Graphene and Beyond:
A Perspective

M. S. Dresselhaus, MIT
May 30, 2012
Europe and Korea are launching large graphene programs

The European Union together with other European countries like the UK are investing 1 billion Euros in graphene research.

Korea is heavily investing in graphene, with an application emphasis.
This conference is looking beyond graphene

• Research presentations from the research community
• Breakout sessions
  • 2D Layered Materials for Electronics Applications
  • 2D Layered Materials for Structural and Energy Applications
  • 2D Layered Materials for Photonic and Sensing Applications
Outline: Graphene and Beyond

• Background
• Introducing Isotopes
• Introducing Dopants
• hBN and Carbon BN Superlattices
• Other Graphene-Like Materials
• Layered Materials Unlike Graphene
Graphene and the field of carbon research

Number of physics-related publications on carbon

- Graphene
- Nanotubes
- Fullerenes
- Early history
  - Graphite intercalation compounds
The Electronic Structure of Graphene

Near the K point

\[ E^\pm (\kappa) = \pm \hbar v_F |\kappa| \]

linear \( \kappa \) relation

where \( v_F = \frac{\sqrt{3} \gamma_0 a}{2 \hbar} \)

and \( a = \sqrt{3} \cdot a_{c-c} \)

and \( \gamma_0 \) is the overlap integral between nearest neighbor \( \pi \)-orbitals (\( \gamma_0 \) values are from 2.9 to 3.1eV).

In 1957-1960 McClure extended the 2D graphene electronic structure to 3D graphite and included the magnetic field dependence

Dünnsste Kohlenstoff-Folien

Von H. P. Boehm, A. Clauss, G. O. Fischer und U. Hofmann

Aus dem Anorganisch-Chemischen Institut der Universität Heidelberg


Thickness determined by TEM

"This means that the thinnest films consist of few carbon layers, maybe even just one layer"
Graphene

(a) monolayer

(b) bilayer

First Brillouin zone

trilayer
Graphene

Electronic structure
Anomalous Quantum Hall Effect in 1-LG Graphene

Three anomalies:
• Half integer quantum Hall effect,
• Factor of 4 in $4e^2/h$
• Berry’s phase of $\pi$

• This work attracted great attention and interest in graphene

Novoselov, Geim et al., *Nature* 438(197) 2005
Graphene: the amazing nanomaterial

✓ Thinnest material sheet imaginable...yet the strongest! (5 times stronger than steel and much lighter!)

✓ Graphene is a zero band gap semiconductor: it conducts as well as the best metals, yet its electrical properties can be modulated (it can be switched “ON” and “OFF”)

✓ High mobility ($\geq 100000$ cm$^2$/Vs @RT) $\Rightarrow$ Ballistic conduction for hundreds of nm

✓ Superb heat conductor ($\sim 5 \cdot 10^3$ W/m·K)

✓ Very high current densities (equivalent to $\sim 10^9$ Å/cm$^2$)
Graphene (mono-, bi- and tri-layer): QUALITATIVELY different materials

- Bipolar materials (electrons and holes)
- Low energy behavior described by Dirac equation
- Truly 2D: pure surface with no bulk!
- Band structure can be modified by application of electromagnetic fields

Band structure of graphene structures depends on geometry (stacking, size, and atomic structure)

Interesting electron spin dynamics (weak spin orbit, nearly absent hyperfine interaction, etc…)
Raman Spectrum for Graphene

Ferrari et al., 2006
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Isotope labeling in 2-LG

Isotopes allow us to study the behavior of individual layers in bilayer graphene

Effect of $^{13}$C isotope doping on the optical phonon modes: Raman spectroscopy and localization

- Phonon lifetimes and localization length affected by the presence of $^{13}$C isotope impurities.
- Measurable effects in Raman spectroscopy

Raman spectra of SWCNT at different $^{13}$C concentrations $\rho$.

G band linewidth $\gamma_G$ as a function of $^{13}$C density $\rho$.

Costa et al., *Carbon* 49:4719-4723, 2011
Phonon Lifetime:

Phonon lifetime due to $^{13}$C scattering:

$$\tau_{qn}^{-1} = \frac{\pi f(\rho)}{N} \sum_{q',n'} \omega_{qn}^0 \omega_{q',n'}^0 (e_{qn}^* \cdot e_{q',n'})^2 \delta(\omega_{qn}^0 - \omega_{q',n'}^0)$$

Decoupling of density dependence and wavevector:

$$\tau_{qn}^{-1}(\rho) = f(\rho)I_{qn}$$

$^{13}$C density $\rho$ dependence of the lifetime.

Plot of $I_{qn}$ for the different phonon modes and wavevectors.

J Rodríguez-Nieva, unpublished
Comparison Theory vs. Experiment:

Typical values of lifetimes at G-band:
- Natural C: \( \tau_{ph-imp} \approx 30 \text{ ps} \)
- 50% doped
- Graphene: \( \tau_{ph-imp} \approx 0.5 \text{ ps} \)

Estimated broadening:
\[ \gamma_G^{exp} \approx 6 \text{ cm}^{-1} \leftrightarrow \gamma_G^{th} \approx \frac{\hbar}{\tau_G} \approx 10 \text{ cm}^{-1} \]

Comparison with other processes (G-band):
- Natural C: \( \tau_{e-ph} \approx 0.6 \text{ ps} \)  
  Negligible
- 50% doped
- Graphene: \( \tau_{ph-imp} \approx 0.5 \text{ ps} \)  
  Comparable
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Similar general behavior for each dopant, but the magnitudes of the bonding interactions differ.


**Unpublished (2012)**

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**Doped Nanoribbons**

(a) Diagram showing dopant atoms in plane and out of plane with growth direction indicated.

(b) Graphs showing quantum conductance (G) vs. energy (eV) for different dopants: Boron, Silicon, Nitrogen, Phosphorous, Oxygen, Sulfur.

(c) Current (µA) vs. voltage (V) graph with lines for different dopants: Pristine, Boron, Nitrogen, Oxygen, Phosphorous, Sulfur, Silicon.
Doping of 2-LG

Electrochemical doping of graphene as observed in Raman scattering

M. Kalbac et al.
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# Graphite/Graphene vs hexagonal Boron Nitride

<table>
<thead>
<tr>
<th>Property</th>
<th>Graphite/Graphene</th>
<th>h-BN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>2.1 g/cm³</td>
<td>2.1 g/cm³</td>
</tr>
<tr>
<td>Stacking</td>
<td>AB</td>
<td>AA'</td>
</tr>
<tr>
<td>C-C/B-N distance</td>
<td>1.421 Å</td>
<td>1.446 Å</td>
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<tr>
<td>Band gap</td>
<td>0</td>
<td>5-6 eV</td>
</tr>
<tr>
<td>Electrical</td>
<td>semimetal</td>
<td>insulator</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>-</td>
<td>3-4</td>
</tr>
</tbody>
</table>
h-BN: an ultraflat high quality insulator

- Ultra-flat
- Chemically inert

Atomic force microscope topography images of boron nitride vs SiO$_2$

Root mean squared roughness of $\text{BN} = 50\text{pm}$! (50-100pm typical)

SiO$_2$ rms = 250pm (200-300pm typical)
Enhancement of the G mode in Raman spectra of 2-LG

Enhancement is similar for the top and bottom layers

Mobility = 110,000 cm$^2$/Vs

Two orders of magnitude higher mobility than previous TLG on SiO$_2$: Cracium et al. Nat. Nano. (2009); Zhu et al. PRB (2009)
ABA Trilayer Graphene

\[ H = \begin{bmatrix} H_s & 0 \\ 0 & H_b \end{bmatrix} \]

\[ H_s = \begin{bmatrix} 0 & v_\pi \dagger \\ v_\pi & 0 \end{bmatrix} \]

\[ H_b = \begin{bmatrix} 0 & v_\pi \dagger & 0 & 0 \\ v_\pi & 0 & \sqrt{2} \gamma_1 & 0 \\ 0 & \sqrt{2} \gamma_1 & 0 & v_\pi \dagger \\ 0 & 0 & v_\pi \dagger & 0 \end{bmatrix} \]

BN substrates useful for studying layer stacking

Twisted Bilayer Graphene

Vary twist angle $\rightarrow$ Rich set of behaviors

Low twist angles $\rightarrow$
- low energy van Hove singularity
- slowdown $v_F$

Large twist angles $\rightarrow$
Single-layer dispersion in both layers

BN substrates useful for studying twisted layer stacking

Lopez et al. PRL 2007
Li et al. Nature Physics 2010
Hass et al. PRL 2008
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Graphene *nanoribbons and flakes* are special forms of graphene with edges.
Edges in graphene nanoribbons

Zigzag ribbons

Armchair ribbons

[From tight binding calculations]

[Spin-resolved band structure]

Metalllic or Semiconductor


Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional Silicon

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FIG. 2 (color). (a) Filled-states STM image of the 2D Si layer on Ag(111)-(1 x 1) (Ubias = −1.3 V, I = 0.35 nA). Clearly visible is the honeycomb-like structure. (b) Line profile along the dashed white line indicated in (a). The dark centers in the STM micrograph are separated by 1.14 nm, corresponding to 4 times the Ag(111) lattice constant, in agreement with the (4 x 4) symmetry. (c) High-resolution STM topograph (3 x 3 nm, Ubias = −1.3 V, I = 0.35 nA) of the Si adlayer.

Also: B. Lalmi et al.

APL 97:223109 (2010)

FIG. 3 (color). (a) ARPES intensity map for the clean Ag surface (left) and after formation of the 2D Si adlayer (right), taken along the Ag $\bar{\Gamma}$-$\bar{K}$ direction through the silicene $\bar{K}(h\nu = 126$ eV). (b) Brillouin-zone (BZ) scheme of the 2D Si layer with respect to the Ag(111)-(1 x 1) surface. The red arrow indicates the ARPES measurement direction.
Evidence of graphene-like electronic signature in silicene nanoribbons

Paola De Padova, Claudio Quaresima, Carlo Ottaviani, Polina M. Sheverdyaeva, Paolo Moras, Carlo Carbone, Dinesh Topwal, Bruno Olivieri, Abdelkader Kara, Hamid Oughaddou, Bernard Auffray, and Guy Le Lay

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FIG. 1. (Color online) Filled-states STM image, 11 × 10 nm² (V = −3.3 V, I = 1.90 nA) of the dense array of SiNRs forming a 1D grating with a pitch of ~2 nm (a); ball model of the corresponding calculated atomic structure [see Ref. 12] (b).

FIG. 3. (Color online) Horizontal slice |E(E, k_x)| along the [−110] Ag direction integrated on k_y from 0.55 to 0.7 Å⁻¹ for the dense array of SiNRs on Ag(110). The 1D projection of the π and π* cones around the Dirac points is shown on the left side of the figure.
A Stable “Flat” Form of Two-Dimensional Crystals: Could Graphene, Silicene, Germanene Be Minigap Semiconductors?

A. O’Hare, a F. V. Kusmartsev, b and K. I. Kugel c, d

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Also the Germanium-based 2D-material
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Molybdenum Sulfide

Single-layer MoS$_2$ is a direct gap semiconductor while multi-layer MoS$_2$ is an indirect gap semiconductor.
Oxides and Hydroxides
Transition metal dichalcogenides are semiconductors.

Figure 2. Structure of typical oxide nanosheets. A) Titanium oxide; B) calcium niobium oxide; C) manganese oxide; D) niobium oxide; E) tantalum oxide; F) titanium niobium oxide; and G) cesium tungsten oxide.

Figure 8. Representative AFM images of nanosheets. A) $\text{Ti}_{0.33}\text{O}_{2.052}$; B) $\text{Ca}_2\text{Nb}_2\text{O}_{10}$; and C) $\text{Mg}_{2/3}\text{Al}_{1/3}\text{(OH)}_{2.138}$. Panel (C) adapted with permission. Copyright 2005, American Chemical Society.

More complex layered structures including transition metal dichalcogenides are in this class.
Topological Insulators: Bi$_2$Se$_3$, Bi$_2$Te$_3$ …

SCIENCE 325, 278 (2009)

Edge-State Physics Without Magnetic Fields

Markus Büttiker

L. A. Wray et al. (2010)

Nano Lett. 10:1209 (2010)
Surface State Transport and Ambipolar Electric Field Effect in Bi₂Se₃ Nanodevices

Hadar Steinberg, Dillon R. Gardner, Young S. Lee, and Pablo Jarillo-Herrero*

FIGURE 1. Device geometry. (a) AFM image of a 17 nm thick Bi₂Se₃ device contacted in a Hall bar geometry. (b) Schematic variation of the band structure along the z direction, showing the bulk conduction (purple) and valence (green) bands bending. The topological surface states bands (light blue) can be shifted by application of a gate voltage or surface doping. (c) Scheme of a back-gated/top-gated device. The device appearing in panel a (light blue) is coated by a layer of high-k dielectric (dark blue), followed by evaporation of a Ti/Au gate. The device is also gated from the bottom by a doped Si back-gate. The top and bottom surface states are indicated by red lines.
Six varieties of Dirac cones in $\text{Bi}_{1-x}\text{Sb}_x$

- Review of bulk bismuth, bulk $\text{Bi}_{1-x}\text{Sb}_x$
- Construct various Dirac-cone-materials
  - Single-, bi-, and tri-Dirac-cone
  - Exact-, quasi-, and semi-Dirac-cone
  - Dirac cones with various anisotropies
- Different high-symmetry orientations of two-dimensional $\text{Bi}_{1-x}\text{Sb}_x$
Crystal Structure of Bi$_{1-x}$Sb$_x$

- Rhombohedral structure
- 2 atoms in each unit cell (red and green)
- 2 FCC sub-lattices elongated along the trigonal axis and inter-penetrating
- Trigonal axis has three-fold symmetry
- The bisectrix axis and the trigonal axis form a mirror plane.
Carrier-Pockets in the First Brillouin Zone of Bi$_{1-x}$Sb$_x$

- The Brillouin Zone contains 1 $T$ point, 3 three-fold symmetrical $L$ points and 6 $H$ points with inversion symmetry and three-fold symmetry along the $\Gamma T$ axis.
- The bottom of the conduction band is located at the $L$ points.
- The top of the valence band is at the $L$ point for bulk Bi and at the $H$ point for bulk Sb, and the exact location depends on $x$ for Bi$_{1-x}$Sb$_x$. 
Band Structure of Bi$_{1-x}$Sb$_x$ in 3D

- The $L$-point conduction band edge and valence band edge are close to each other and strongly coupled.
- The dispersion relation at the $L$ points is non-parabolic or linear:
  \[ E(k) = \pm (v \cdot k)^2 + E_g^2 \]

- $x < 0.07$: Semimetal
- $x = 0.07$~$0.09$: Indirect-Semiconductor
- $x = 0.09$~$0.15$: Direct-Semiconductor
- $x = 0.15$~$0.22$: Indirect-Semiconductor
- $x > 0.22$: Semimetal
Different types of Dirac cones in $\text{Bi}_{1-x}\text{Sb}_x$

- **Dirac Point**: $E(k) = v \cdot \hbar k$
- **Dirac Cone**: 2D projection of Dirac Point
  - Single-Dirac-cone: Topological Insulator ($\text{Bi}_2\text{Se}_3$ surface states)
  - Bi-Dirac-cone: Graphene
  - Tri-Dirac-cone—$\text{Bi}_{1-x}\text{Sb}_x$
- **Quasi-Dirac-cone**
- **Semi-Dirac-cone**: semi-classically dispersive and semi-relativistically dispersive

Anisotropic Single-Dirac-Cone in Bi$_{1-x}$Sb$_x$ Thin Film
Prediction only—no experiments

*Bisectrix-Oriented Growth—2D

Thermal smearing of $\left( -\frac{\partial f}{\partial E} \right)$, where $f$ is the Fermi-Dirac Distribution.
The effective range of smearing is $\sim k_B T$
Single-, Bi-, and Tri-Dirac-Cones in Bi$_{1-x}$Sb$_x$

**Single-Dirac-Cone Material:**
Bisectrix Oriented Growth

**Bi-Dirac-Cone Material:**
Binary Oriented Growth

**Tri-Dirac-Cone Material:**
Trigonal Oriented Growth

$l_z = 100$ nm

Group Velocity and Anisotropy

Bisectrix Growth Oriented $l_z=300\text{nm}$

$[60\bar{6}1]$ Growth Oriented $l_z=300\text{nm}$

$v^\text{Dirac}_{ij} \approx 10^{-2} c_{\text{light}}$
Anisotropy Coefficient

\[ \gamma = \frac{|v_{\text{max}}|}{|v_{\text{min}}|} \]

velocity anisotropy for different in-film directions
Controlling the \( L \)-point Mini-Gap

\[ E_g \text{ vs. } l_z \text{ and growth orientation} \]

\[ E_g \text{ vs. } l_z \text{ and } x \]
Phase Diagrams for Thin Film Bi$_{1-x}$S$_x$

SM: semi-metal
ISC: indirect-semiconductor
DSC: direct-semiconductor

S. Tang & M. S. Dresselhaus, Phase Diagrams of Bi$_{1-x}$Sb$_x$ Thin Films with Different Growth Orientations, to be submitted
Summary of Dirac Cone Types

• Predicted construction of different Dirac cones:
  – single-, bi-, and tri-Dirac-cone materials
  – exact-, quasi-, and semi-Dirac-cone materials
  – Dirac cones with different anisotropies

All are based on Bi$_{1-x}$Sb$_x$ thin films.
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