Unique Thermal Properties of Graphene:

Implications for Graphene Devices and Electronics





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Profile: experimental and theoretical research in phonon engineering and nanodevices







- Motivations
- Thermal Properties of Graphene
 - Experiments and theoretical interpretation
 - Comparisons with other materials
- Graphene Applications in Thermal Management
 - Lateral heat spreaders and thermal interface materials TIMs
- Graphene Device Applications
 - Transparent electrodes and interconnects
 - Transistors for high-frequency communications
- From Graphene to Topological Insulators
 - Exfoliated topological insulators
 - Device applications of topological insulators
- Conclusions



The Nobel Prize in Physics 2010

The Royal Swedish Academy of Sciences has decided to award the Nobel Prize in Physics for 2010 to

Andre	Geim
University of	Manchester, UK

and

Konstantin Novoselov

University of Manchester, UK

"for groundbreaking experiments regarding the two-dimensional material graphene"

Graphene - the perfect atomic lattice

A thin flake of ordinary carbon, just one atom thick, lies behind this year's Nobel Prize in Physics. Andre Geim and Konstantin Novoselov have shown that carbon in such a flat form has exceptional properties that originate from the remarkable world of quantum physics.

Graphene is a form of carbon. As a material it is completely new – not only the thinnest ever but also the strongest. As a conductor of electricity it performs as well as copper. As a conductor of heat it outperforms all other known materials. It is almost completely transparent, yet so dense that not even helium, the smallest gas atom, can pass through it. Carbon, the basis of all known life on earth, has surprised us once again.



OCTOBER 5, 2010

Using the layer thickness we get a bulk conductivity of $0.96 \times 10^6 \Omega^{-1} \text{cm}^{-1}$ for graphene. This is somewhat higher than the conductivity of copper which is $0.60 \times 10^6 \Omega^{-1} \text{cm}^{-1}$.

Thermal conductivity

The thermal conductivity of graphene is dominated by phonons and has been measured to be approximately 5000 $Wm^{-1}K^{-1}$. Copper at room temperature has a thermal conductivity of 401 $Wm^{-1}K^{-1}$. Thus graphene conducts heat 10 times better than copper.

This year's Laureates have been working together for a long time now. Konstantin Novoselov, 36, first worked with Andre Geim, 51, as a PhD-student in the Netherlands. He subsequently followed Geim to the United Kingdom. Both of them originally studied and began their careers as physicists in Russia. Now they are both professors at the University of Manchester.

http://nobelprize.org/nobel_prizes/physics/laureates/2010/press.html



3200

Practical Motivation: Thermal Bottleneck for CMOS Downscaling



IEEE Spectrum illustration of the thermal issues in the feature article *Chill Out: New Materials and Designs Can Keep Chips Cool* by A.A. Balandin.

100.0 Pentium@ 90.0 Pentium@ II A Pentium@ III 80.0 Pentium® 4 70.0 (Matts) 50.0 40.0 30.0 20.0 10.0 Data is after R. Mahajan et al., Proceed. IEEE (2006) 0.0 400 Frequency (MHz) 0 800 2400 2800 1200 2000

No BIG fan solutions!



→The switch to multi-core designs alleviates the growth in the thermal design power (TDP) increase but does not solve the hot-spot problem

→ Non-uniform power densities leading to hot-spots (>500 W/cm²)



Basics of Heat Conduction

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 :



<u>RT thermal conductivity of important materials:</u> Silicon (Si): 145 W/mK SiO₂: 0.5-1.4 W/mK Copper: 400 W/mK

RT thermal conductivity for carbon materials: Diamond: 1000 – 2200 W/mK Graphite: 200 – 2000 W/mK (orientation) DLC: 0.1 – 10 W/mK CNTs: 3000 – 3500 W/mK → Very wide range of K for carbon materials

depending on their lattice and dimensionality



Degradation of Thermal Conduction in Nanostructures

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

 \rightarrow Phonon thermal conductivity:

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

→ Boundary-limited MFP (Λ = $v\tau$):

$$1/\tau_B = (\upsilon/D)[(1-p)/(1+p)]$$

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

What happens in CNTs and graphene?



Part I: Thermal Conductivity of Graphene





Raman Spectroscopy of Graphene

Visualization on Si/SiO₂ substrates



- \rightarrow low-temperature transport study
- →cross-sectional TEM
- \rightarrow few other costly methods

A.C. Ferrari et al., *Phys. Rev. Lett.* 97, 187401 (2006).
I. Calizo, et al., *Nano Lett.*, 7, 2645 (2007).

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





Temperature Effects on Raman Spectrum – Converting Spectrometer into "Thermometer"

Note: the sign is negative



Temperature is controlled externally; very low excitation power on the sample surface is used (< 0.5 – 1 mW).

Phonon frequency downshift with T is unusual when the bond-bond distances shorten with T since normally lattice contraction leads to the upward shift of the frequencies.



Thermal Conductivity Measurements with Micro-Raman Spectrometer

Idea of the Experiment:

 \rightarrow Induce locale hot spot in the middle of the suspended graphene flake and monitor temperature rise in the middle with increasing excitation laser intensity.



Importance of the Suspended Portion of Graphene

- \rightarrow Formation of the specific in-plane heat front propagating toward the heat sinks
- \rightarrow Reduction in the graphene substrate coupling
- → Determining the fraction of the power dissipated in graphene through callibration procedure

- Graphene Specifics:
- \rightarrow <u>Atomic thickness:</u> good for this method
- \rightarrow <u>Heat transport</u>: diffusive or partially diffusive thermal transport
- \rightarrow In-plane phonon modes: less effect from the substrate and possibility of graphite calibration



Optothermal Method for Measuring Thermal Conductivity of Graphene



Thermal conductivity of rectangular flake (*L* is the half-length):

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

Connect $\Delta P_D \leftarrow \rightarrow \Delta P_G$ through calibration

A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C.N. Lau, *Nano Letters*, **8**: 902 (2008).

- → Laser acts as a heater (confirmed by Stoke Anti-Stoke intensity ratio): ΔP_G
- → Raman "thermometer": $\Delta T_G = \Delta \omega / \chi_G$
- → Thermal conductivity: $K = (L/2a_GW)(\Delta P_G/\Delta T_G)$





Thermal Conductivity of Graphene: Comparison with CNTs and Theory

Sample	K (W/mK) near RT	Method	Comments	Refs
MW-CNT	>3000	electrical self-heating	individual; diffusive	10
SW-CNT	~3500	electrical self-heating	individual; boundary	11
SW-CNTs	1750 - 5800	thermocouples	bundles; diffusive	63
SW-CNT	3000 - 7000	thermocouples	individual; ballistic	64
CNT	1500 - 2900	electrical	individual	65
CNT	~6600	Theory: MD	K _{CNT} < K _{graphene}	66
CNT	~3000	Theory: MD	strong defect dependence	67
SW-CNT	~2500	Theory: BTE	K _{CNT} < K _{graphene}	69
graphene	~2000 - 5000	Raman optothermal	suspended; exfoliated	UCR
FLG	~1300 - 2800	Raman optothermal	suspended; exfoliated; <i>n</i> =4-2	UCR
graphene	~2500	Raman optothermal	suspended; CVD	UTA
graphene	1500 - 5000	Raman optothermal	suspended; CVD	Purdue
graphene	600	Raman optothermal	suspended; exfoliated; T~660 K	CNRS
FLG ribbon	1100	electrical self-heating	supported; exfoliated; <i>n</i> <5	GIT
graphene	600	electrical	supported; exfoliated	UTA
graphene	2000 - 5000	Theory: VFF, BTE, γ(q)	strong width dependence	79
graphene	1 - 5000	Theory: RTA, γ_{TA} , γ_{LA}	strong size dependence	62
graphene	8000 - 10000	Theory: MD, Tersoff	square graphene sheet	80
graphene	1400 - 3400	Theory: BTE	length dependence	69
graphene	~4000	Theory: ballistic	strong width dependence	82



Comparison with Recent Independent Experimental and Theoretical Studies



L. Lindsay, et al., Phys. Rev. B, 82, 161402R (2010);

 \rightarrow Experimental thermal conductivity is above bulk graphite

S. Chen, et al., ACS Nano, 5, 321 (2011).

- ightarrow Theoretical thermal conductivity of graphene is above that of CNTs: ~2500 W/mK at RT for L=3 μ m
- ightarrow Theoretical value is size dependent: Balandin group and Mingo Broido group
- → Ballistic limit for graphene: ~12800 W/mK



Part II: Practical Applications of Graphene

technology review



Communications

Graphene Transistors Do Triple Duty in Wireless Communications

A single graphene transistor that does the job of many conventional ones could lead to compact chips for cell phones.

Friday, October 22, 2010

By Katherine Bourzac

Triple transistor: Single graphene transistors like this one can be made to operate in three modes and perform functions that usually require multiple transistors in a circuit.

Credit: Alexander Balandin



Passive High-Heat Flux Thermal Management



High thermal conductivity materials can be used as lateral hot-spot spreaders or thermal interface materials (TIM)

Issues:

- → Compatibility with Si CMOS technology
- \rightarrow Electrical insulator vs conductor
- \rightarrow Bulk vs nanostructure
- → Anisotropy
- \rightarrow Coefficient of thermal expansion
- \rightarrow Temperature stability

Sample	K (W/mK)	Method	Comments	Reference
diamond	~ 1000 – 2200	3-omega; other	bulk	Berman <i>et al.</i>
MW-CNT	> 3000	electrical	individual	Kim <i>et al</i> .
SW-CNT	~ 3500	electrical	individual	Pop <i>et al</i> .
SW-CNT	1750 – 5800	thermocouples	bundles	Hone <i>et al</i> .

Table : Room-temperature thermal conductivity of best heat conductors

Theoretical Suggestions:

→ Graphene should have very high thermal conductivity; flat geometry is a major benefit

Extra Benefits:

→ Graphene and CNTs can become foundations of the carbon or hybrid Si-carbon electronics 17



Graphene as Interconnects and Laterals Heat Spreaders





580

Experimental Demonstration of Graphene Lateral Heat Spreaders for GaN FETs





I-V characteristics before (solid line) and after (dashed) introducing graphene heat spreader.

→ Red lines were measured at 2V gate bias; Black lines were measured at 0V gate bias; Blue lines were measured at -2V gate bias.





Graphene-on-Diamond Top-Gate Transistors with Enhanced Performance

STUDENT TALK



M. Freitag, et al., *Nano Letters*, 9, 1883 (2008)



Schematic of graphene on diamond top gated devices the green part is the HfO_2 dioxide and the yellow are the metal pads (Ti 10 nm / Au 60 nm).





SEM of the top-gate graphene-on-diamond FET.



Thermal Conduction in Composite Synthetic Diamond – Silicon Substrates





Characteristics of Graphene-on-Diamond Field-Effect Transistors

UNCD: D=5-10 nm

Roughness: ~ 1nm

Leakage: ~1 nA



J. Yu, G. Liu and A.A. Balandin, *Proceedings of IEEE Nano*, Portland, Oregon (2011)

 → Dielectric constants: 5.68 for
 Diamond; 11.7 for Si; 3.9 for SiO₂
 → Typical mobility in graphene-ondiamond FETs is ~ 2500 cm²/Vs for
 holes and ~ 1500 cm²/Vs for electrons



Drain



 \rightarrow Graphene-on-SI revealed the breakdown current density ~ 10⁸ A/cm².

→ Average J_{BR} ~2 x 10⁸ A/cm² for UNCD/Si substrates

→ Order of magnitude improvement in J_{BR} of graphene FETs on the highquality synthetic diamond with larger grains and on single-crystal diamond.



Increasing Importance of the Thermal Interface Materials - TIMs



F. Sarvar et al. Elect. Sys. Technology Conference (2006) http://www.ecnmag.com/tags/products/Materials/



Hybrid Graphene – Nanoparticles Composites as Efficient TIMs

STUDENT TALK



Preliminary Experimental Data

pristine silver epoxy: K~1.67 W/mK

K increases with T

→ Pristine epoxy: K ~0.21 W/mK → Epoxy with graphene: K~ 2.35 W/mK at 4.3 % vol.

 \rightarrow Conventional TIMs: require 50-70 vol % to achieve comparable K



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→ The RT thermal conductivity of silver epoxy increases by ~500% with a graphene loading of ~5 vol %.

→ The RT thermal conductivity of pristine epoxy increases by ~1000% with a graphene loading of ~5 vol %. 24



Graphene – Epoxy Composite as TIMs

Effective Medium Approximation Predictions: Graphene is better than CNTs Preliminary Experimental Data after K.M.F. Shahil and A.A. Balandin, UCR, 2010





Graphene-Polymer TIM Composites: **Comparison with CNT Composites**

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	Interfees		naa Math	a d Dafar	
				Balandin	fr
Graphene	1000%	5.0 vol%	ероху	Balandin Shahil,	e
Graphene	500%	5.0 vol%	silver epoxy	Goyal, Shahil,	€ p
SW-CNT	200%	5.0 wt%	ероху	A. Yu et al.	t
SW-CNT	125%	1.0 wt%	ероху	Biercuk et al.	r
MW-CNT	160%	1.0 vol%	oil	Choi et al	
Filler	Enhancement	Volume Fraction	Base Material	Refs	

Simulation ndings: Kapitza sistance duction is the key better composite IM performance

Graphene ovides strongest hancement at /en volume ction

TBR not s depe the r mate

	Interface	Thermal Resistance	Method	Reference
does	Graphene/SiO ₂	~4 × 10⁻ଃ (Km²/W)	Raman/Electrical	Freitag et al. (2008)
strongly	Graphene/SiO ₂	~(0.6-12) × 10 ⁻⁸ (Km²/W)	Electrical	Chen et al. (2009)
end on	Graphene/SiO ₂	~2 × 10⁻ଃ (Km²/W)	Pump-Probe	Mak et al. (2010)
matrix	Au/Ti/graphene/SiO ₂	~4 × 10 ⁻⁸ (Km²/W)	Raman/Electrical	Koh et al. (2010)
	Bulk Graphite/Metal	~(1 - 3) × 10 ⁻⁸ (Km²/W)	Reflectance	Schmidt et al.(2010)
	Graphene/a-SiO ₂	~4 × 10⁻ଃ (Km²/W)	Theory	Persson et al. (2010)
	Graphene/Oil	~(0.4-4) × 10 ⁻⁸ (Km²/W)	Theory	Konatham (2009)



Graphene as Transparent Electrode for Touch Screens and Flexible Electronics





Flexible graphene sheet with silver electrodes printed on it can be used as a touch screen when connected to control software. Credit: Byung Hee Hong, SKKU.

http://www.technologyreview.com/computing/25633/page1/





Bottom-Gate and Top-Gate Graphene Field-Effect Transistors









Top Gate Function of Single

Layer Graphene Device

22.0u

The fabrication of pads and contact bars was performed using electron beam lithography Cr/Au metal deposition by electron beam evaporator.

Top gate dielectric of \sim 20 nm HfO2 is grown by the atomic layer deposition (ALD). The low-temperature ALD allows for fabrication of the dielectric with low leakage.



Demonstration of the Triple-Mode Graphene Amplifier and Phase Detector



 \leftarrow c) common-drain mode: output has the same frequency and phase as the input; d) frequency multiplication mode: *f* of the output is doubled as compared to *f* of input; e) commonsource mode: the same frequency but 180° shifted as compared to the input.

The graphene circuit can realize the modulation necessary for phase shift keying and frequency shift keying



X. Yang, et al., ACS Nano, **4**, 5532 (2010).²⁹



Electronic Noise Reduction in Graphene Transistors





S. Rumyantsev, G. Liu, W. Stillman, M. Shur and A.A. Balandin, *J. Physics: Condensed Matter*, 22, 395302 (2010).

→The noise level in graphene transistors scales with the graphene channel area, which suggests that the dominant noise source is graphene channel itself.

→ No clear G-R peaks observed in graphene devices.





Graphene vs. CNT Transistors: Flicker Noise Levels





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 \rightarrow Upper bound: number of carriers equal to the number of atoms in CNTs.

- \rightarrow Different role of contacts
- \rightarrow Different exposure to environment

$$\alpha_H = \frac{S_I}{I^2} f N$$

$$\alpha_H \sim 1 - 10$$

Graphene $\alpha_{\rm H} \approx 10^{-3}$



Part II: Dirac Materials: From Graphene to Topological Insulators



 ← D. Teweldebrhan, V. Goyal,
 M. Rahman and A.A. Balandin,
 "Atomically-thin crystalline films and ribbons of bismuth telluride,"
 Applied Physics Letters, 96,
 053107 (2010). - Issue's Cover





"Graphene-Like" Exfoliation of Different Type of Materials



1 μm

D. Teweldebrhan, V. Goyal and A.A. Balandin, "Exfoliation and characterization of bismuth telluride atomic *quintuples* and quasi-2D crystals," *Nano Letters*, 10, 1209 (2010).



Raman Spectroscopy of the Atomically Thin Films of Bi-Te Topological Insulators







K.M.F. Shahil, M.Z. Hossain, D. Teweldebrhan and A.A. Balandin, "Crystal symmetry breaking in few-quintuple Bi_2Te_3 films: Applications in nanometrology of topological insulators," *Appl. Phys. Lett.*, **96**, 153103 (2010).



Room-Temperature Electrical Characterization Bi-Te Atomic Films





Thermoelectric Topological Insulators

Raman Intensity (Arb. Units)



ZT increase by $\sim 140 - 250\%$ at room temperature

The enhancement is expected to be larger at low T





V. Goyal, D. Teweldebrhan and A.A. Balandin, "Mechanically exfoliated stacks of thin films of Bi₂Te₃ topological insulator films", Appl. Phys. Lett. (2010).





Distinguishing between Surface and Volume Transport in Topological Insulator Films



M.Z. Hossain, S.L. Rumyantsev, D. Teweldebrhan, K.M.F. Shahil, M. Shur and A.A. Balandin, "Low-frequency current fluctuations in "graphene-like" exfoliated thin-films of bismuth selenide topological insulators," *ACS Nano*, ASAP (2011).

The absence of scaling of the normalized resistance with the film thickness indicates that surface transport is dominant in the exfoliated films.

Contacts: 20 nm Ti / 180 nm Au 37Resistance: 1 k Ω to 100 k Ω



Topological Insulators as Low-Noise Interconnects





"Carbon World" vs. "Hybrid Carbon-Silicon World" vs. "Dirac World" vs.?



IEEE Spectrum artistic rendering of the hybrid silicon – carbon 3D chip with graphene heat spreaders, interconnects and gtransistors. IEEE Spectrum illustration of the thermal issues in the feature article *Chill Out: New Materials and Designs Can Keep Chips Cool* by A.A. Balandin. **Graphene Applications**

- *→Transparent electrodes*
- \rightarrow Touch screens
- \rightarrow Heat spreaders
- \rightarrow TIMs
- \rightarrow Sensors
- → Super-capacitor electrodes
- → Battery electrodes
- *→High-frequency*
- \rightarrow Interconnects
- \rightarrow Analog, RF, mixed signal



Thermal properties of graphene and nanostructured carbon materials





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