Phononics in Low-Dimensional Materials: Engineering Phonon Spectrum

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Profile: experimental and theoretical research in advanced materials and nano-devices

Phononics Research & Applications
- Electronic Devices and Circuits
- Direct Energy Conversion
- Raman, Fluorescence and PL Spectroscopy
- Optoelectronics
- Bio-Nanotech

Nanoscale Characterization

PI: Alexander A. Balandin
- Thermal and Electrical Characterization
- Device Design and Characterization

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Outline

- **Part I: Overview of Phononics and Phonon Engineering**
- **Part II: Phonons in Graphene**
  - Specifics of 2D phonon thermal transport
  - Engineering phonons by twisting atomic planes
- **Part III: Phonons in van der Waals Materials**
  - Restacking the layers
  - Charge-density waves
- **Part IV: Applications of Phononics**
  - Thermal interface materials
  - Heat spreaders
  - Thermoelectric energy generation
  - Low-power information processing
- **Conclusions**
Part I: Overview of Phononics and Phonon Engineering

Cross sections of polar optical phonon modes with $l = 3, 4$ and for the spherical ZnO quantum dot. Blue and red colors denote negative and positive values of phonon potentials, correspondingly.
**Phononics → Nanoscale Phonon Engineering**

**Definition:** phonon engineering is an approach for modifying the thermal, electrical and optical properties of materials via tuning the phonon characteristics at nanometer scale through the spatial confinement-induced changes in the phonon spectrum.

**Goals:**
- Change in electron–phonon scattering → drift mobility
- Change in phonon group velocity → thermal conductivity
- Control of the phonon energies → optical response

**Tuning Parameters:**
- Crystalline structure
- Dimensions
- Sound velocity
- Mass density
- Acoustic Impedance
- Interface
- Optical phonon frequencies

**Band-structure engineering:** mismatch of \(E_G\)

**Phonon engineering:** mismatch of \(Z = \rho V_{sound}\)

Rytov Model for Folded Phonons in Thinly Laminated Media

\[ \omega = Vq \]

\[ \cos(qD) = \cos\left(\frac{\omega D_1}{V_1}\right) \cos\left(\frac{\omega D_2}{V_2}\right) - \frac{1 + \varsigma^2}{2\varsigma} \sin\left(\frac{\omega D_1}{V_1}\right) \sin\left(\frac{\omega D_2}{V_2}\right) \]

\( V_i \) is the sound velocity in each layer, and \( \varsigma = \rho_2 V_2 / \rho_1 V_1 \) is the acoustic mismatch between the layers, \( D = D_1 + D_2 \) is the period of the superlattice.


Raman spectrum of superlattice. Inset is Rytov-model calculations showing \( q \) of the folded LA peaks. The arrows indicate predicted peak frequencies corresponding to a superlattice period of 52 Å.

The data is after C. Colvard et al., *Phys. Rev. B*, 31, 2080 (1985)

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Bulk vs. Confined Acoustic Phonons


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Thermal Conductivity of Nanostructures Beyond “Classical” Size Effects

“Classical” size effects on heat conduction:
phonon – boundary scattering

Casimir (1938), Berman (1955), Ziman (1960)

Phonon – boundary scattering rate:

\[ \frac{1}{\tau_B} = \zeta \frac{1 - p}{1 + p} \frac{<\nu>}{L} \]

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Significant decrease of the lattice thermal conductivity due to phonon confinement in a free-standing semiconductor quantum well

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Tuning thermal conductivity can be approached with appropriate modification of phonon modes, e.g., phonon engineering.
Thermal Conductivity of Nanowires: Boundary Size Effects


- Predicted decrease of the thermal conductivity from 148 W/m-K in bulk to about 13 W/m-K in 20 nm Si crystalline nanowire at T=300 K (2001).

- Agreement with experimental study: ~ 9 W/m-K in 22 nm nanowire at T=300K; strong diameter dependence; deviation from Debye T^3 law at low T, Majumdar Group, UCB (2003).
Thermal Conductivity Inhibition in Phonon Engineered Nanowires

Models:
- Five-parameter Born-von Karman
- Six-parameter valence-force field

\[ \kappa_{\text{mod}} = 6.76 \text{ W m}^{-1}\text{K}^{-1} \text{ at RT} \]
\[ \kappa_{\text{ref}} = 0.25 \text{ W m}^{-1}\text{K}^{-1} \text{ at RT} \]

K of Si/Ge cross-section modulated nanowires is three orders of magnitude lower than that of bulk Si.

Thermal flux in the modulated nanowires is suppressed by an order of magnitude in comparison with generic Si nanowires.

Modification of phonon spectra in modulated nanowires leading to decrease of the phonon group velocities and localization of the certain phonon modes.

K inhibition is achieved in nanowires without additional surface roughness.


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Electron Mobility in Nanowires: Effect of the Electron Confinement

Assumptions:
- confined electrons (infinite potential well)
- remote ionized impurity scattering

Predictions: mobility increase $> 10^6$ cm$^2$/Vs


GaAs nanowire at $T=200$ K

Assumptions:
- confined electrons (infinite potential well)
- bulk phonons (acoustic and polar optical)
- ground state sub-band only
- ionized impurity scattering

Conclusions: $1/\tau_{ph}$ increases with decreasing $a$
Mobility Calculation in Silicon Nanowires: Bulk vs. Confined Phonons

Momentum relaxation rate due to phonons:

\[
\tau_{\text{ph}}^{-1}(k_z) = \frac{2\pi}{\hbar^2} E_a^2 \sum_q \| \mathbf{\nabla} \cdot \mathbf{u}_q \|^2 \frac{q_z}{k_z} \left[ (N_q + 1) \delta(\varepsilon_{q_z} - \varepsilon_{k_z}) + \hbar \omega_q - \varepsilon_{k_z} \right] + N_{-q} \delta(\varepsilon_{q_z} - \varepsilon_{k_z}) \]

Momentum relaxation rate due to ionized impurities:

\[
\tau_{\text{imp}}^{-1}(k_z) = \frac{2\pi m N_f R_1^2}{\hbar^2 k_z} \left( \frac{Z e^2}{2\pi e_0 e} \right)^2 \left[ \ln(k_z R_1) \right]^2
\]

The low-field electron mobility in the nanowire:

\[
\mu = -\frac{2e}{m} \int_0^\infty \varepsilon^{1/2} \frac{\partial f_0}{\partial \varepsilon} \tau(\varepsilon) d\varepsilon /
\int_0^\infty \varepsilon^{-1/2} f_0(\varepsilon) d\varepsilon
\]

\( f_0(\varepsilon) \) is the electron occupation number given by the Fermi-Dirac distribution. In the non-degenerate case, it is given by a Maxwellian distribution.

\( \mu_i \sim (m^*)^{-5/2} T^{-3/2} \) \( \leftarrow \) acoustic phonons

\( \mu_i \sim (m^*)^{-1/2} N_I^{-1} T^{3/2} \) \( \leftarrow \) ionized impurities

Phonons in a cylindrical nanowire:

\[
\mathbf{u}_{\text{ph},q} = \left[ \left( \frac{dG}{dr_\perp} + q_z \frac{dF}{dr_\perp} \right) e_\rho + i \left( -q_z G(r_\perp) + q_z^2 F(r_\perp) \right) e_z \right] e^{-iq_r}
\]

\[
G^{(n)}(r_\perp) = C_1^{(n)} J_0(q_z r_\perp) + C_2^{(n)} N_0(q_z r_\perp)
\]

\[
F^{(n)}(r_\perp) = C_3^{(n)} J_0(q_z r_\perp) + C_4^{(n)} N_0(q_z r_\perp)
\]

\[
q_z^2 = (\omega/q_e)^2 - q_z^2
\]

\[
q_z^2 = (\omega/q_i)^2 - q_z^2
\]

\[
\omega_q = c_i q
\]

\[
\mathbf{u}_q = \sqrt{\frac{\hbar}{2c_i \rho V}} q \frac{3}{2} e^{-iq_r}
\]
Evolution of Phonon Transport in Nanowires with “Acoustically Hard” Barriers

The size of the circles is proportional to the average divergence of displacement vector.

Contribution of higher energy modes is negligible compared to the shown modes.

“True” acoustic mode changes velocity from that in Si to the diamond.

Contribution of the “true” acoustic mode to scattering decreases with increasing coating thickness.

Phonon Engineering of Electron Mobility in Silicon Nanowires

- At low $T$ the mobility is limited by impurities and is proportional to $T^{1/2}$, while at high $T$ it is limited by phonons and is proportional to $T^{-1/2}$.

- Electron mobility for diamond coated Si nanowire is between the limits corresponding to free-standing and clamped nanowire.

A. A. Balandin and V. A. Fonoberov, "Nanometer-Scale Transistor Architecture Providing Enhanced Carrier Mobility," U.S. Patent 8,097,922
Experimental Evidence of Phonon Confinement Effects in GaN Nanowires

Brillouin-light-scattering measurements and finite-element modeling of vibrational spectra in mono-crystalline GaN nanowires

Experimental Evidence of Phonon Confinement Effects in Nanostructures

“We report the changes in dispersion relations of hypersonic acoustic phonons in free-standing silicon membranes as thin as ~8 nm. We observe a reduction of the phase and group velocities of the fundamental flexural mode by more than 1 order of magnitude compared to bulk values.”


“Thermal conductivities of the sub-20 nm diameter NWs are further suppressed by the phonon confinement effect beyond the diffusive boundary scattering limit.”

Part II: Phonons in Graphene

IEEE Spectrum illustration of the discovery of unique thermal properties of graphene at UC Riverside (IEEE Spectrum, October, 2009)
Optical Phonons in Graphene: Raman Spectroscopy

Visualization on Si/SiO₂ substrates

- **D band**: A₁g (~1350 cm⁻¹); **G peak**: E₂g; **2D band**

Other techniques:

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

Temperature Effects on Raman Spectrum – Converting Spectrometer into “Thermometer”

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.

Optothermal technique for measuring thermal conductivity of graphene
Raman Optothermal Measurement Procedure for Graphene

- Laser acts as a heater: $\Delta P_G$
- Raman “thermometer”: $\Delta T_G = \Delta \omega / \chi_G$
- Thermal conductivity: $K = (L / 2a_GW)(\Delta P_D / \Delta T_G)$

Bilayer graphene ribbon bridging 3-µm trench in Si/SiO$_2$ wafer

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

Connect $\Delta P_D$ to $\Delta P_G$ through calibration


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Evolution of the Intrinsic Thermal Conductivity in Low-Dimensional Systems


Experiment and Umklapp Scattering Theory

Nonequilibrium Molecular Dynamics Study

Simulations for graphene and FLG ribbons


Consistent with the prediction:

Phonons in Isotopically Engineered Graphene

The thermal conductivity, $K$, of isotopically pure $^{12}$C (0.01% $^{13}$C) graphene was higher than 4000 W/mK at $T \sim 320$ K and more than a factor of two higher than in 50%-50% $^{12}$C and $^{13}$C graphene.

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

Klemens Model of Heat Conduction: Bulk Graphite vs. Graphene

Phonon Thermal Conductivity:

\[ K_p = \sum_j \int C_j(\omega) \nu_j^2(\omega) \tau_j(\omega) d\omega \]


Umklapp life-time, which defines MFP:

\[ \tau_{U,s} = \frac{1}{\gamma_s^2} \frac{M \nu_s^2}{k_B T} \frac{\omega_{s,max}}{\omega^2} \]

2-D: \( C(\omega) \sim \omega \rightarrow K \sim T^{-1}\omega \)

3-D: \( C(\omega) \sim \omega^2 \)

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

Thermal conductivity in graphene:

\[ K \propto \int_{\omega_m}^{\omega_c} \frac{d\omega}{\omega} \int_{\omega_m}^{\omega_c} \frac{1}{\omega_m} \ln\left(\frac{\omega_m}{\omega_c}\right) \]

Graphene:

\[ \tau_{U,s} = \frac{1}{\gamma_s^2} \frac{M \nu_s^2}{k_B T} \frac{\omega_{s,\text{max}}}{\omega^2} \]

\[ \omega_{s,\text{min}} = \frac{\nu_s}{\gamma_s} \sqrt{\frac{M \nu_s \omega_{s,\text{max}}}{k_B T L}} \]

\[ K = (2\pi \gamma^2)^{-1} \rho(\nu^4 / f_m T) \ln(f_m / f_B) \]

\[ f_B = \left( M \nu^3 f_m / 4\pi \gamma^2 k_B T L \right)^{1/2} \]
Divergence of the Lattice Thermal Conductivity in 2-D Crystal Lattices

\[ K \sim \log(N) \text{ in 2D} \]
\[ K \sim N^\alpha \text{ in 1D, } \alpha \neq 1 \]

N – system size

\[ \rightarrow \text{Consensus: The intrinsic thermal conductivity of 2-D or 1-D anharmonic crystals is anomalous.} \]

Uniqueness of Heat Conduction in Graphene

Breakdown of Fourier’s Law vs. Size-Dependent Intrinsic Thermal Conductivity

The phonon transport in graphene is 2D all the way down to zero frequency

Low-bound cut-off frequency is defined by the condition that the phonon MFP can not exceed the physical size of the graphene flake:

\[ \omega_{s,\text{min}} = \frac{\nu_s}{\gamma_s} \sqrt{\frac{M \nu_s \omega_{s,\text{max}}}{k_B T L}} \]

\[ K(W/mK) \]

Engineering Phonons by Twisting Atomic Planes

Phonons in Twisted Bilayer Graphene

- Born-von Karman model for description of the carbon-carbon intra-layer interactions
- Lennard-Jones potential for the inter-layer interactions


Please see POSTER for details
**Part III: Phonons in van der Waals Materials**

Van der Waals Materials: Two-Dimensional Materials Beyond Graphene


Topological Insulators
→ Benefits of Few-Quintuple Films
→ Predicted High Thermoelectric Figure of Merit
Thermoelectric Motivation for Atomically Thin Films of Bi$_2$Te$_3$

The thermoelectric figure of merit: $ZT = S^2\sigma T/(K_e+K_p)$

$S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity and $K$ is the thermal conductivity.

Electron Quantum Confinement

Acoustic Phonon Confinement


Low potential barrier in Bi$_2$Te$_3$/Bi$_2$Se$_3$; Bi$_2$Te$_3$/Sb$_2$Te$_3$
Raman Spectroscopy of the Atomically Thin Films of Bi-Te Topological Insulators

Weak gating at RT

Resistivity is \( \sim 10^{-4} \, \Omega \text{m} \)

Thermoelectric Energy Conversion with Stacks of Bi$_2$Te$_3$ Exfoliated Films


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

The enhancement is expected to be larger at low $T$
Charge Density Waves: Macroscopic Quantum State

Normal state $T > T_c$

Electron Density $\rho_e = \text{const}$

Peierls state $T < T_c$

Electron Density $\rho_e = \rho_0 + \rho_1 \cos(qx + \lambda_c) / \lambda_c$

$\xrightarrow{\text{CDW is a cooperative state of the ionic lattice and electron gas}}$

$\xrightarrow{\text{1D and 2D metal-chalcogenides: \(NbSe_2, NbSe_3, TaS_2, TiSe_2\)}}$

$\xrightarrow{\text{CDW can move in electric field}}$

$\xrightarrow{\text{Progress in 1970 – 1980}}$

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Phonon Spectrum Evolution with the TiSe₂ Film Thickness

Main features are A₁g peak at ~207 cm⁻¹ and E₉ peak at 233 cm⁻¹.

Peak at 316 cm⁻¹ is more pronounced and appears near T_c.

Temperature at which the spectrum modification is observed is shifted to about ~225 K.

Intensity of the low-T Raman peaks varies from sample to sample.

Emergence of the new Raman lines in TiSe₂ is explained by formation of the CDW superlattice below the phase transition temperature.

CDW Transition Temperature Scaling with Decreasing Thickness

- CDW transition temperature vs. thickness of the exfoliated TiSe$_2$ thin films.

- temperature increases from ~200 K in the thick films ($H \sim 2 \mu m$) to ~240 K in the thin films ($H \sim 100$ nm).

- Major benefit for the proposed electronic applications

Recent theoretical work: M. Calandra, et al., PRB, 80, 241108 (2009)

Collective Current Regime in TaSe$_2$ Channel Devices

Increase in the apparent threshold voltage is owing to:

(i) High concentration of defects
(ii) Size effects
(iii) Possible voltage drop on electrodes
(iv) Channel non-linearity
Part IV: Practical Applications of Phononics

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.

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Data is after R. Mahajan et al., Proceed. IEEE (2006)

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)

No BIG fan solutions!
Increasing Importance of the Thermal Interface Materials - TIMs

TIMs are materials with the relatively high thermal conductivity introduced to the joint to fill the air gaps.

\[ R_{\text{effective}} = \frac{BLT}{k_{TIM} A} + R_{c1} + R_{c2} \]

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

- Conventional TIMs: K=1-5 W/mK at the volume fractions of filler ~50% at RT
- Companies need K=25-30 W/mK

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Graphene Enhanced Thermal Interface Materials

Graphene TIMs with Strongly Enhanced Thermal Conductivity

- Record-high enhancement of $K$ by 2300 % in the graphene-polymer at the loading fraction $f=10$ vol. %.
- $K$ of the commercial thermal grease was increased to $K=14$ W/mK at the small loading $f=2$ vol. %

Can Graphene Make PCM Not Only to Store Heat but also to Conduct it Away?

Hydrocarbon – Graphene Composites as PCMs with Enhanced Thermal Conductivity

The thermal conductivity enhancement factor, $h = (K - K_m)/K_m$, of about 60 at the 1 wt. % loading fraction is exceptionally high.

It is unlikely that uniformly dispersed graphene flakes with a lateral size in the range from 150 to 3000 nm form a thermally percolating network at 1 wt. %.

Strongly increased thermal conductivity of the composite is explained by good attachment of hydrocarbon molecules to graphene flakes.

Testing C\textsubscript{n}H\textsubscript{2n+2} – Graphene Composites for PCM for Battery Thermal Management

Reduced temperature rise and increased reliability of Li-ion batteries
GaN HFETs were used as examples of high-power density transistors; PMMA was utilized as the supporting membrane for graphene transfer to a desired location; the alignment was achieved with the help of a micromanipulator.


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Reduction of the Hot-Spot Temperature

The hot-spots temperature near drain contacts can be lowered by as much as ~20°C in such devices operating at ~13-W/mm – translates to an order of magnitude improvement in MTTF.

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Typical graphene FETs on SiO$_2$/Si reveal $J_{BR}$ on the order of $10^8$ A/cm$^2$, which is $\sim 100 \times$ larger than the limit for the metals but still smaller than the maximum achieved in CNTs.
Graphene Interconnects with Extraordinary High Breakdown Current Density

Basics of CDW Logic Gates

Schematic view of the CDW-based EX-NOR gate. Input data is encoded into the phase of the CDW (e.g. $\phi = 0$ corresponds to logic 0, and $\phi = \pi$ corresponds to logic 1). The amplitude of the applied voltage is just below the threshold (e.g. $V_{in} = 8 \text{ mV}$; $V_{th} = 9 \text{ mV}$). The constructive interference produces CDW of the double amplitude sufficient for de-pinning, which opens the channel. There is no electric current flow in the case of destructive interference.
Practical Motivations for Collective State as Computational State Variables

- Power dissipation became the limiting factor to the continued scaling of size and speed of the CMOS transistors

- If $N$ electrons are in a collective state then the minimum dissipation limit for one switching cycle can be reduced from $Nk_B T \ln(2)$ to $k_B T \ln(2)$

- Charge density waves (CDW) are collective states, which can exist on a macroscopic scale near room temperature

- CDW can be utilized for Boolean and non-Boolean logic gates and information processing similar to spin waves

- Unconventional materials require innovative techniques for material synthesis and device fabrication
RT Thermal Conductivity of Carbon Materials:
- Diamond: 1000 – 2200 W/mK
- Graphite: 20 – 2000 W/mK
- DLC: 0.1 – 10 W/mK
- a-C: 0.01 – 1 W/mK
- NCD-MCD: 1 – 1000 W/mK
- CNTs: 1000 – 3500 W/mK
- Graphene: 2000 – 5000 W/mK

Take Home Message: Thermal Properties of Carbon Materials
Outlook for Phonon Engineering

- Phonon confinement effects in nanostructures are observed at room temperature
- Nanometer scale is essential for observing and utilizing the phonon confinement effects
- Technology has reached the state required for engineering phonon modes
- Strong practical motivation due to the problems of heat removal from downscaled computer architectures
- Phonon engineering combined with electron band-structure engineering can bring previously unattainable functionality
- Graphene and van der Waals materials offer new opportunities for phonon engineering
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