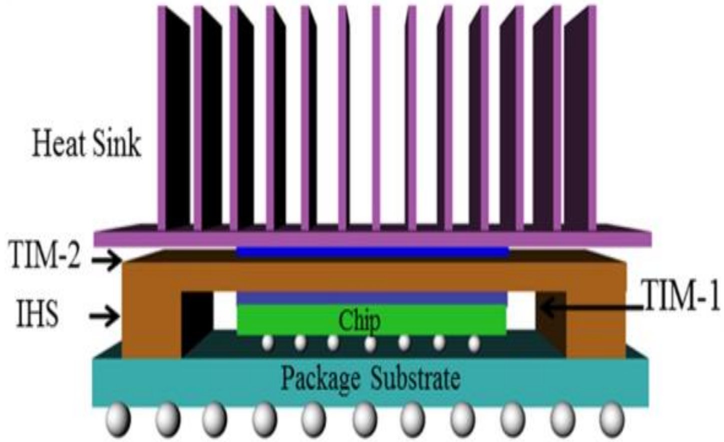
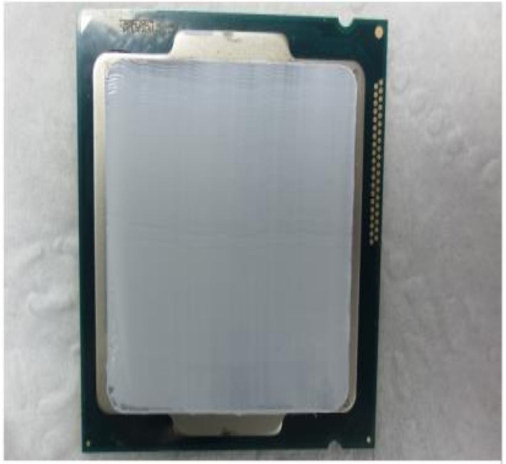
Thermal Interface Materials







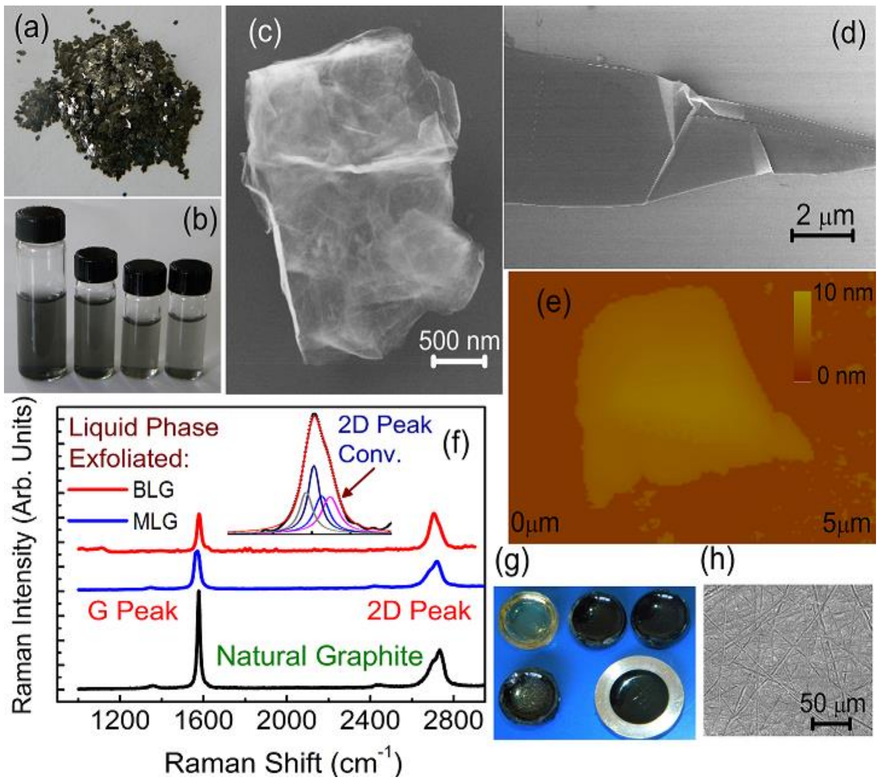
- → Conventional TIMs: K=1-5 W/mK at the volume fractions *f* of filler ~50% at room temperature
- → Companies need K=10-30 W/mK

$$R_{effective} = \frac{BLT}{k_{TIM} A} + R_{c_1} + R_{c_2}$$

Current TIM based on polymer, grease filled with silver, alumina require 50-70% loading to achieve 1-5 W/mk.

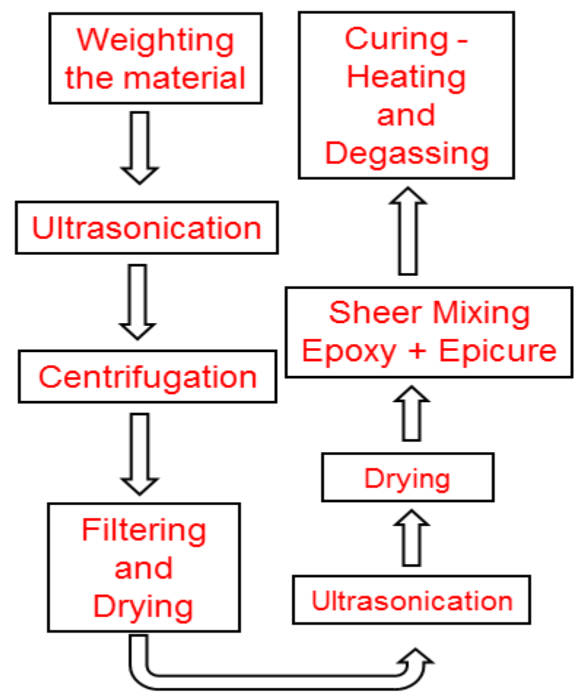
Graphene Enhanced TIMs

What is specifically good about graphene for composites?

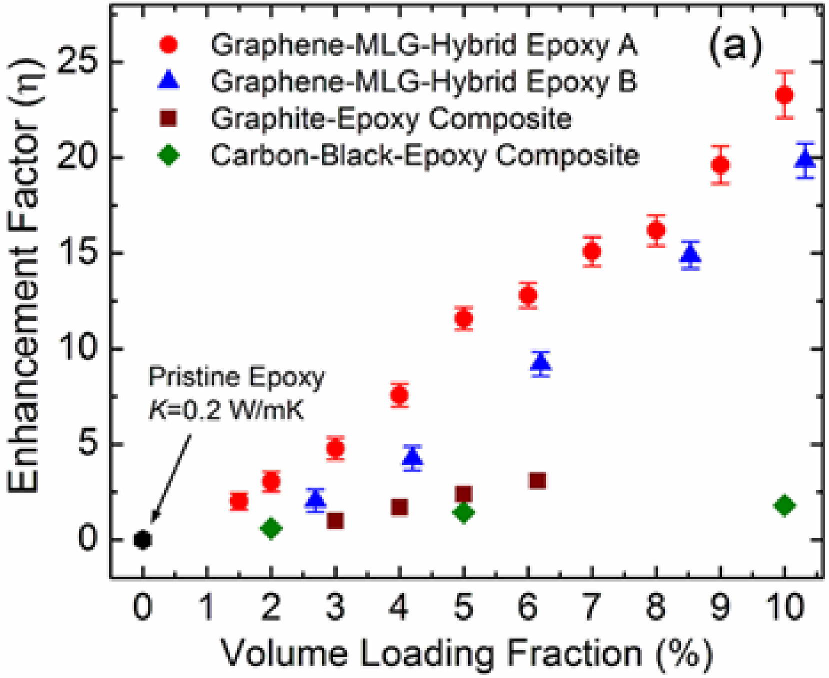


K.M.F. Shahil and A.A. Balandin, "Graphene - multilayer graphene nanocomposites as highly efficient thermal interface materials," *Nano Letters*, 12, 861 (2012).

- Few-layer graphene maintains high thermal conductivity owing to its van der Waals nature
- Better coupling to matrix than CNTs
- Inexpensive mass-production is possible

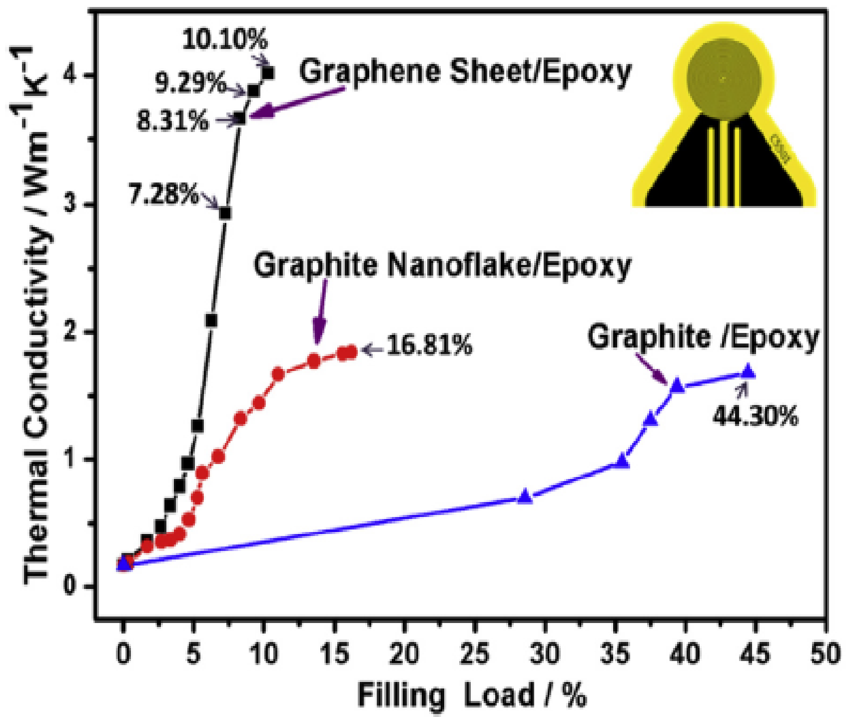


Initial Results: Thermal Interface Materials Base on Epoxy Composites



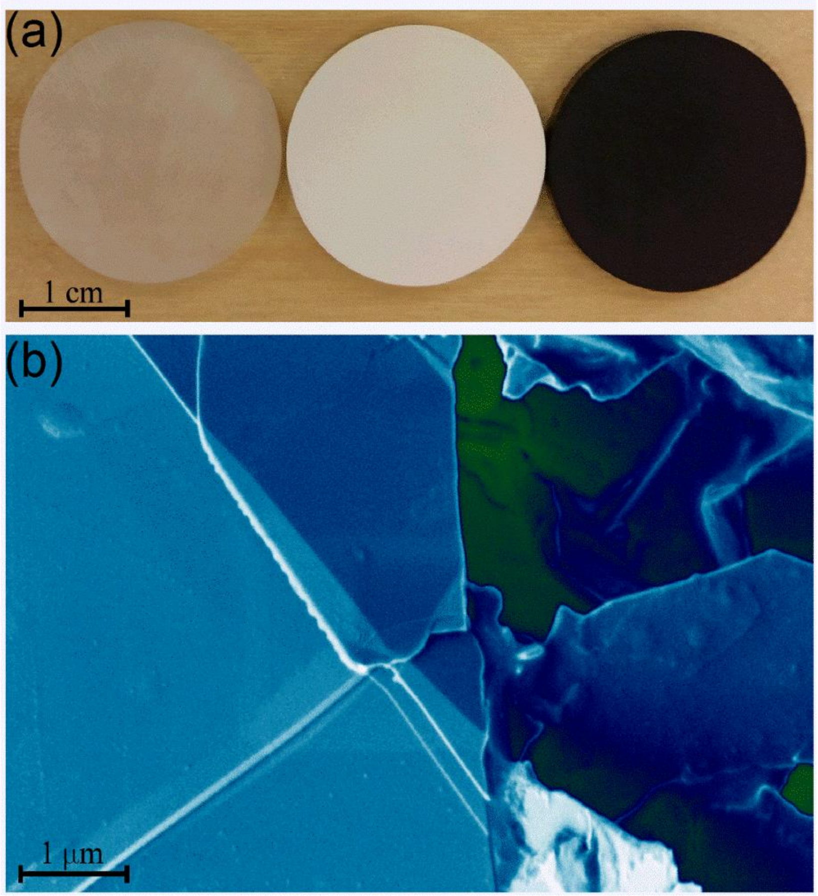
K.M.F. Shahil and A.A. Balandin, "Graphene - multilayer graphene nanocomposites as highly efficient thermal interface materials," *Nano Letters*, 12, 861 (2012).

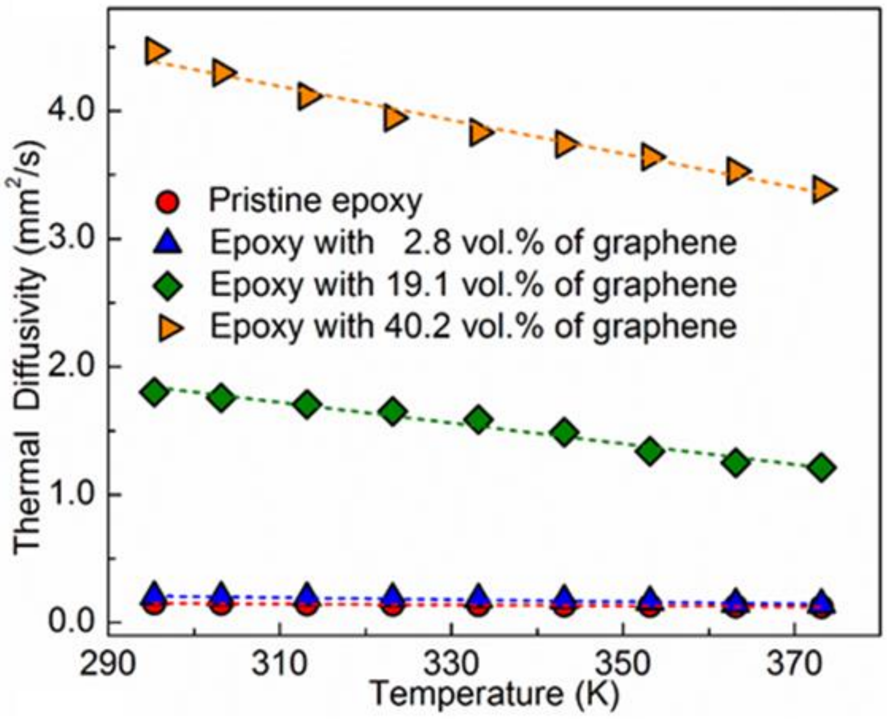
Independent Experimental Confirmation:



Y.-X. Fu et al. / International Journal of Thermal Sciences 86 (2014) 276–283

Composites with Graphene and Boron Nitride





F. Kargar, et al., "Thermal percolation threshold and thermal properties of composites with high loading of graphene and boron nitride fillers," ACS Appl. Mater. Interfaces, 10, 37555 (2018).

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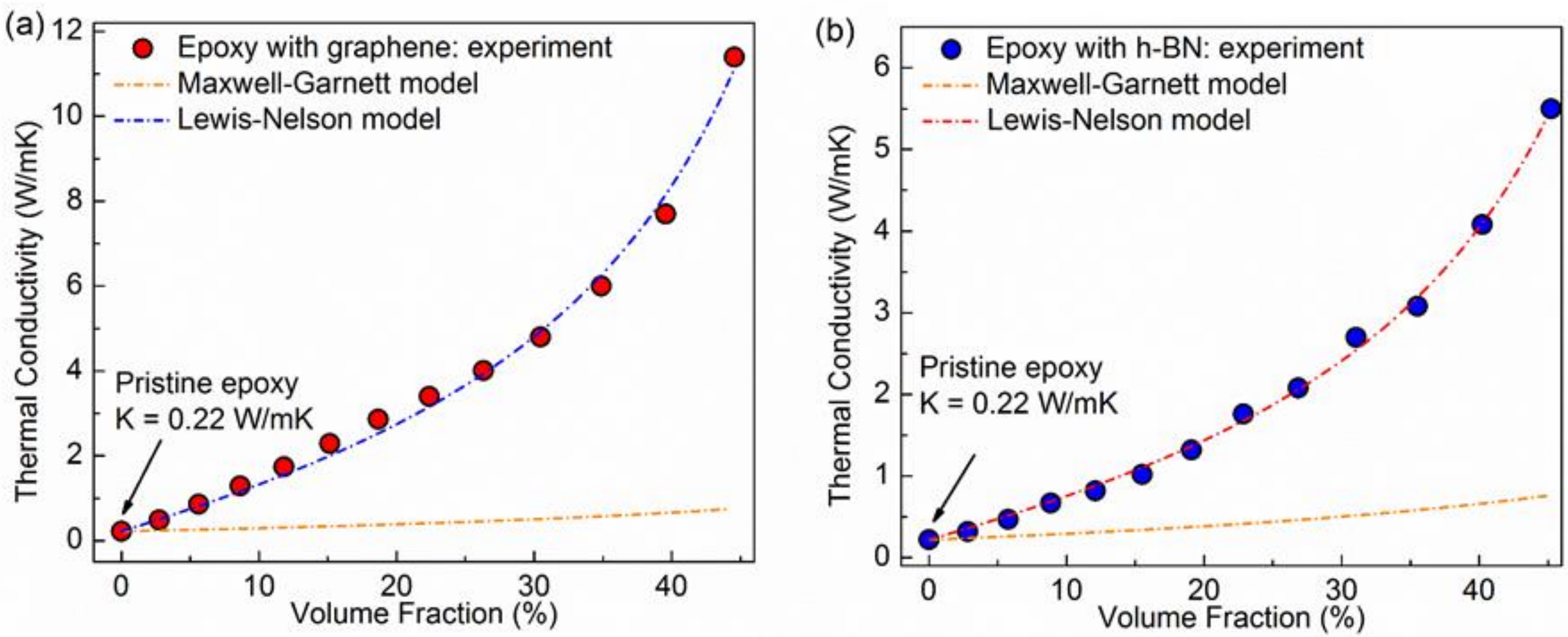
Thermal Percolation Threshold



Thermal conductivity of the epoxy composites with (a) graphene and (b) h-BN fillers. The thermal conductivity depends approximately linear on the loading fraction till $f_T \approx 30$ vol.% in graphene composites and $f_T \approx 23$ vol.% in h-BN composites. The maximum thermal conductivity enhancements of ×51 and ×24 are achieved for the epoxy composites with graphene (f=43 vol.%) and h-BN (f=45 vol.%), respectively.

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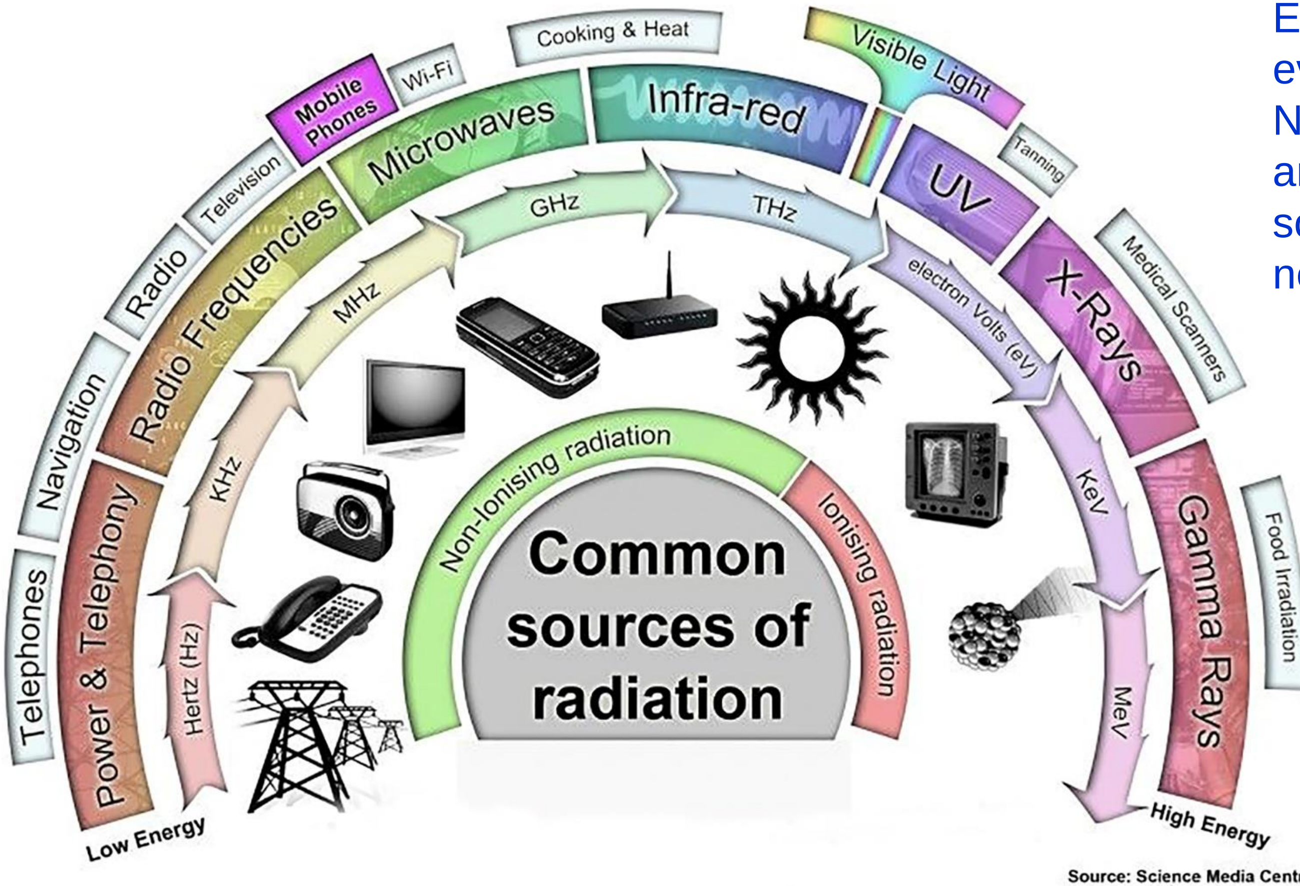
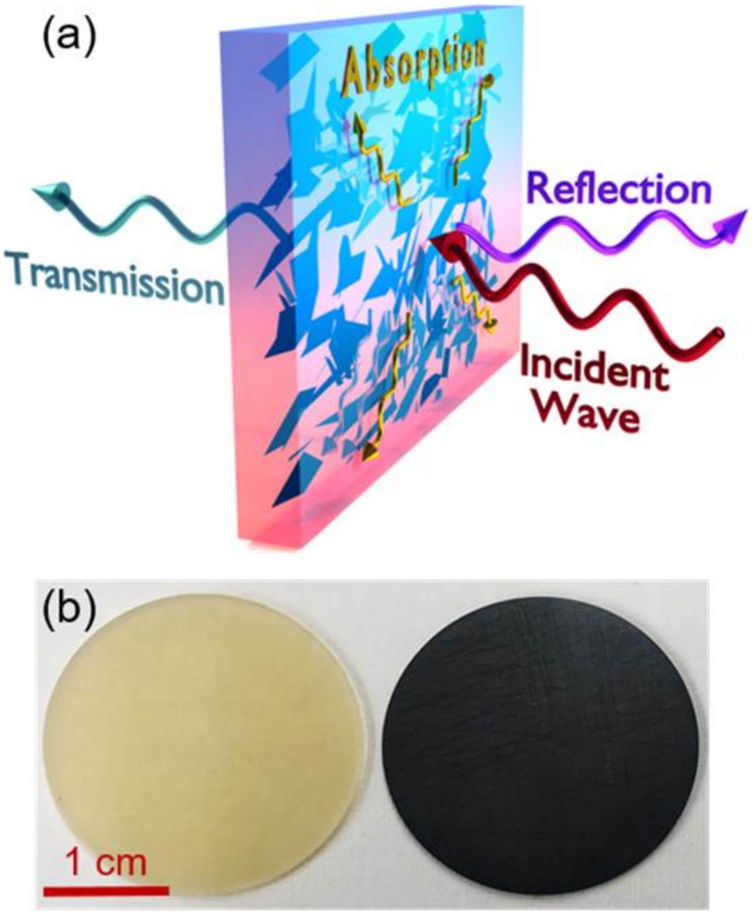
Electromagnetic Interference Shielding



EM waves are everywhere - New materials and technical solutions are needed!

EMI Background and Basics



→ The reflection and transmission coefficients of the EMI shielding composite can be calculated as $R = |S_{11}|^2$ and $T = |S_{21}|^2$.

→ Knowing R and T, one can calculate the absorption coefficient, A, for any incident EM wave as $A = 1 - R - T$.

→ The effective absorption coefficient, $A_{eff} = (1 - R - T)/(1 - R)$ defines the actual absorption characteristic of the EMI shielding material since some part of the incident EM wave energy is reflected at the interface prior to being absorbed or transmitted through it.

→ The total shielding efficiency (SE_{tot}), which defines the ability of the material to block the incident EM radiation, is the sum of the shielding by reflection, $SE_R = -10\log(1 - R)$, and absorption, $SE_A = -10\log(T/1 - R) = 10\log\left(1 - A_{eff}\right)$.

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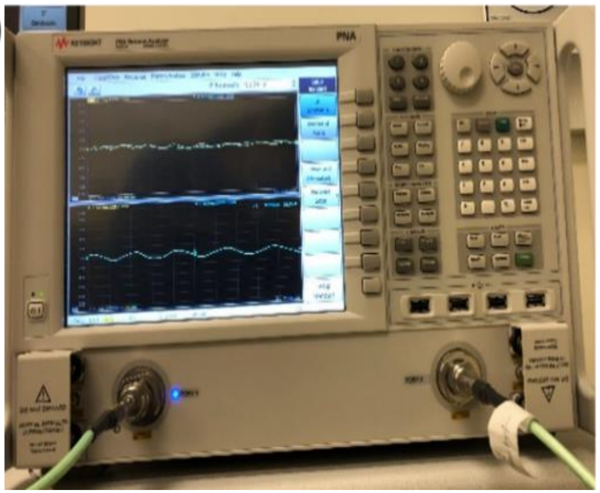
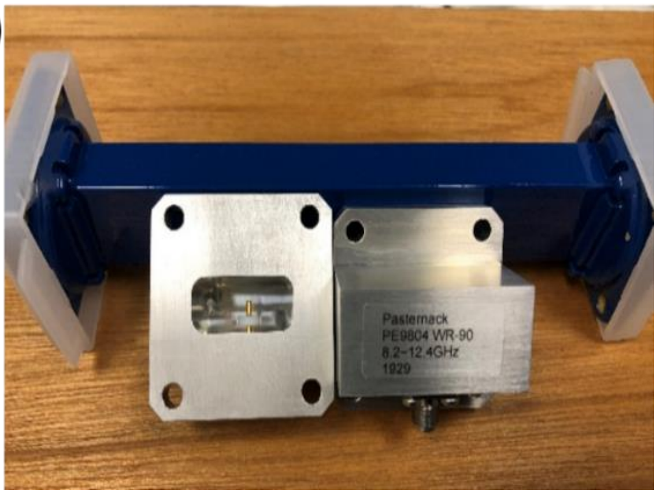
Electromagnetic Interference EMI Shielding – Measurements

X-Band frequency range: 8.2 GHz – 12.4 GHz

(a)



(b)



EMI characteristics - the scattering parameters, S_{ij}, measured using the two-port PNA system.

Extremely High Frequency (EHF) band: 220 GHz – 320 GHz

EMI shielding efficiency was determined from the measured scattering parameters using Agilent N5245A vector network analyzer (VNA) with a pair of frequency extenders

Z. Barani, et al., “Graphene epoxy-based composites as efficient electromagnetic absorbers in the extremely high-frequency band,” ACS Appl. Mater. Interfaces, 12, 28635 (2020).

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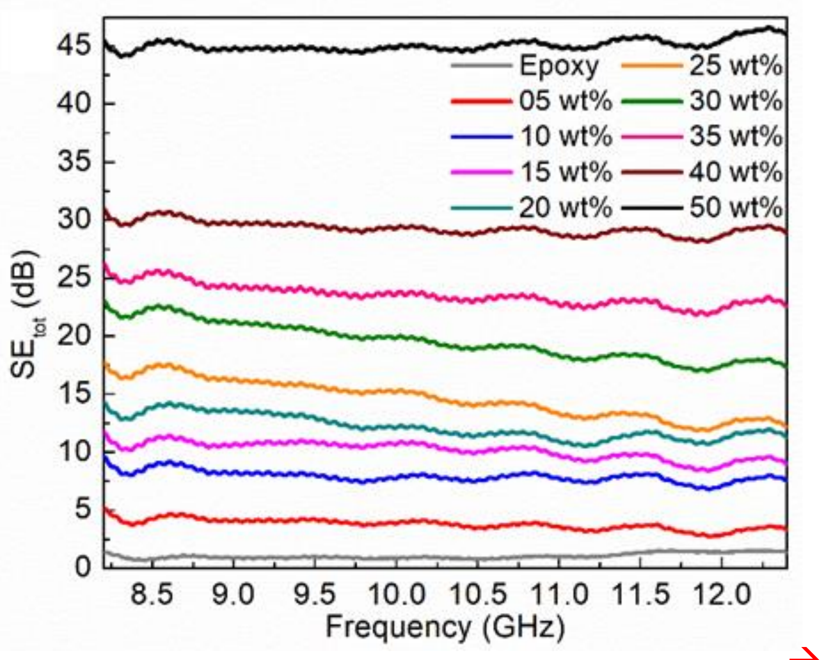
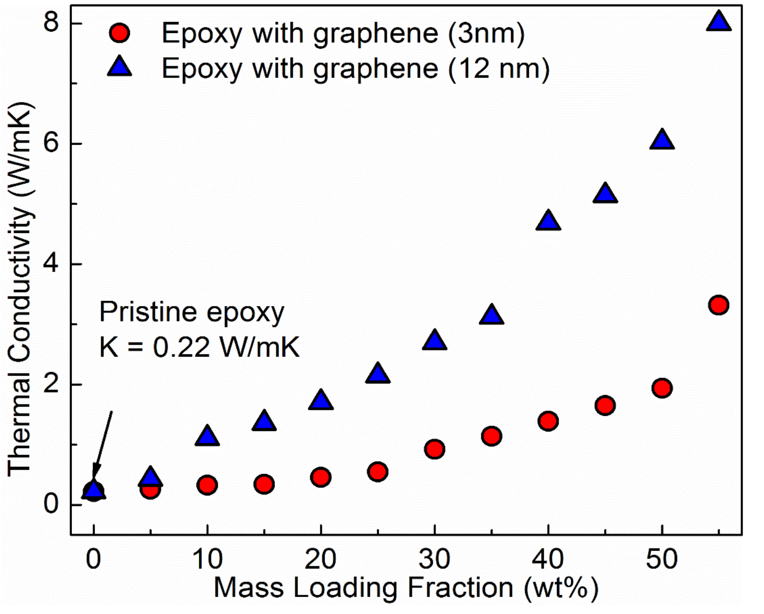
Dual Functionality of Graphene Composites – EMI Shielding and Thermal Management





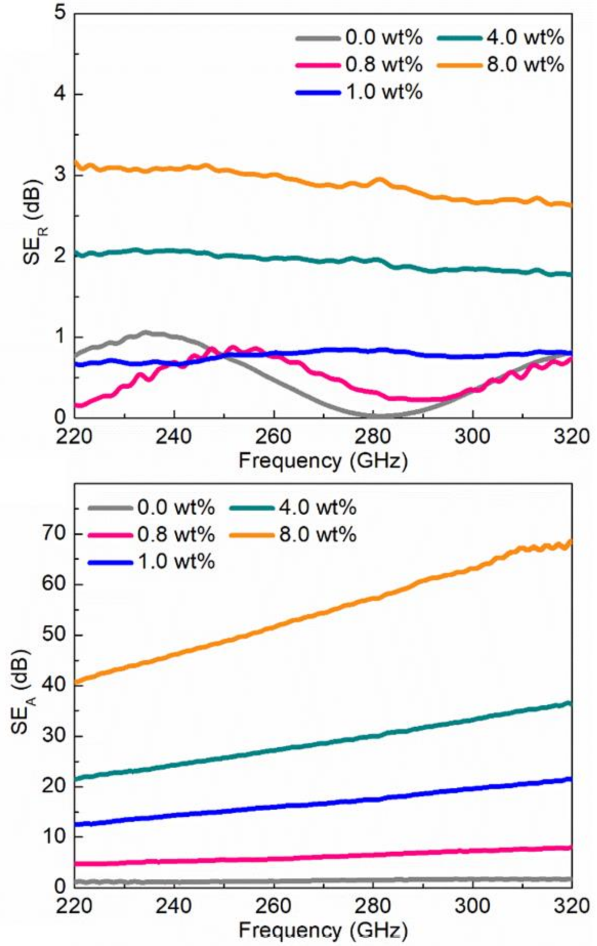
Efficient total EMI shielding, $SE_{tot} \sim 45$ dB, in the X-band frequency range, $f = 8.2$ GHz $- 12.4$ GHz, while simultaneously providing the high thermal conductivity, $K \approx 8$ Wm^{-1}K^{-1}, which is a factor of ×35 larger than that of the base matrix material.

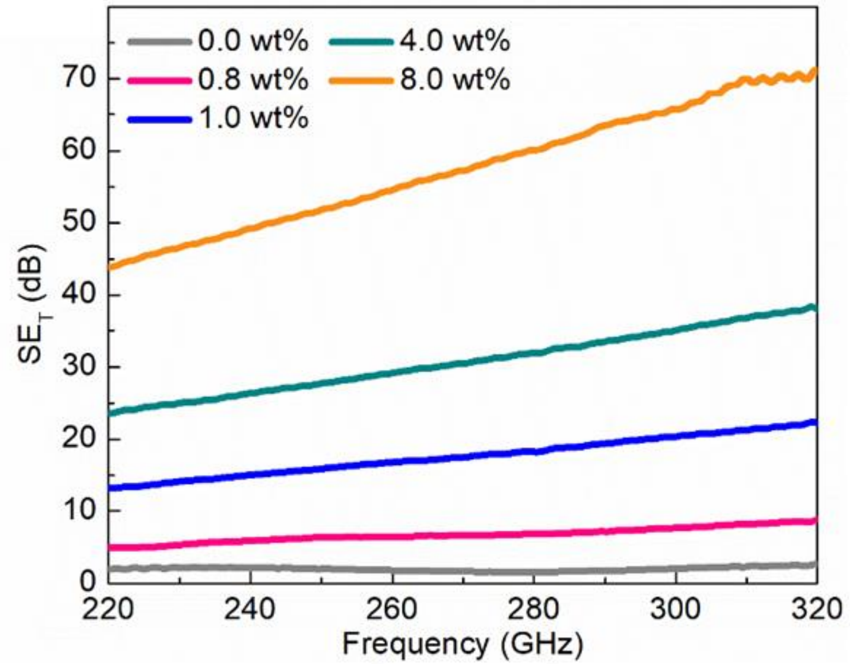
→The composite works even below the electrical percolation threshold – local coupling of EM wave to the filler

→Electrically insulating films can be efficient EMI shield and dissipate the heat

F. Kargar, et al., "Dual-functional graphene composites for electromagnetic shielding and thermal management," Adv. Electron. Mater., 5, 1800558 (2019).

Graphene Composites as EM Absorbers in the Extremely High Frequency Band





→ The main shielding mechanism in composites with the low graphene loading in the sub-THz range is absorption.

Z. Barani, et al., "Graphene epoxy-based composites as efficient electromagnetic absorbers in the extremely high-frequency band," ACS Appl. Mater. Interfaces, 12, 28635 (2020).

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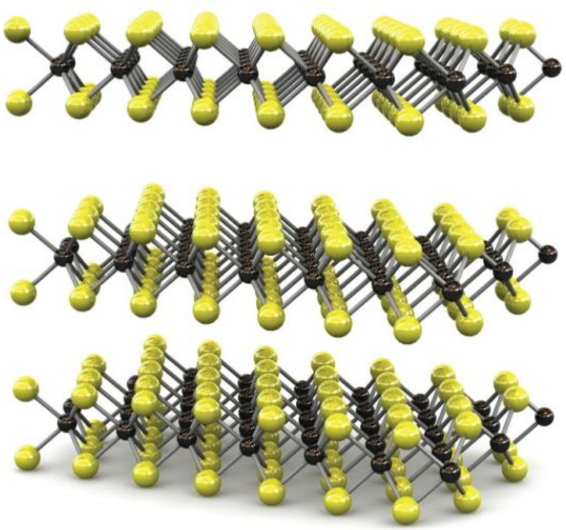
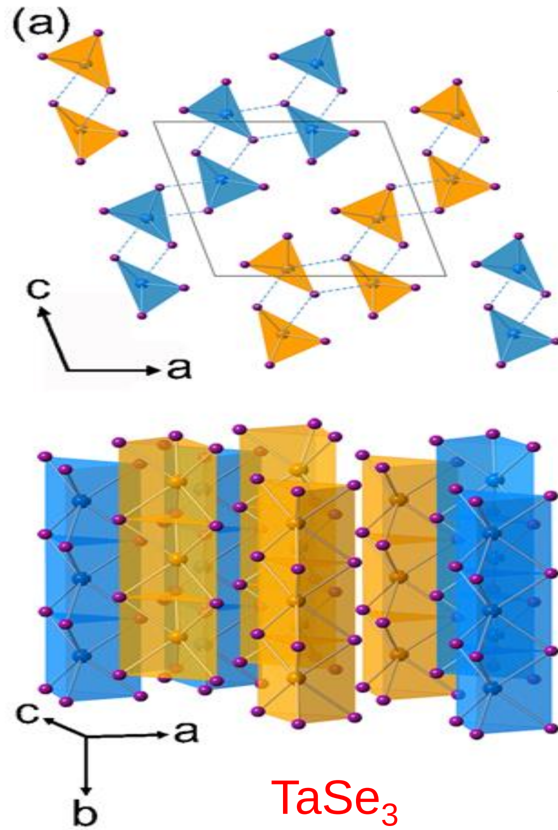
Going from 2D to 1D Van der Waals Materials

Quasi-2D van der Waals Materials



MoS_2



Quasi-1D van der Waals Materials

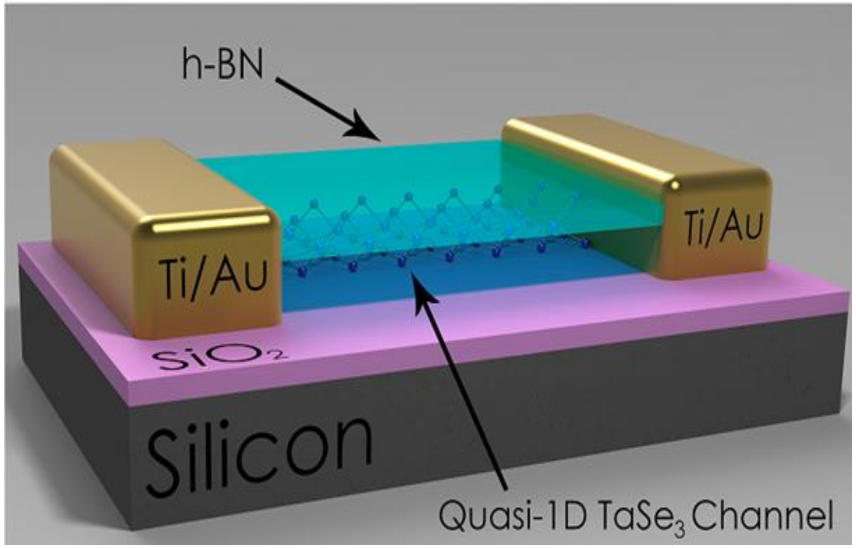
- → Crystal structure of monoclinic $TaSe_3$, with alternating layers of $TaSe_3$
- → Cross section of the unit cell, perpendicular to the chain axis (b axis).
- → The side view: 1D nature of $TaSe_3$ chains along the b axis.

$TaSe_3$

atomic threads

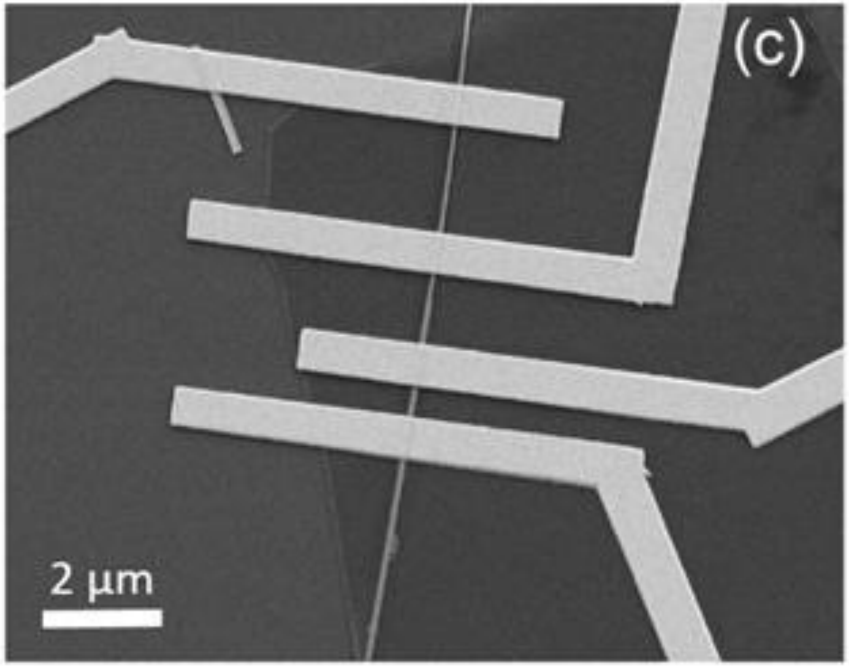
Quasi-1D Channel $TaSe_3$ Devices Fabricated by Electron Beam Lithography

Quasi-1D bundles and BN capping



Schematic of the $TaSe_3$/h-BN quasi-1D / quasi-2D nanowire heterostructures used for the I-V testing.

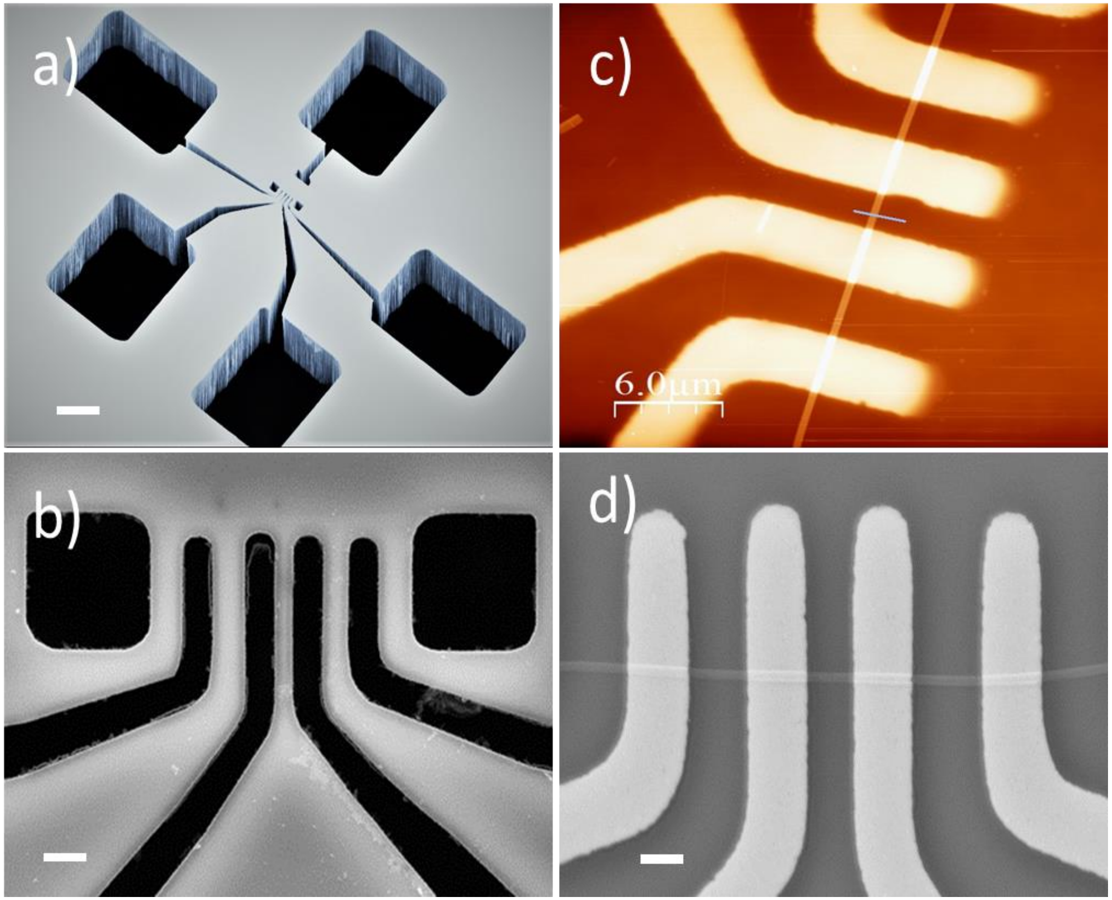
Range: 20 nm to 100 nm



The metals tested for fabrication of Ohmic contacts included combinations of thin layers of Cr, Ti, Au, Pd together with a thicker Au layer.

Alexander A. Balandin, University of California, Riverside

Quasi-1D Channel $ZrTe_3$ Devices Fabricated by Shadow Mask Method



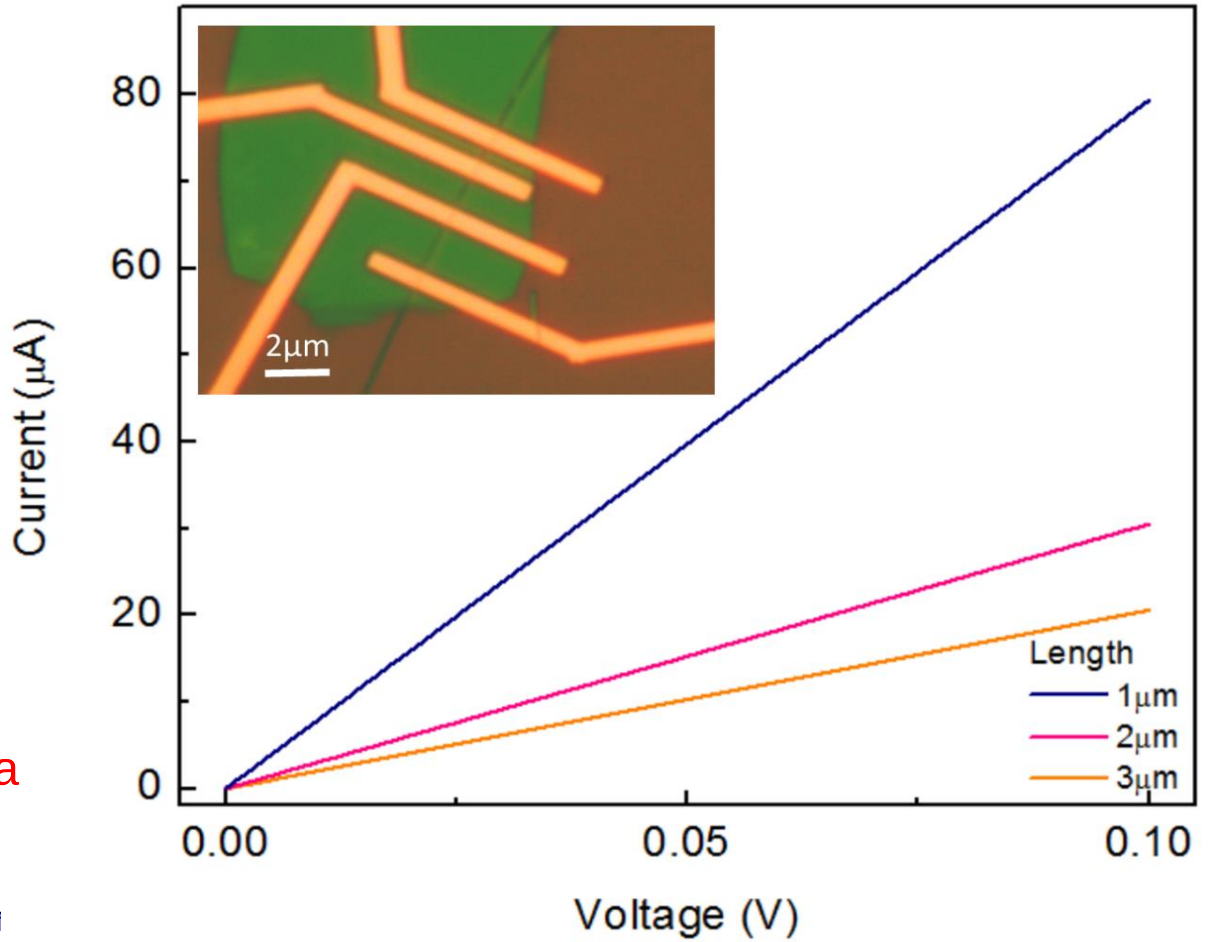
(a) SEM image of a shadow mask. (b) SEM image of the pattern for Ti and Au evaporation to create the contacts. (c) AFM image of the quasi-1D $ZrTe_3$ nanoribbon device. AFM characterization was used to determine the nanowire width and thickness (33-nm in the present case). (d) SEM image of another quasi-1D ZrTe3 nanowire device with a different cross-sectional area. The scale bars in (a), (b) and (d) are 50 μm, 2 μm and 1 μm respectively.

Electrical Characteristics of Devices with Quasi-1D $TaSe_3$ Channels – Ohmic Contacts

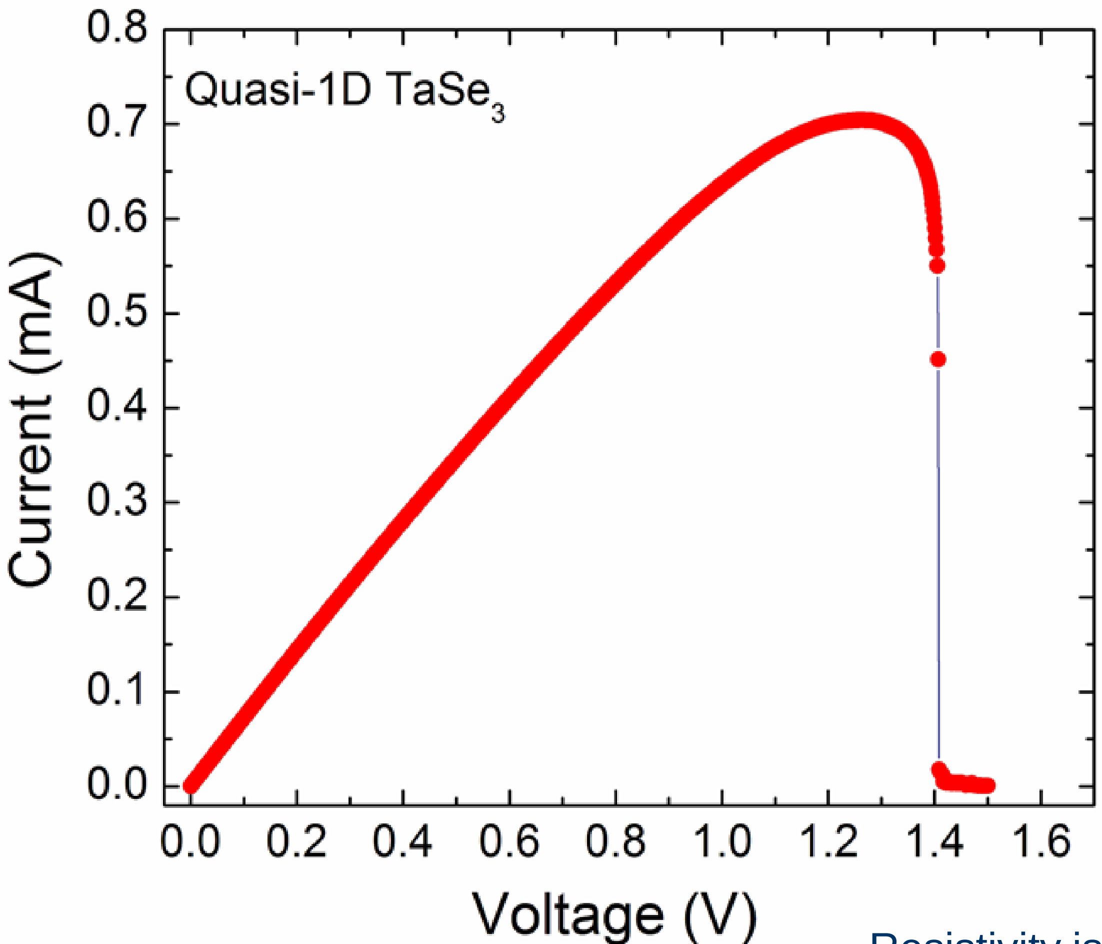
→ Current-voltage characteristics of $TaSe_3$ devices with different channel length.

→ Linear characteristics at low voltage indicates good Ohmic contact of $TaSe_3$ channel with the metal electrodes.

The contact resistance extracted from TLM data is $2R_C$=22 Ω-μm



Current Density in Quasi-1D $TaSe_3$ Nanowires – Bundles of Atomic Chains



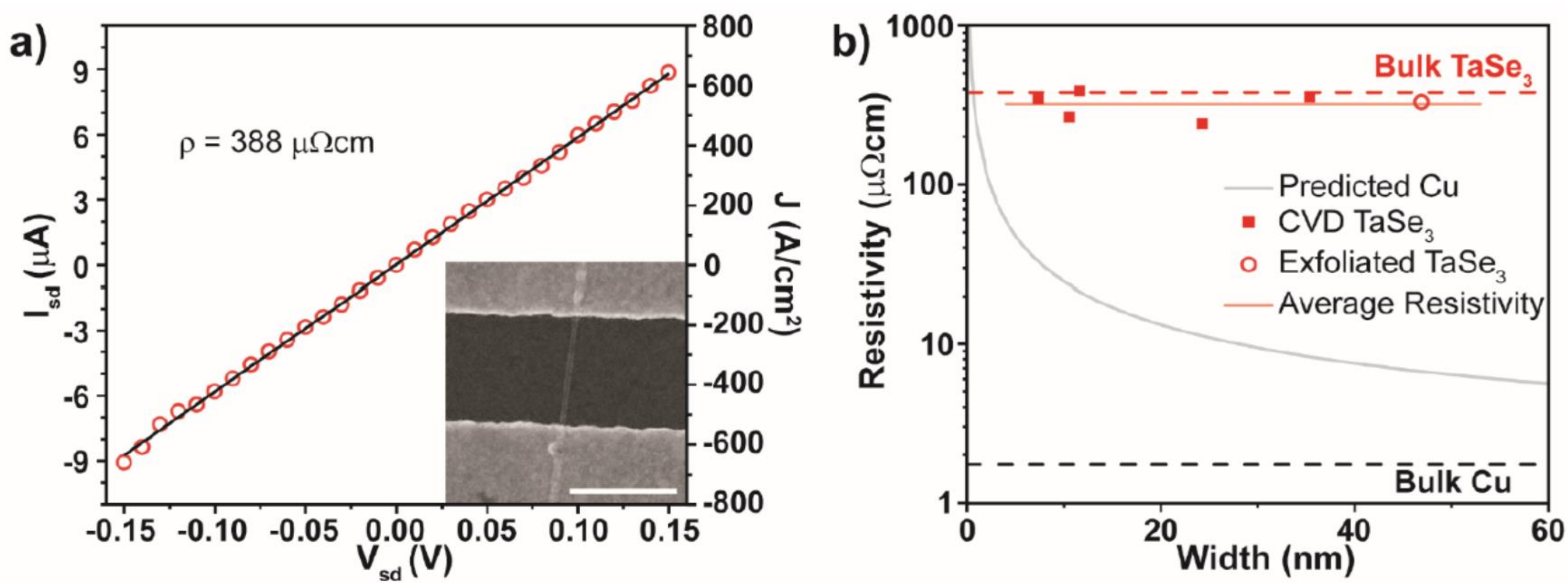
→ High-field I-V characteristics showing the breakdown point. In this specific device the breakdown is gradual.

→ Breakdown current density of about 32 MA/cm^2 — an order-of-magnitude higher than that for copper.

Open question: high currents are sustained in materials with low thermal conductivity

Resistivity is 2.6 – 6.4×10^{-4} Ω-cm.

Testing Prototype Interconnects Implemented with CVD Grown Quasi-1D Bundles of $TaSe_3$



A.A. Balandin and L. Bartels, SRC – Intel Corporation: Task 2796.001
Fabrication and Testing of Quasi-1D van der Waals Metal Interconnects

T. A. Empante, et al., "Low resistivity and high breakdown current density of 10 nm diameter van der Waals $TaSe_3$ nanowires by chemical vapor deposition," Nano Letters 19, 4355 (2019).

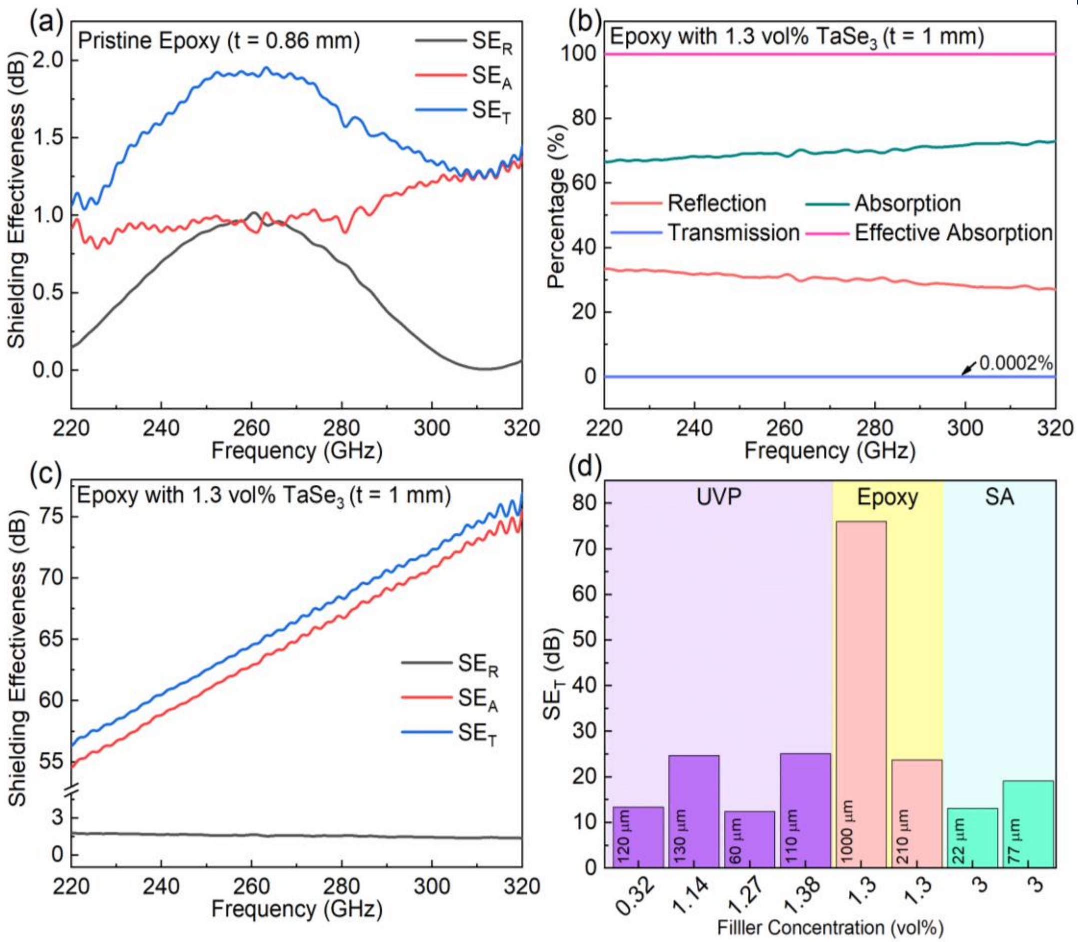
Chemical Exfoliation of Bundles of Quasi-1D van der Waals Materials

Polymer composite films containing fillers comprised of quasi-1D van der Waals materials.

Fillers can exfoliation into bundles of *atomic threads.*

These nanostructures are characterized by extremely large aspect ratios of up to ~10^6.

Electrically-Insulating Films with Quasi-1D Fillers as EMI Shields in Sub-THz



→ The EMI shielding performance of the films with the quasi-1D fillers in EHF-band of sub-THz frequencies: 60 dB to 70 dB.

→ Composite films with only 1.3 vol% loading of exfoliated quasi-1D fillers of TaSe3 and the film thickness of 1 mm.

Z. Barani, F. Kargar, Y. Ghafouri, S. Ghosh, K. Godziszewski, S. Baraghani, Y. Yashchyshyn, G. Cywiński, S. Rumyantsev, T. T. Salguero, and A. A. Balandin, “Electrically insulating flexible films with quasi-1D van der Waals fillers as efficient electromagnetic shields in the GHz and sub-THz frequency bands” Adv. Mater., 2007286, 2021.

Outlook – Take Home Message

- The actual large-scale industrial applications of graphene may not be what you thought they would - think thermal.

- The low-dimensionality game does not end with the 2D van der Waals materials – there are 1D van der Waals materials out there.

Jackets, rackets, hair dye and satellites: How graphene is changing the global economy

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To learn more about applications of 2D and 1D materials visit the group site:

https://balandingroup.ucr.edu/

Acknowledgements

Riverside, California, 2020