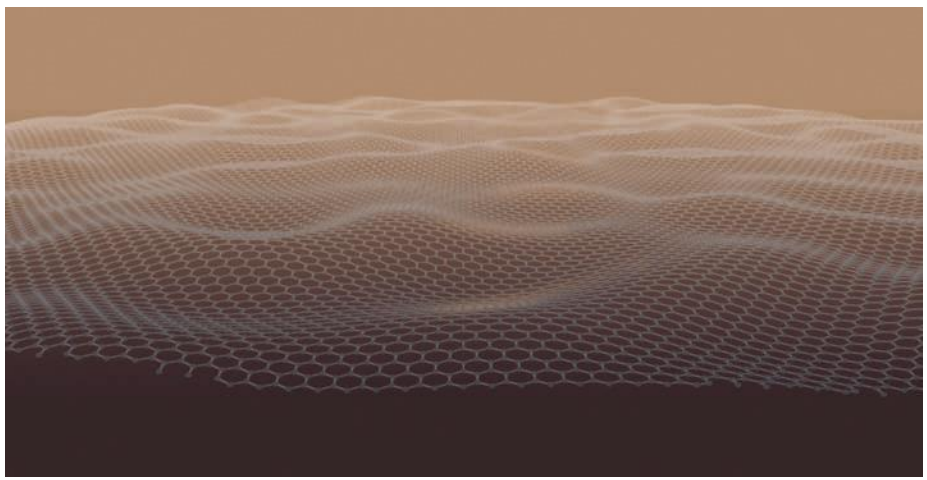
Emergent Properties of Two-Dimensional Materials

Flatlands beyond Graphene



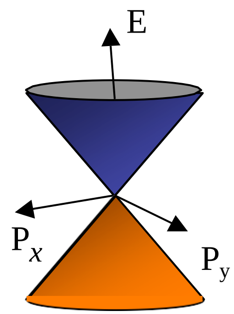
Prof. J. Raynien Kwo
Department of Physics,
National Tsing Hua University

2-D Materials

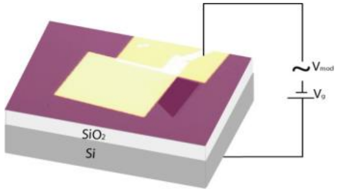
- graphene
- transition metal di-chalcogenides
- graphene like materials

Why the interest?

- **2D crystal with extraordinarily few defects**



- **Exotic electrical behaviors**
  - E = $\mathbf{v_F} \bullet \mathbf{P}$ (massless Dirac fermions)
  - Efficient tunneling through energy barrier, quantum Hall effects (QHE), …
- **Excellent materials properties**
  - Electrical -- high electron mobility, high current carrying capacity,…
  - Mechanical -- large Young's modulus, high tensile strength, low friction, …
  - Thermal -- high thermal conductivity
- **Excellent controllability**
  - Electrical gating, structural patterning, etc



Attractive for fundamental physics and technological applications

Hot spots of graphene

Nobel Prize in Physics for 2010

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

Andre Geim Konstantin Novoselov

www.graphene-flagship.eu

GRAPHENE FLAGSHIP

European Commission has chosen graphene as a ten-year, 1 billion euro Future Emerging Technology flagship. (Jan 28, 2013)

Aim to get graphene into industry and product development

http://www.graphene-flagship.eu/GF/index.php

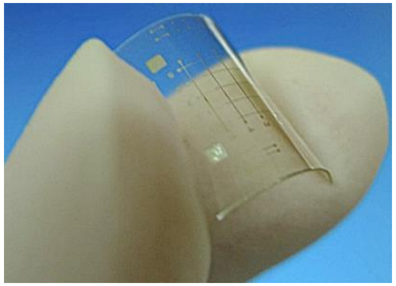
SAMSUNG

SAMSUNG TECHWIN

The South Korean government has invested $200 million, beating the amount actually spent on graphene by the UK government so far at least twenty times over. Samsung has added another $200million in South Korean spend.

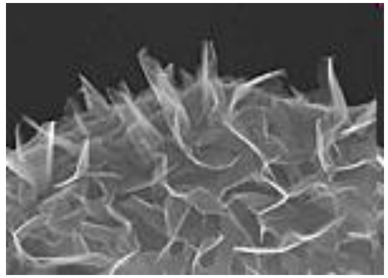
http://www.cambridgenetwork.co.uk/news/is-the-uk-set-to-miss-out-on-the-graphene-revolution/

Graphene's Applications



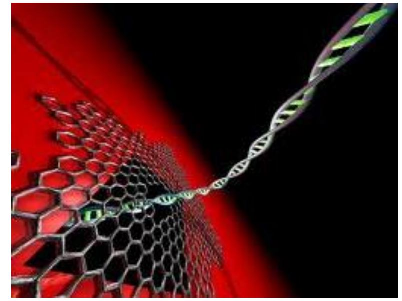
Flexible Memristors

Photo: Sung-Yool Choi
Nano Lett., ***10*** (11), 4381 (2010)



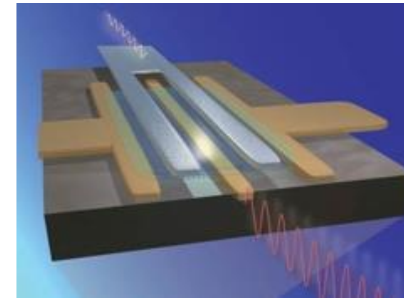
Ultracapacitor

Image: Ron Outlaw
Science **329** (5999) 1637 (2010)



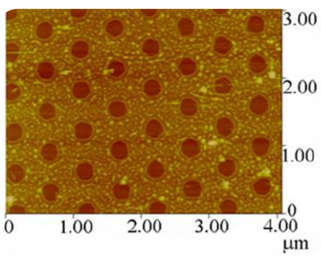
DNA graphene nanopore

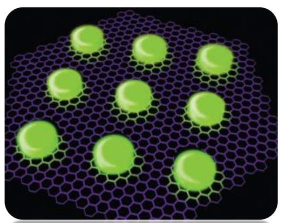
Nano Lett., ***10*** (8), 3163 (2010)
Nano Lett.,, ***10*** (8), 2915 (2010)
Nature **467**, 190–193 (2010)



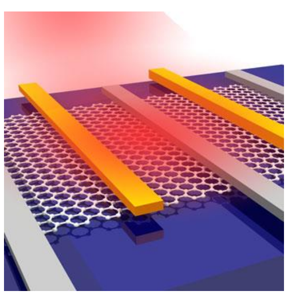
RF transistors

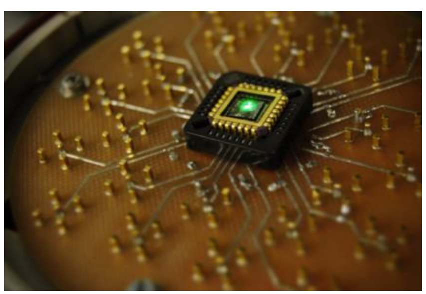
Nano Letters **9** (1), 422 (2009)
Nano Letters, **9** (12), 4474 (2009)
Science, **327**(5966), 662 (2010)
IEEE EDL, **31**(1), 68 (2010)
Nature **467**, 305–308 (2010)





Graphene Transparent Conductors
APL **99**, 023111 (2011) and Adv. Mater. **24**, 71 (2012)





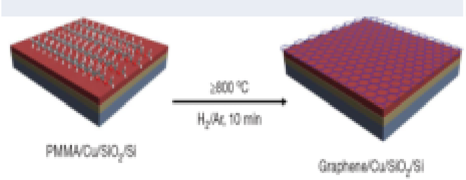
Graphene Photodetector
Nature Photonics **4**, 297 - 301 (2010)
Nature Nanotechnology **7**, 363–368 (2012)

Graphene Commercialization Breakthrough*

- OLED Lighting
- Transparent Conductors
- Logic & Memory
- Printed Electronics Manufacturing
- Catalytic support
- Stretchable and Sensing Electronics
- Solar Opportunities
- Energy Storage
- Advanced carbon based materials for Lithium Ion battery electrodes

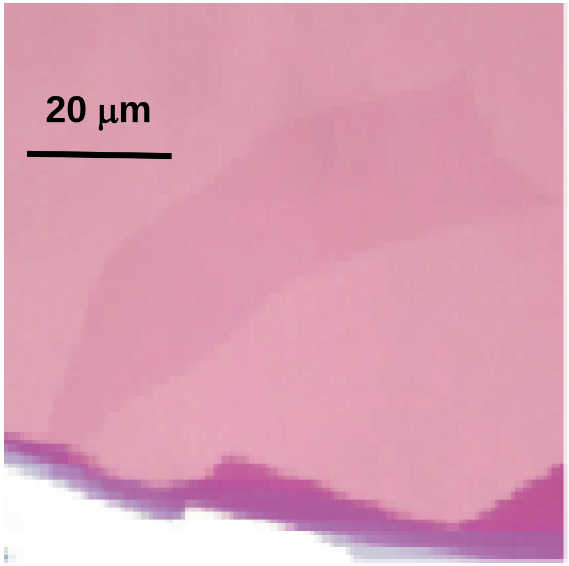
*http://www.nanowerk.com/news2/newsid=27702.php

Fabrication of graphene

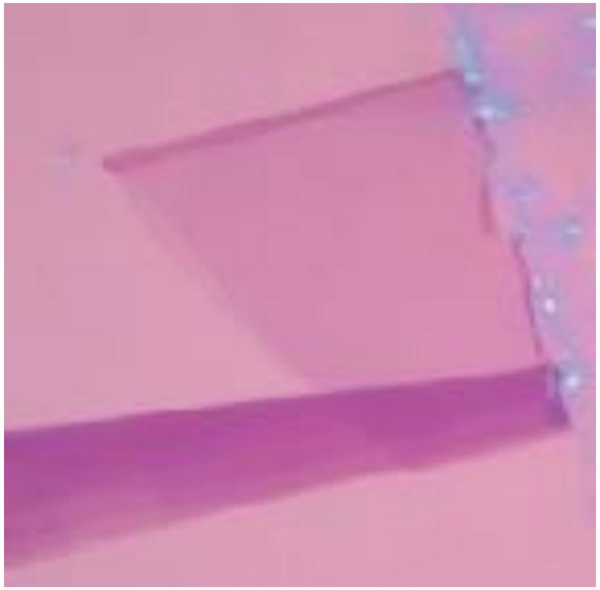
Method	Descriptions	Merits	References
Mechanical cleavage or exfoliation	Scotch Tape 	Minimal defects Intrinsic properties Small sizes	Science 306, 666 (2004)
Chemical oxidized process	Producing GO by the oxidation of graphite with acid	Large scale flakes Composite	Nature 442, 282 (2006)
Epitaxial growth on SiC	Epitaxial growing graphene on SiC	Large area Multilayer High temperature	J. Phys. Chem. B 108, 19912 (2004)
Chemical vapor deposition on Ni	Ambient-pressure CVD on evaporated polycrystalline Ni	Large area multilayer	Nano Lett., Vol. 9, No. 1, 200
Chemical vapor deposition on Cu	Growing graphene on Cu with methane and hydrogen.	Large area, one-layer Defect Mechanism	Science 324, 1312 (2009)
Solid carbon source to graphene		Poly (methyl methacrylate) One step to doped graphene	Nature, 468, 549 (2010)

Exfoliated Graphene Monolayers and Bilayers

Reflecting microscope images.



Monolayer



Bilayer

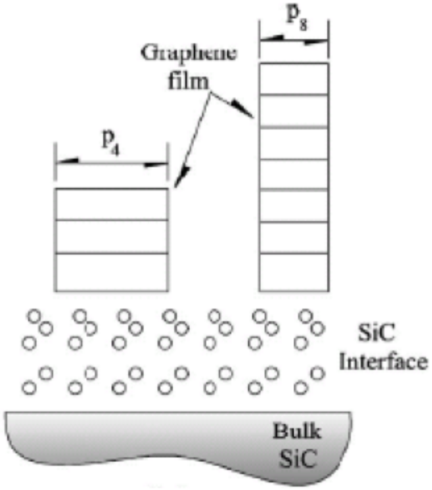
Graphene's unique optical properties produce an unexpectedly high opacity for an atomic monolayer in vacuum, absorbing $\pi\alpha \approx 2.3\%$ of red light, where α is the fine structure constant. This one-atom-thick crystal can be seen with the naked eye, because it absorbs approximately 2.6% of green light, and 2.3% of red light

K. S. Novoselov *et al.*, *Science* **306**, 666 (2004).

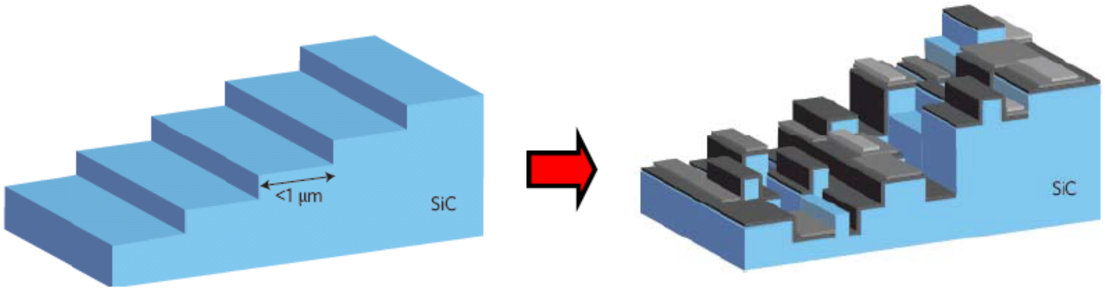
Epitaxial growth of graphene

Epitaxial graphene grown on SiC(0001) surfaces

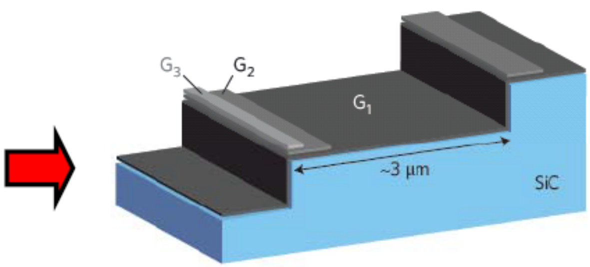
One often ends up with multi-layers of graphene with small grains 30nm-200nm



Recent progress:

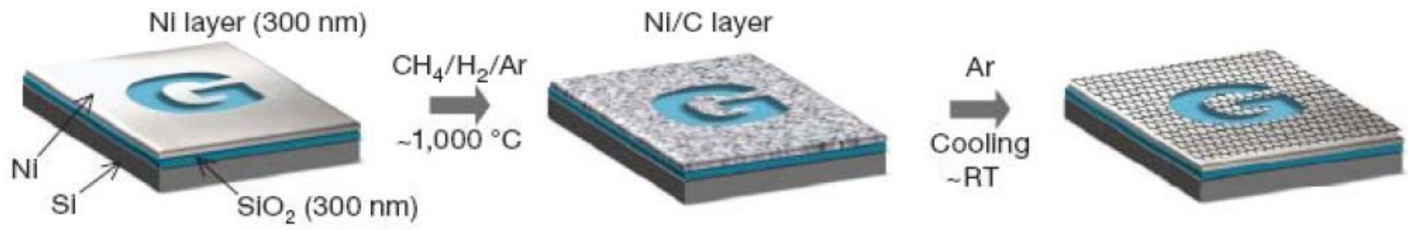


UHV

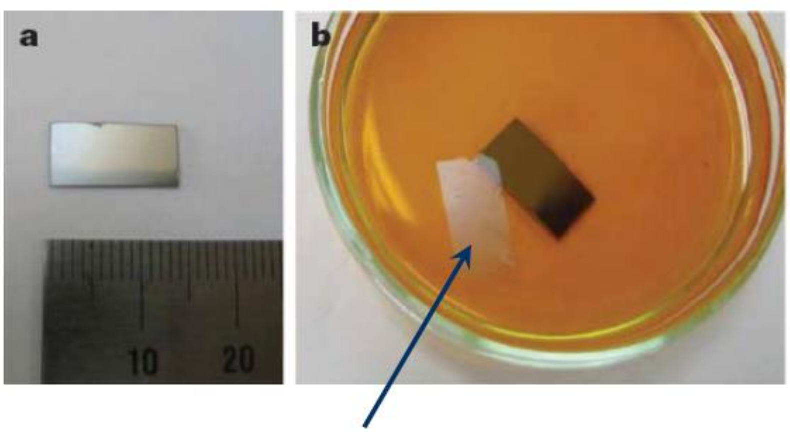


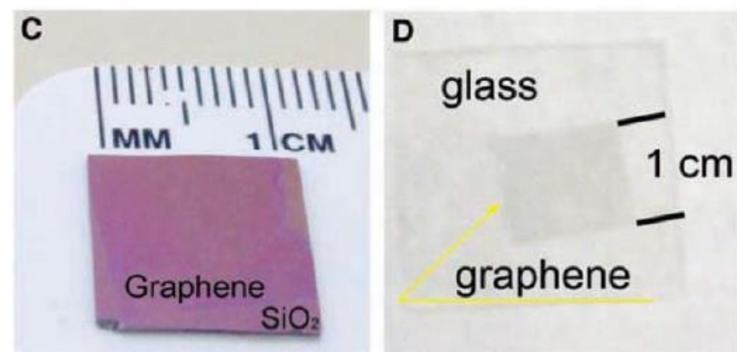
In the presence of pressurized Ar
K.V. Emvsev et al., Nature Materials 8, 203 (2009)

CVD graphene on metal substrates



Etching and transfer





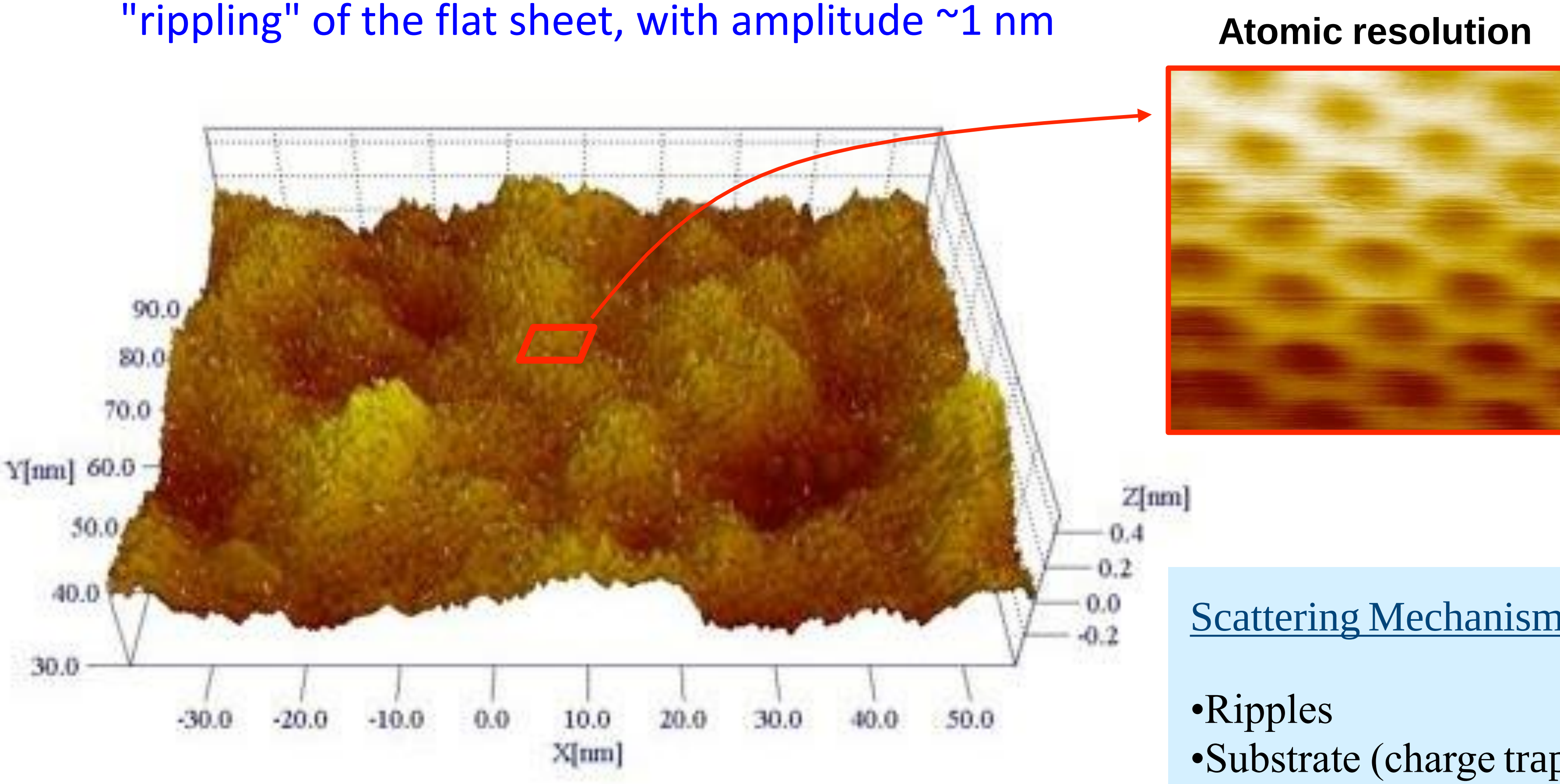
Cu: Li et al., Science 324, 1312 (2009)

Floating graphene after Ni being etched

Ni: Kim et al., Nature 457, 706 (2009)

Ripples of graphene on a SiO_2 substrate

"rippling" of the flat sheet, with amplitude ~1 nm



Scattering Mechanism?

- Ripples
- Substrate (charge trap)
- Absorption
- Structural defects

Elena Polyakova et al (Columbia Groups), PNAS (2007)

See also Meyer et al, Nature (2007) and Ishigami et al, Nano Letters (2007)

Extraordinary Properties of Graphene

- **Room-temperature electron mobility of 2.5×10^5 cm^2V^{-1} s^{-1}**

  Nano Lett. 11, 2396–2399 (2011).

- **Young's modulus of 1 TPa and intrinsic strength of 130 Gpa, the strongest materials ever tested.**

  Cu: 0.117 TPa

  Phys. Rev. B 76, 064120 (2007).

- **High thermal conductivity: above 3,000$Wm^{-1}K^{-1}$**

  Cu: 401$Wm^{-1}K^{-1}$

  Nature Mater. 10, 569–581 (2011).

- **A prediction in 2015 suggested a melting point at least 5000K.**

- **Optical absorption of 2.3%**

  Science 320, 1308 (2008).

- **No band gap for undoped graphene**

- **The electrical resistivity of graphene < 10^{-6} Ω·cm, less than silver, the lowest known at RT.**

Super-Qualities

★ $m^* = 0$ expect huge mobility

Carrier mobility: 200000 $cm^2/V.s$

(Geim, 2008, 300K, $n \approx 10^{13} cm^{-2}$)

Ballistic transport at micronscale

Epitaxial graphene: 2000 $cm^2/V.s$ **(27K)** $\lambda_\phi \geq 1\mu m$

CVD graphene: 4050 $cm^2/V.s$ **(room temp)**

Si 1500 $cm^2/V.s$ **high speed GaAs 8500** $cm^2/V.s$

InSb (undoped) 77000 $cm^2/V.s$

★ Thermal conductivity (room temp)

$\approx 5 \times 10^3 Wm^{-1}K^{-1}$ ~ 10 × Cu or Al

$\mu = v/E$

$\sigma = ne\mu_e + ne\mu_h$

$\mu_e = e\,\tau_e/m_e$

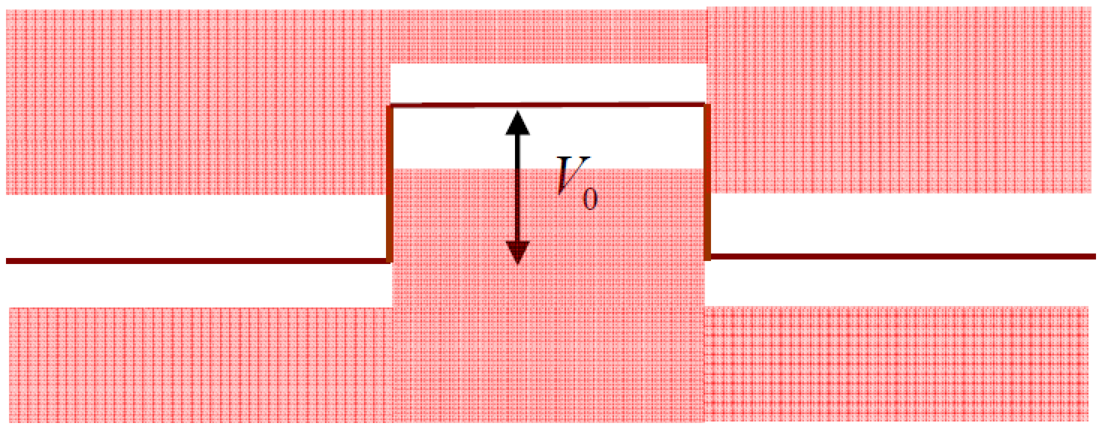
$\mu_h = e\,\tau_h/m_h$

Exotic Behaviors

- **Klein’s paradox**
- **Quantum Hall effect**
- **Berry Phase**
- **Ballistic transport**
- **Others**

Electron scattering from a potential barrier in applying the Dirac equation (1929)

Potential complication: Klein Paradox



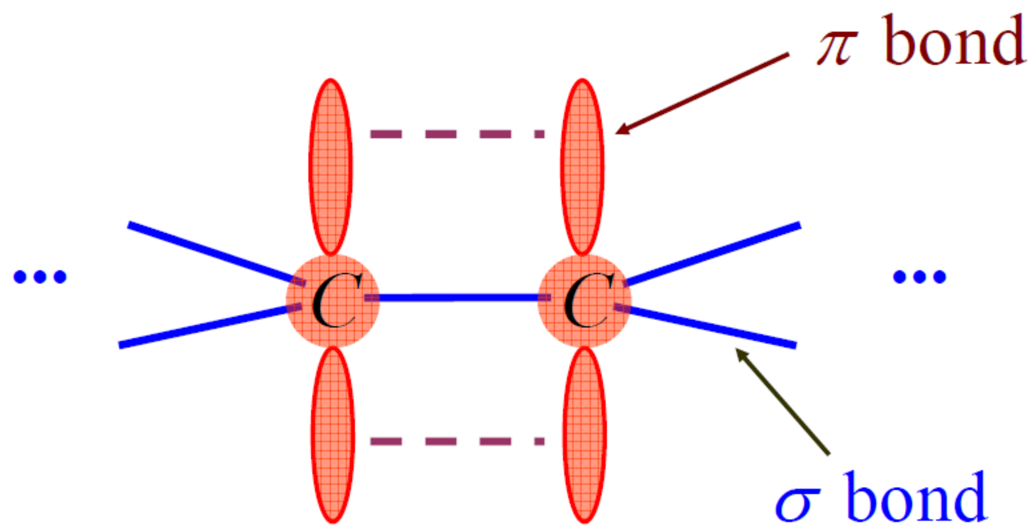
As V_o ~mC^2, $T \to 1$, $R \to 0$

As the potential approaches infinity,
the reflection diminishes, the electron always transmit

No confinement for electrons

On/off ratio is reduced in graphene FET

Element of Carbon Network

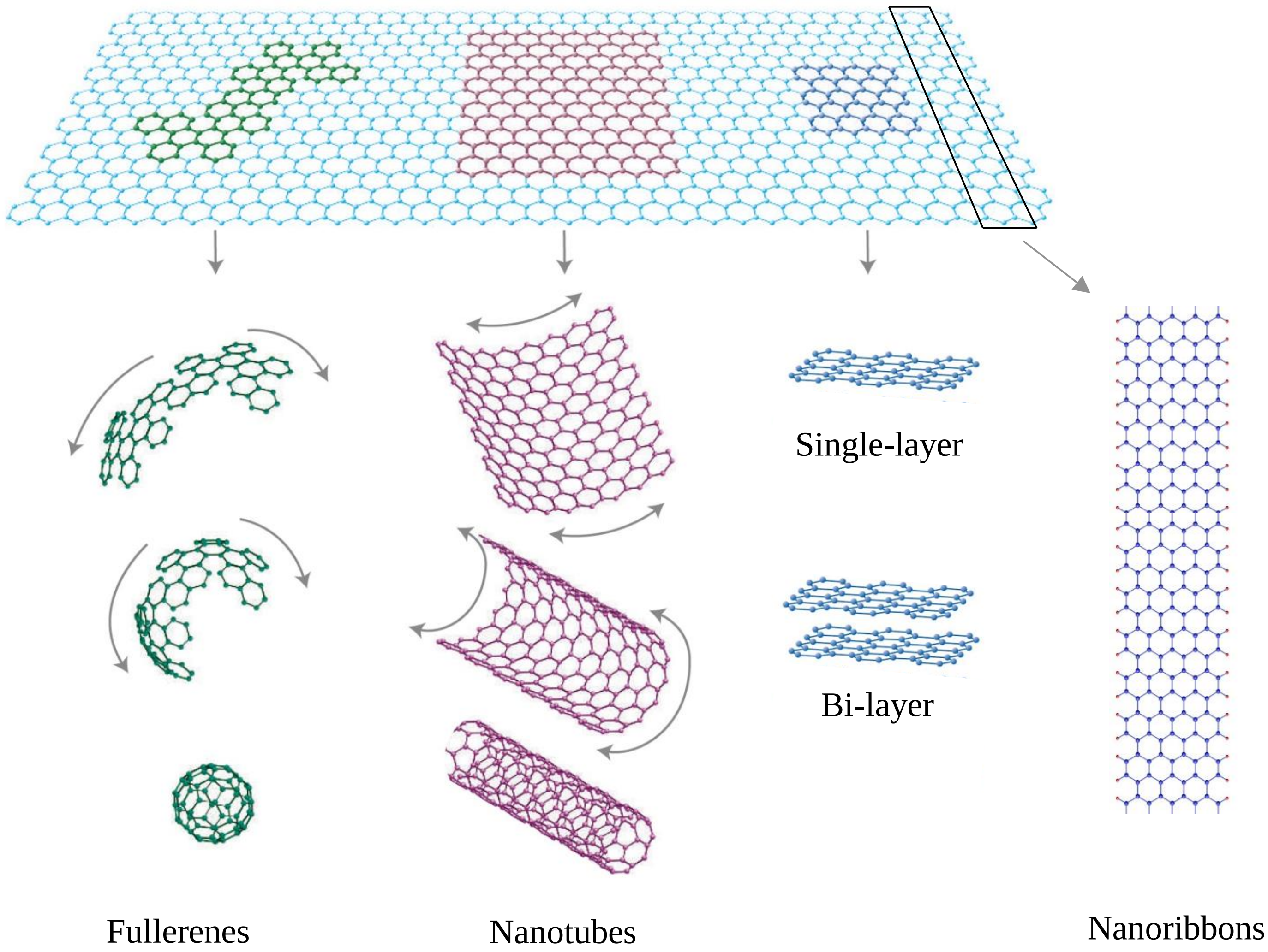


Carbon $1S^2\,\underbrace{2S^2\,2P^2}$

4 electrons in σ bonds (SP^2) + π bond or SP^3

(s, p_x, p_y orbitals) p_z orbital

Graphene and Related Carbon sp^2-bonded Structures



Honeycomb lattice and Brillouin zone of graphene

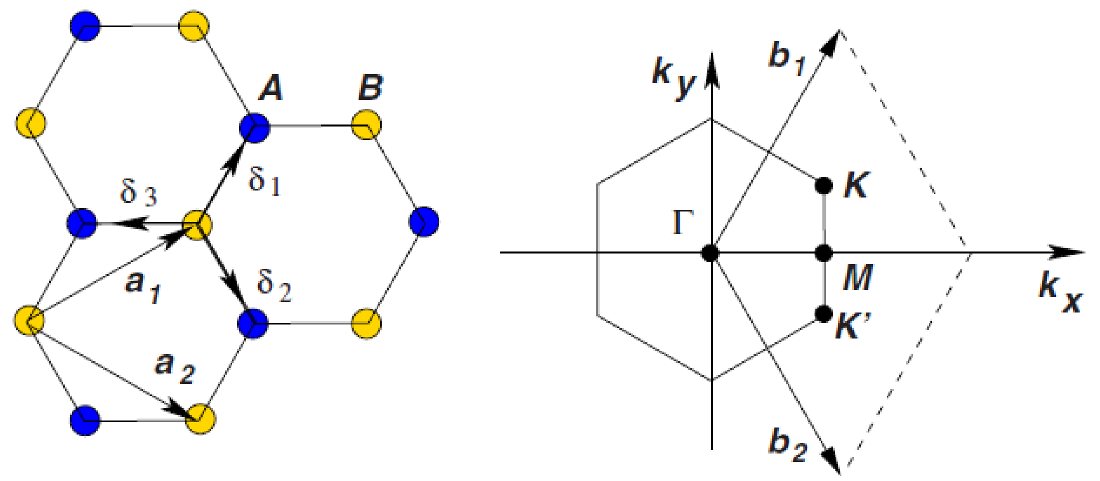
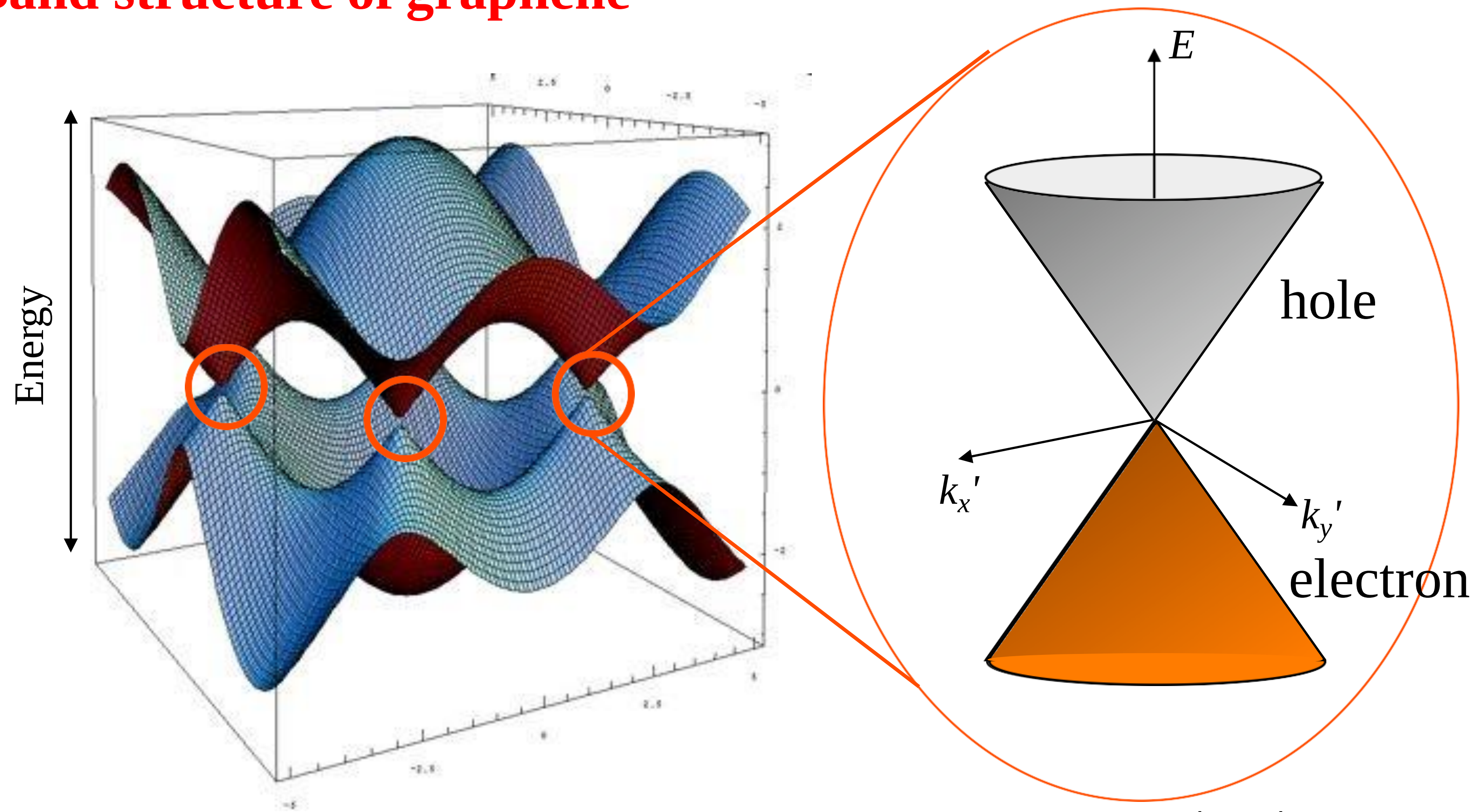


FIG. 2. (Color online) Honeycomb lattice and its Brillouin zone. Left: lattice structure of graphene, made out of two interpenetrating triangular lattices ($\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are the lattice unit vectors, and δ_i, $i=1,2,3$ are the nearest-neighbor vectors). Right: corresponding Brillouin zone. The Dirac cones are located at the K and K' points.

Graphene : 2-D Massless Dirac Fermions

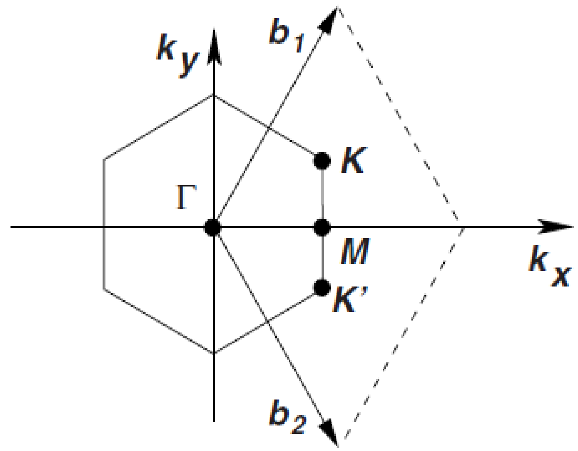
Band structure of graphene



$$E \approx \hbar v_F \left| \vec{k}'_\perp \right|$$

Zero effective mass particles moving with a constant speed v_F

Graphene electronic structures

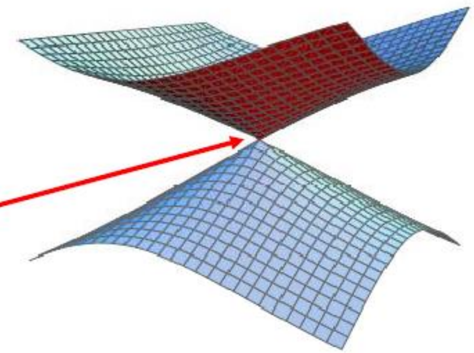


- The *E–K* relation is linear for low energies near the six corners of the 2-D hexagonal Brillouin zone, leading to zero effective mass for electrons and holes.
- Due to this linear dispersion relation at low energies, electrons and holes near these six points, two of which are inequivalent, behave like relativistic particles described by the Dirac equation for spin 1/2 particles.
- The electrons and holes are called Dirac Fermions, and the six corners of the Brillouin zone are called the Dirac points. The equation describing the *E–K* relation is $\boxed{E = \hbar v_F \sqrt{k_x^2 + k_y^2}}$

  , where the Fermi velocity v_F ~10^6 m/s.

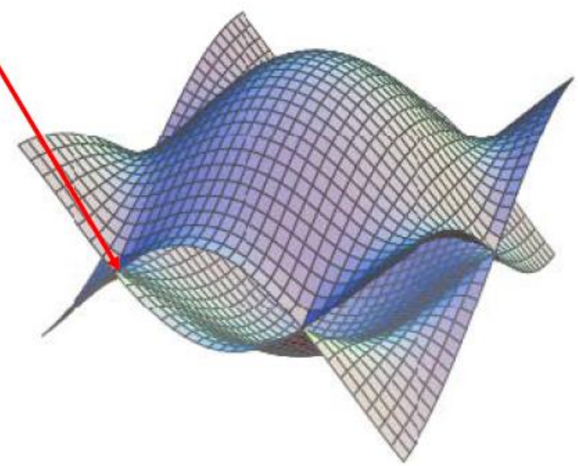
Quasi-Dirac Fermions

$E = \hbar \upsilon k$ with $m = 0$



Dirac points

New playground for testing
relativistic QM and QED!



Not exactly Dirac Fermions

$\upsilon \approx c / 300$

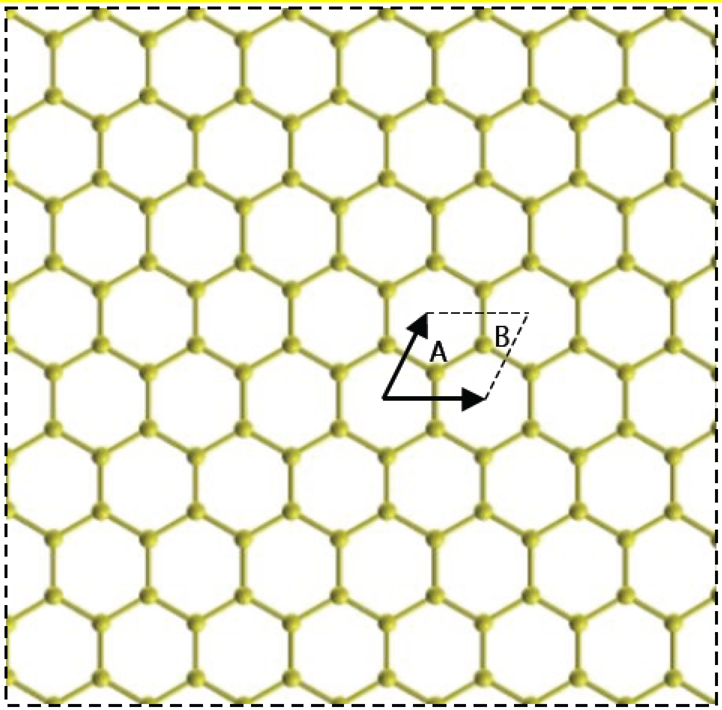
$k_D \neq 0$ and inter-Dirac point scatterings!

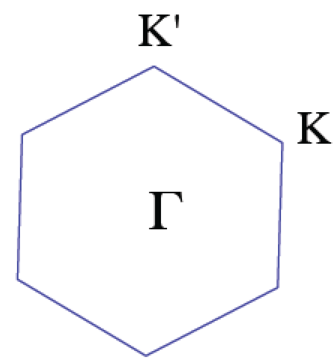
Graphene

Single layer of graphite
Two carbon atoms per unit cell
in a honeycomb structure

For a nanoribbon, in zig-zag orientation, always metallic, zero bandgap

In arm chair, semiconducting or metallic, nonzero band gap





Brillouin zone

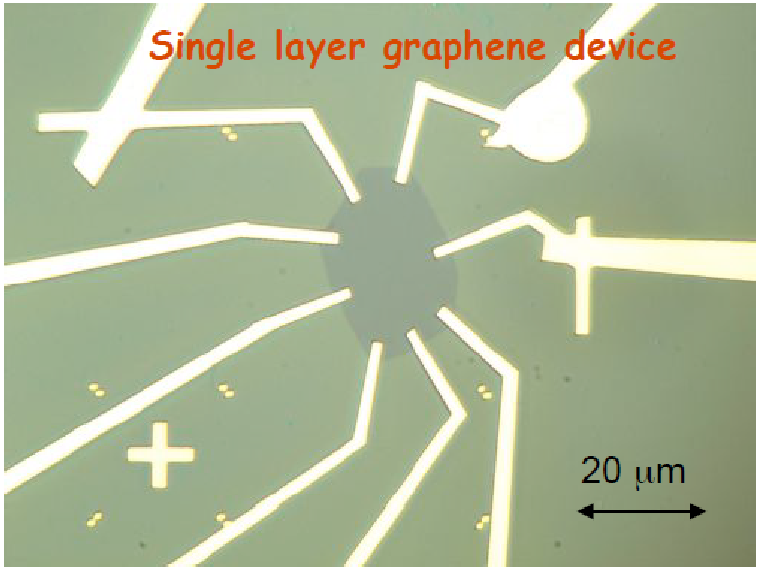
The **quantum Hall effect** is a quantum mechanical version of the Hall effect, which is the production of transverse (perpendicular to the main current) conductivity in the presence of a magnetic field. The quantization of the Hall effect σ_{xy} at integer multiples (the "Landau level") of the basic quantity e^2/h (where e is the elementary electric charge and h is Planck's constant). $\sigma_{xy} = \pm N e^2/h$. It can usually be observed only in very clean silicon or gallium arsenide solids at temperatures around 3 K and high magnetic fields.

Graphene shows the quantum Hall effect with respect to conductivity quantization: the effect is anomalous in that the sequence of steps is shifted by **1/2** with respect to the standard sequence and with an additional factor of **4**. Graphene's Hall conductivity is $\sigma_{xy} = \pm 4 \cdot (N + 1/2) e^2/h$, where N is the Landau level and the double valley and double spin degeneracies give the factor of 4. These anomalies are present at room temperature, i.e. at roughly 20 °C (293 K).

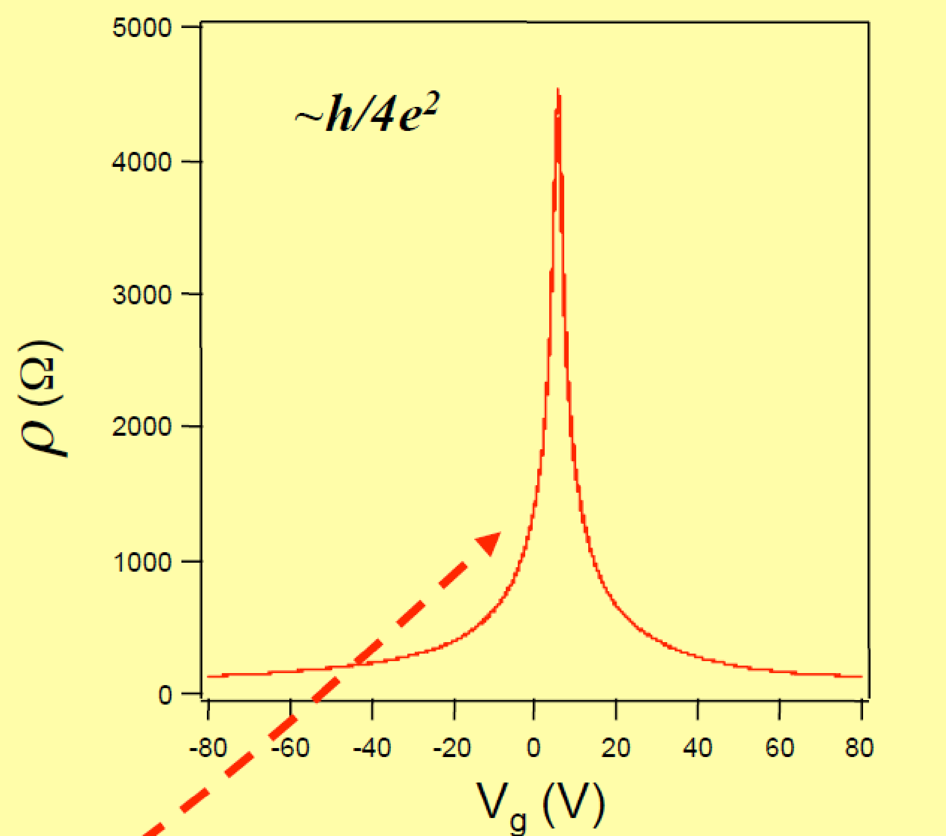
This behavior is a direct result of graphene's **massless Dirac electrons**. In a magnetic field, their spectrum has a Landau level with energy precisely at the Dirac point. This level is a consequence of the Atiyah–Singer index theorem and is half-filled in neutral graphene, leading to the "+1/2" in the Hall conductivity. **Bilayer graphene** also shows the quantum Hall effect, but with only one of the two anomalies, i.e. $\sigma_{xy} = \pm 4 \cdot N \cdot e^2/h$. In the second anomaly, the first plateau at N=0 is absent, indicating that bilayer graphene stays metallic at the neutrality point.

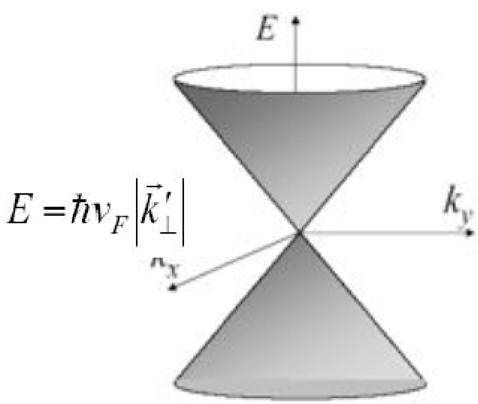
Unlike normal metals, graphene's longitudinal resistance shows maxima rather than minima for integral values of the Landau filling factor in measurements of the Shubnikov–de Haas oscillations, whereby the term integral quantum Hall effect. **These oscillations show a phase shift of π, known as Berry's phase.** Berry's phase arises due to the zero effective carrier mass near the Dirac points. The temperature dependence of the oscillations reveals that the carriers have a non-zero cyclotron mass, despite their zero effective mass.

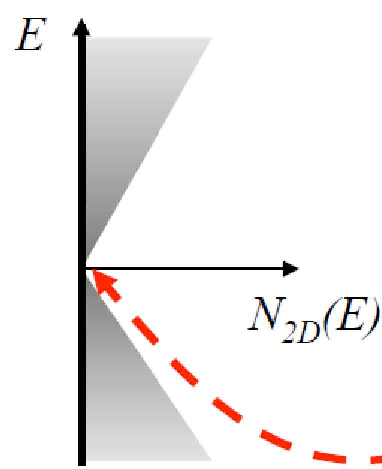
Transport Single Layer Graphene



Resistivity vs Gate Voltage







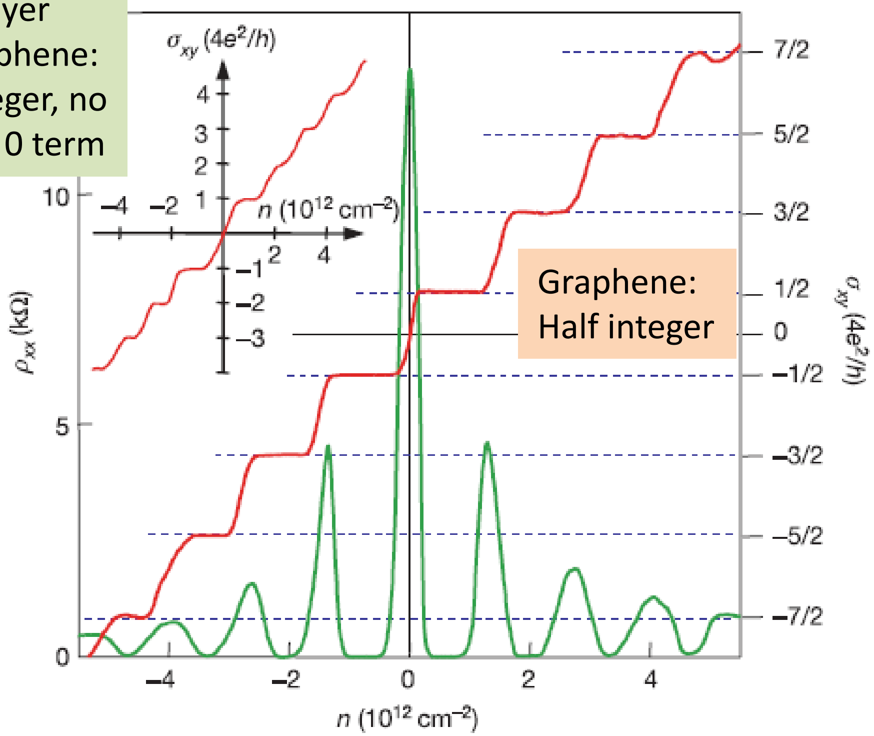
$$\rho^{-1} = e^2 v_F\, l_e\, N_{2D}$$

P. Kim et al , Nature (2005)

Quantum Hall Effect in Graphene

B= 14T, T = 4K

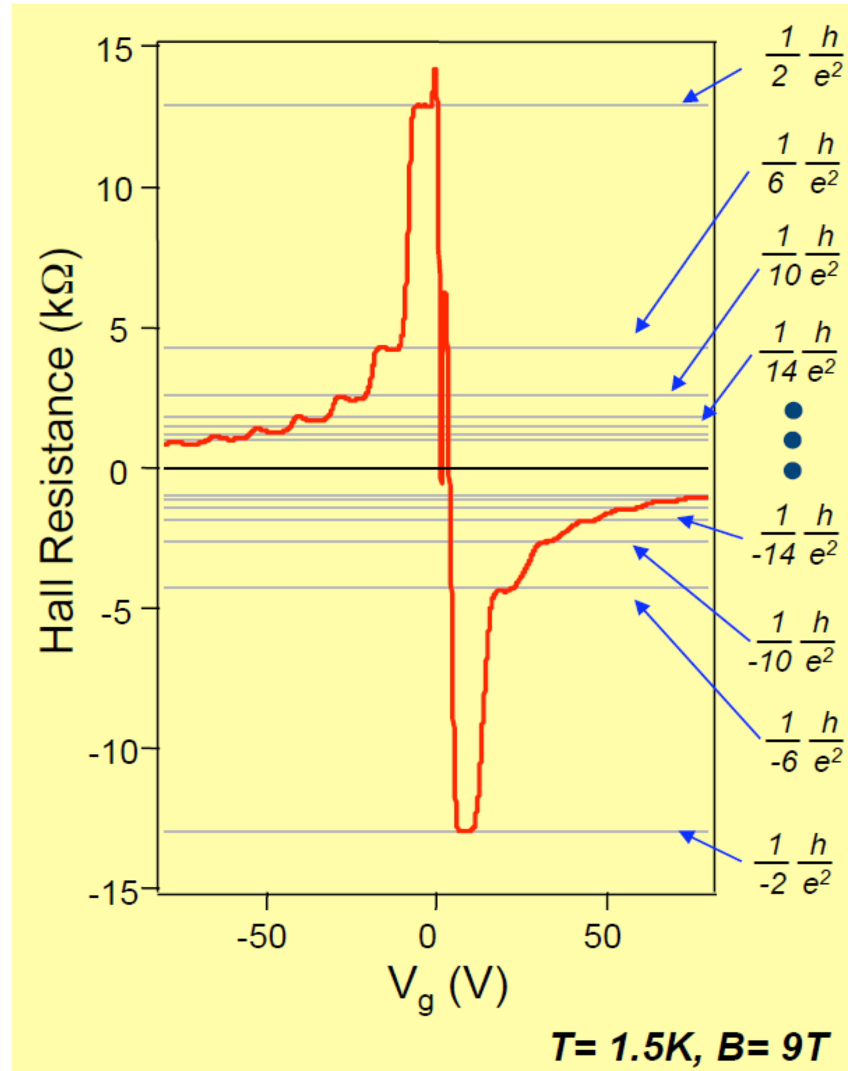
2-layer graphene: Integer, no N = 0 term



Graphene: Half integer

Figure 4 | QHE for massless Dirac fermions. Hall conductivity σ_{xy} and longitudinal resistivity ρ_{xx} of graphene as a function of their concentration at $B = 14$ T and $T = 4$ K. $\sigma_{xy} \equiv (4e^2/h)\nu$ is calculated from the measured dependences of $\rho_{xy}(V_g)$ and $\rho_{xx}(V_g)$ as $\sigma_{xy} = \rho_{xy}/(\rho_{xy}^2 + \rho_{xx}^2)$. The behaviour of $1/\rho_{xy}$ is similar but exhibits a discontinuity at $V_g \approx 0$, which is avoided by plotting σ_{xy}. Inset: σ_{xy} in 'two-layer graphene' where the quantization sequence is normal and occurs at integer ν. The latter shows that the half-integer QHE is exclusive to 'ideal' graphene.

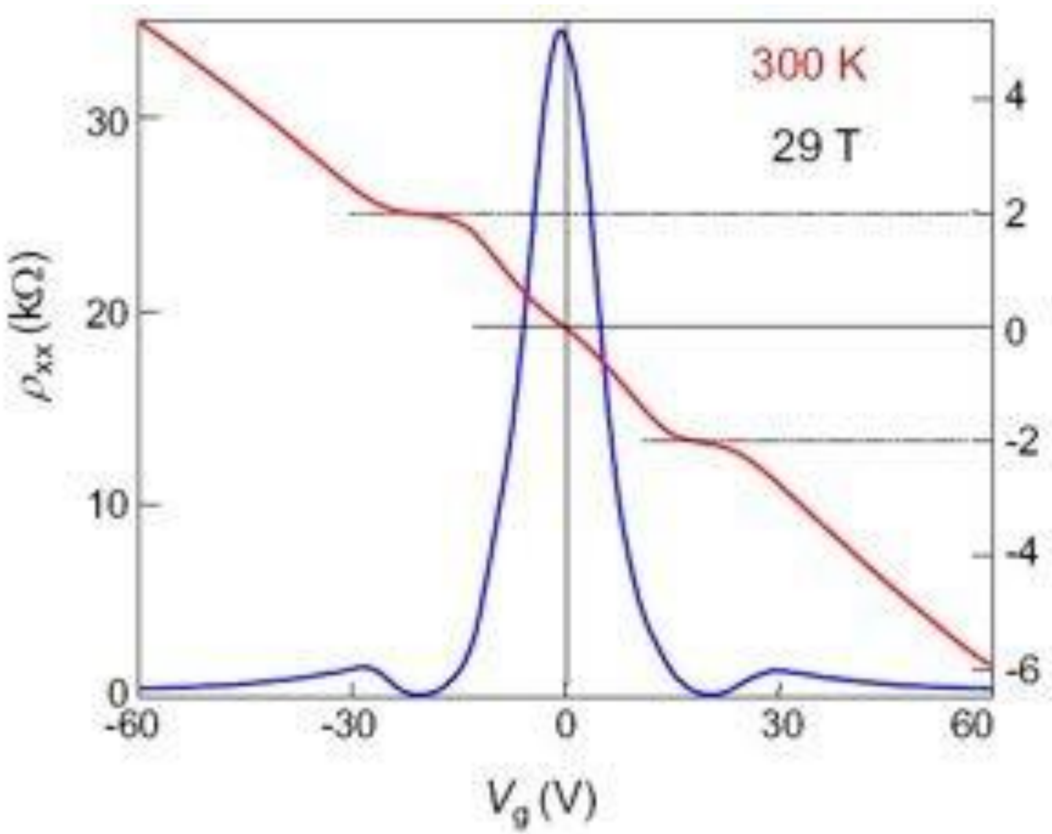
Novoselov et al, Nature, 438, 197, (2005)
Zhang et al, Nature, 438, 201, (2005)

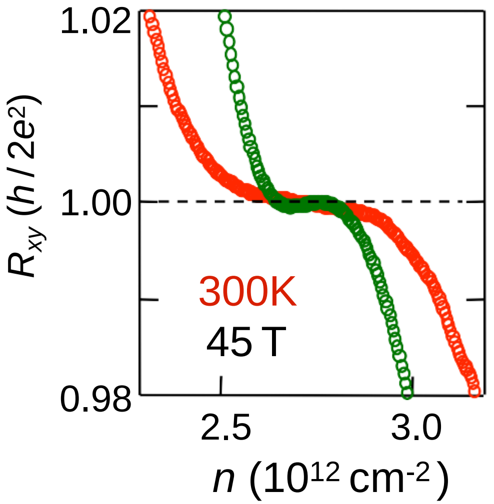


Quantization:

$$R_{xy}^{-1} = 4\left(n + \frac{1}{2}\right)\frac{e^2}{h}$$

Room Temperature Quantum Hall Effect





Deviation < 0.3%

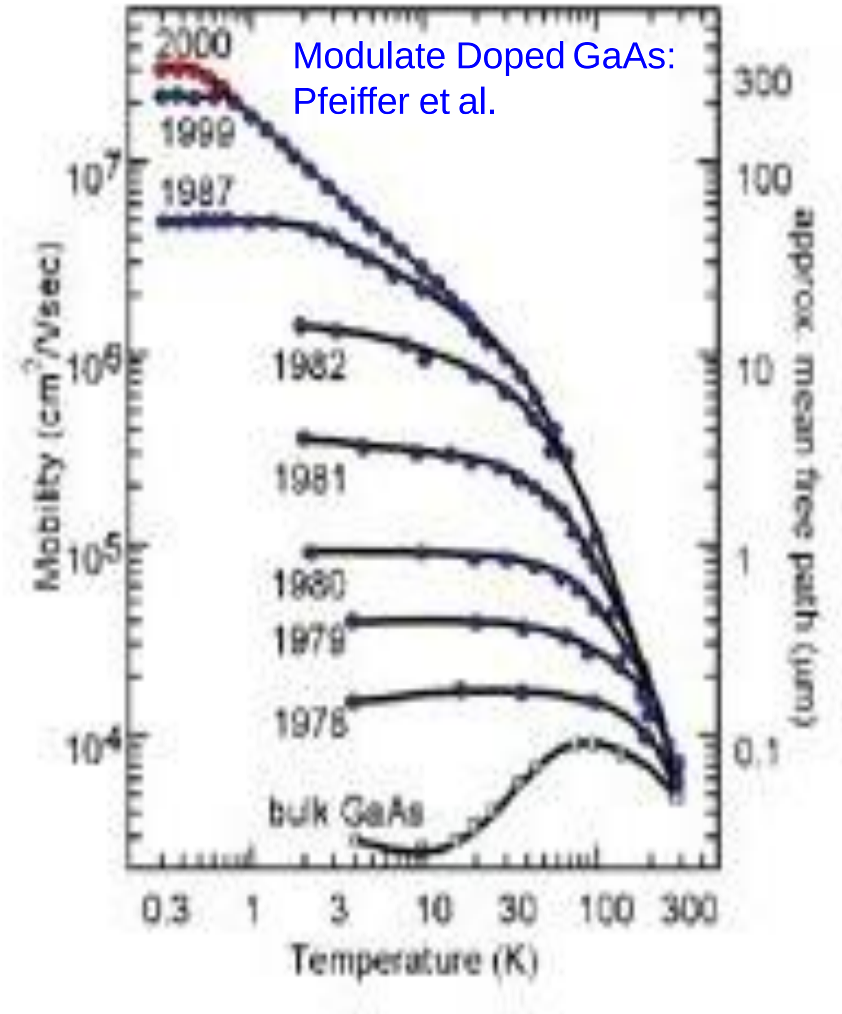
$$E_n = \pm\sqrt{2e\hbar v_F^2 |n| B}$$

$$E_1 \sim 100 \text{ meV @ 5 T}$$

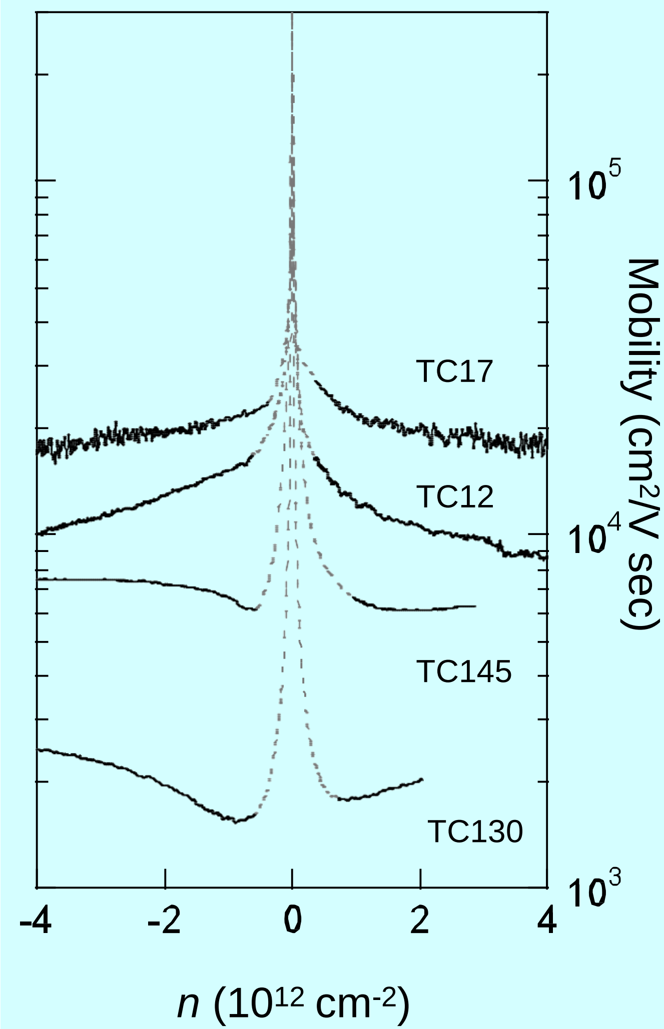
Novoselov, Jiang, Zhang, Morozov, Stormer, Zeitler, Maan, Boebinger, Kim, and Geim *Science* (2007)

Graphene Mobility

GaAs HEMT



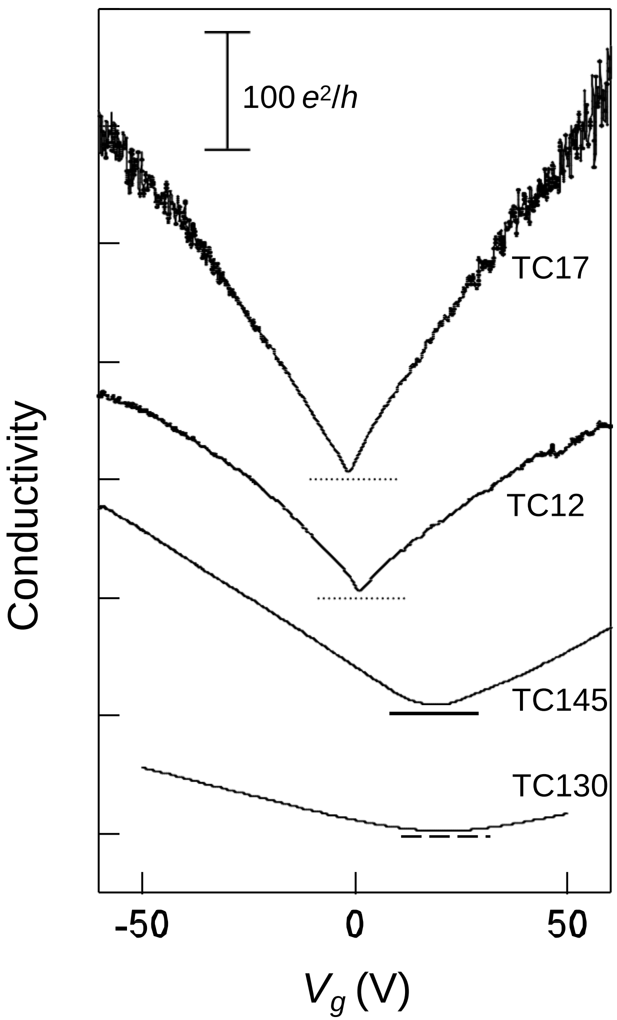
Graphene Mobility

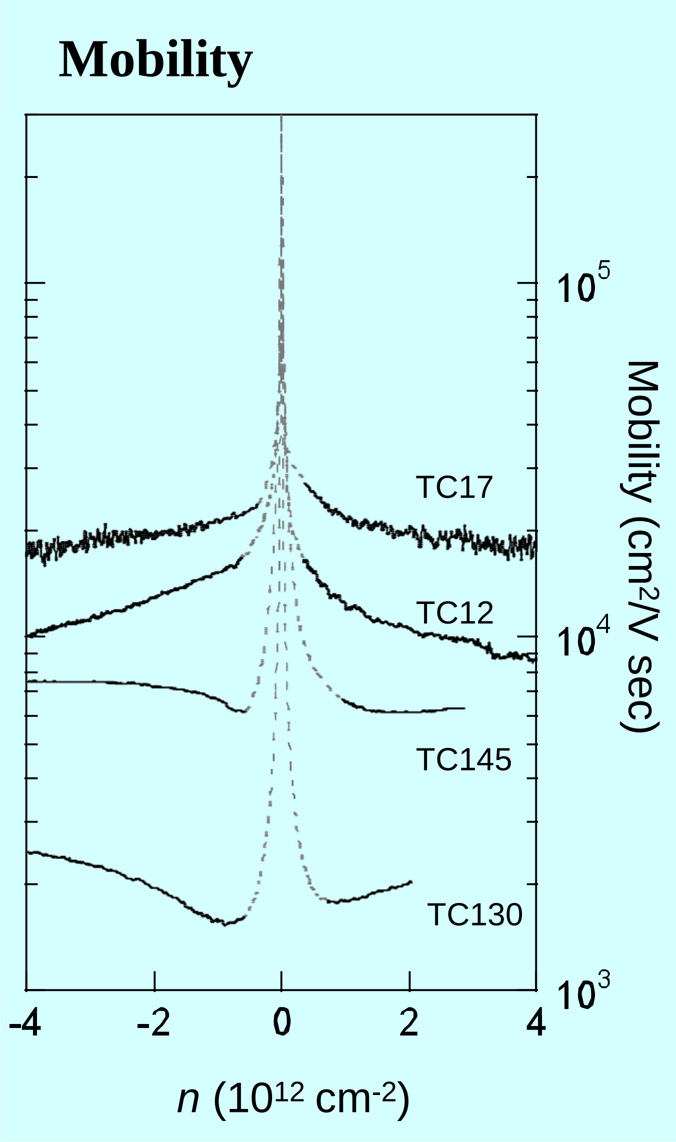


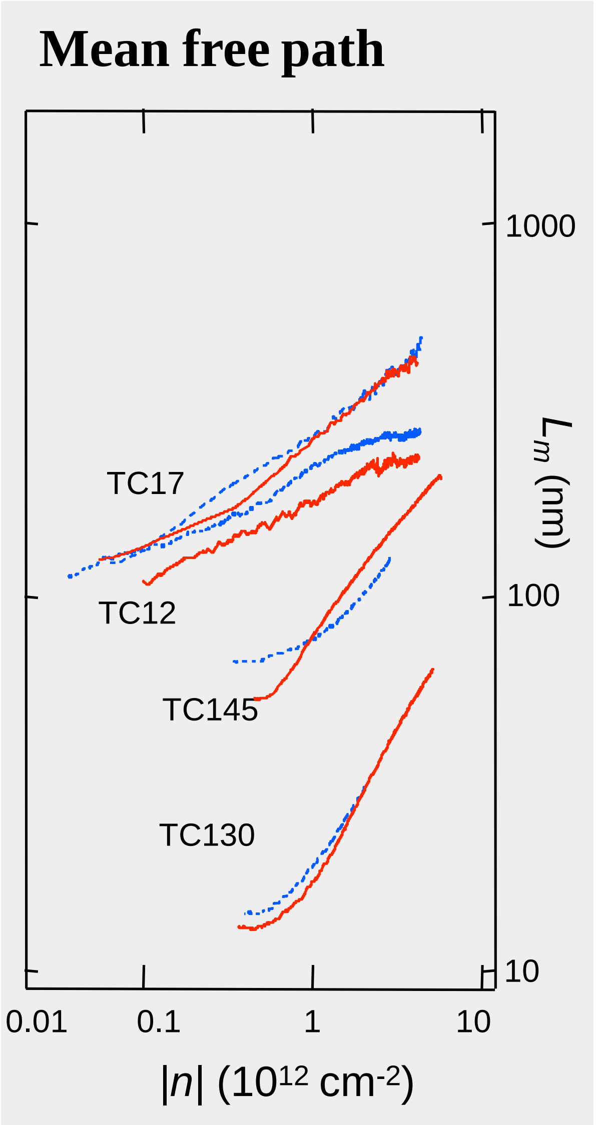
Tan al. PRL (2007)

Conductivity, Mobility, & Mean Free Path

$$\sigma = en\mu = \frac{e^2}{\hbar}\ell\sqrt{\frac{n}{\pi}}$$



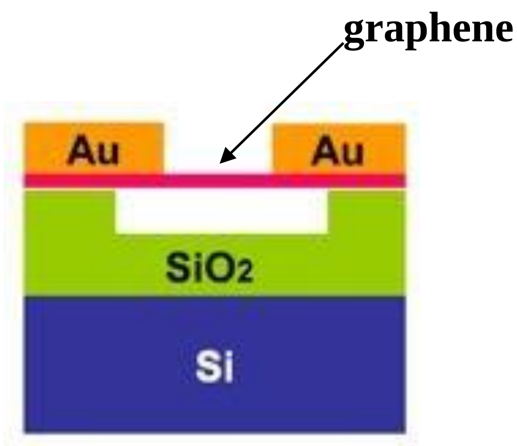




Spin transport

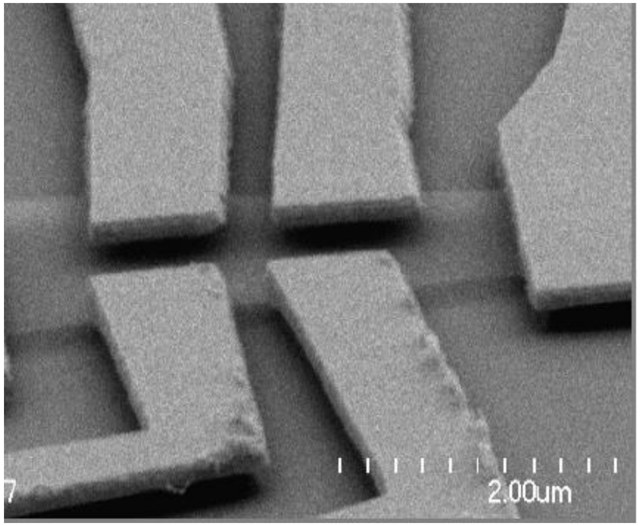
- Graphene is claimed to be an ideal material for spintronics due to its small spin orbit interaction and the near absence of nuclear magnetic moment in carbon.
- Electrical spin current injection and detection has been demonstrated up to room temperature.
- Spin coherence length λ over 1 μm at room temperature was observed, and control of the spin current polarity with an electrical gate was observed at low temperature.
- Spintronic and magnetic properties can be present in graphene simultaneously.

Toward High Mobility: Suspending Samples



HF etching
-> critical pointing drying

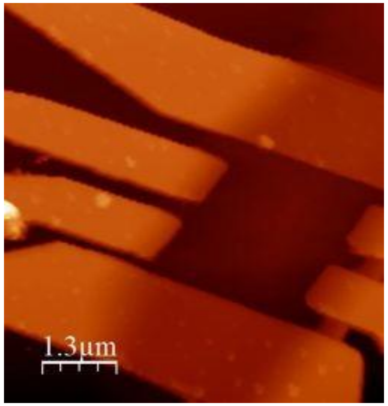
SEM image of suspended graphene

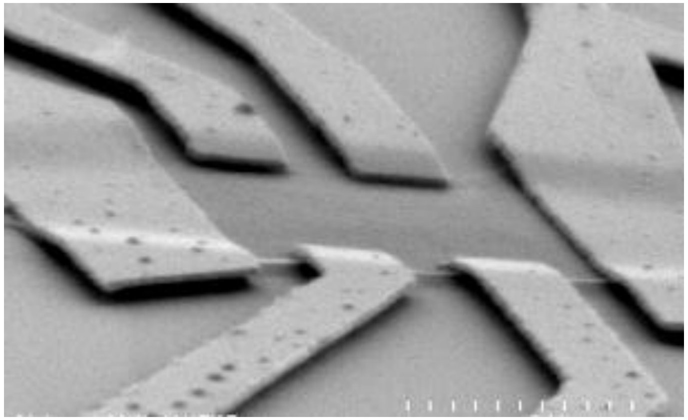


AFM image of suspended graphene

You should not apply to high gate voltage, otherwise…

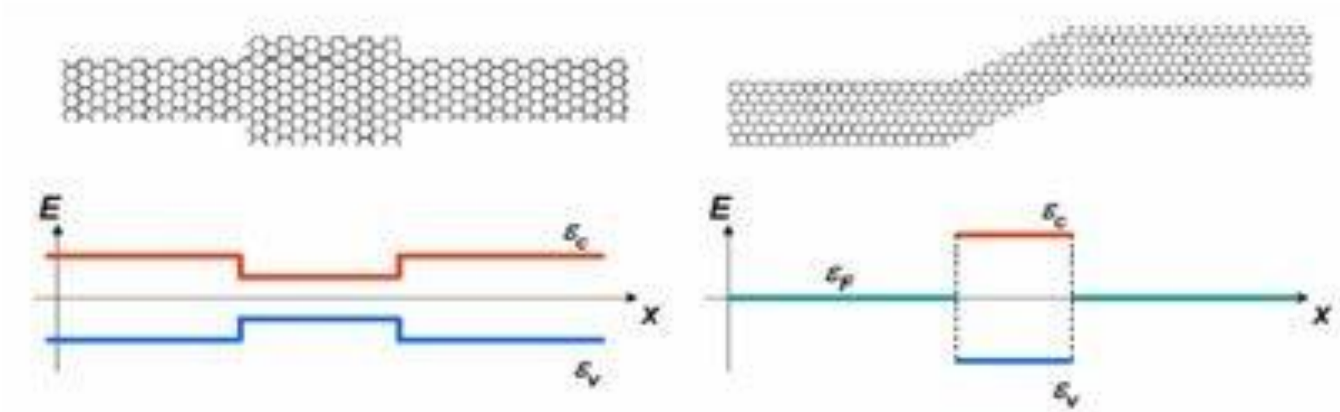
Collapsed graphene devices…



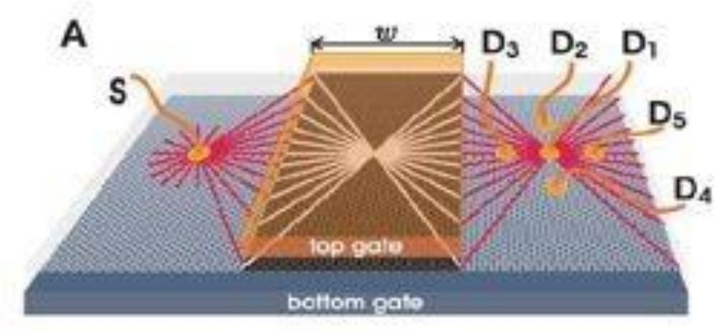


Graphene Electronics

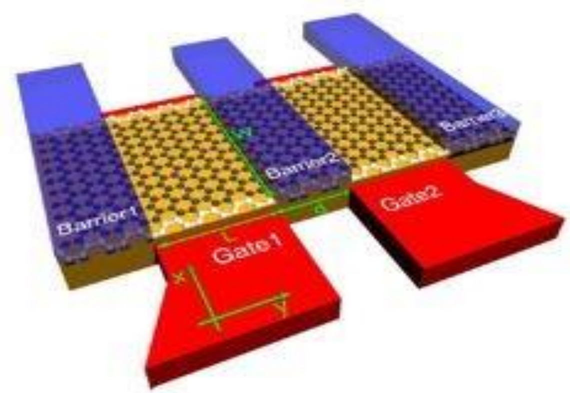
Engineer Dreams



Theorist Dreams



Graphene Veselago lense
Cheianov *et al. Science* (07)



Graphene q-bits
Trauzettel *et al. Nature Phys.* (07)

and more …

The Focusing of Electron Flow and a Veselago Lens in Graphene p-n Junctions

Science, VOL 315, 1252 (2007)

The focusing of electric current by a single *p-n* junction in graphene is theoretically predicted, as achieved by fine-tuning the densities of carriers on the *n-* and *p*-sides of the junction to equal values. This finding is useful for the engineering of electronic lenses and focused beam splitters using gate-controlled *n-p-n* junctions in graphene-based transistors.

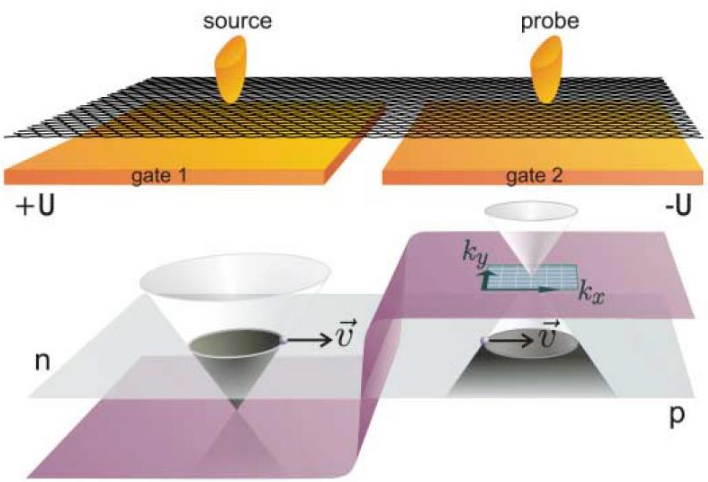


Fig. 1. Graphene *p-n* junction (PNJ). Monolayer of graphite is placed over the split gate, which is used to create *n*- (**left**) and *p*-doped (**right**) regions. The energy diagram shows the position of the Fermi level with respect to the touching point of the valence and the conduction bands.

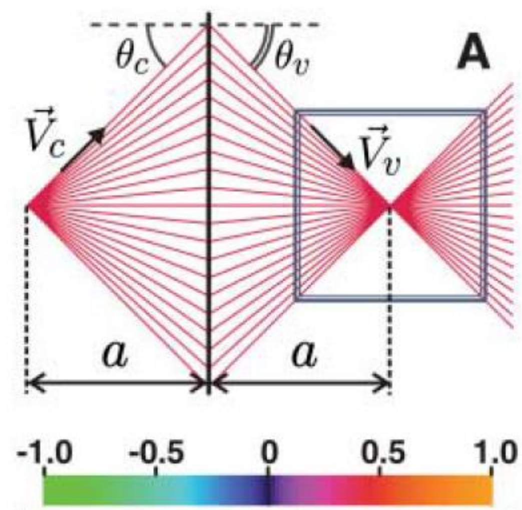


Fig. 2. Focusing of electrons by symmetric PNJ, $\rho_h = \rho_e$. (**A**) Classical trajectories of electrons diverging from a source at distance *a* from the junction become convergent after refraction. (**B**)

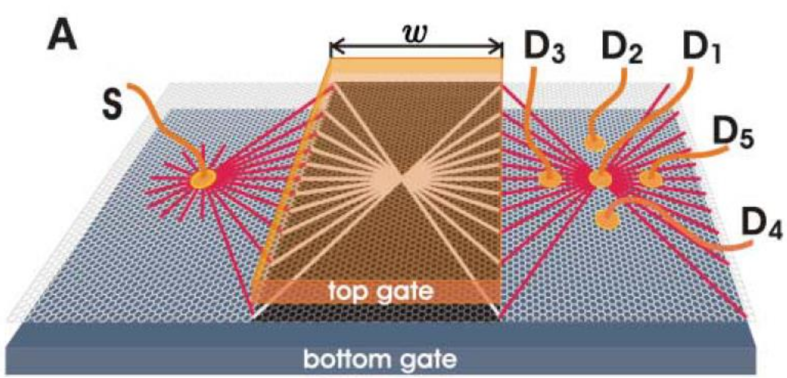
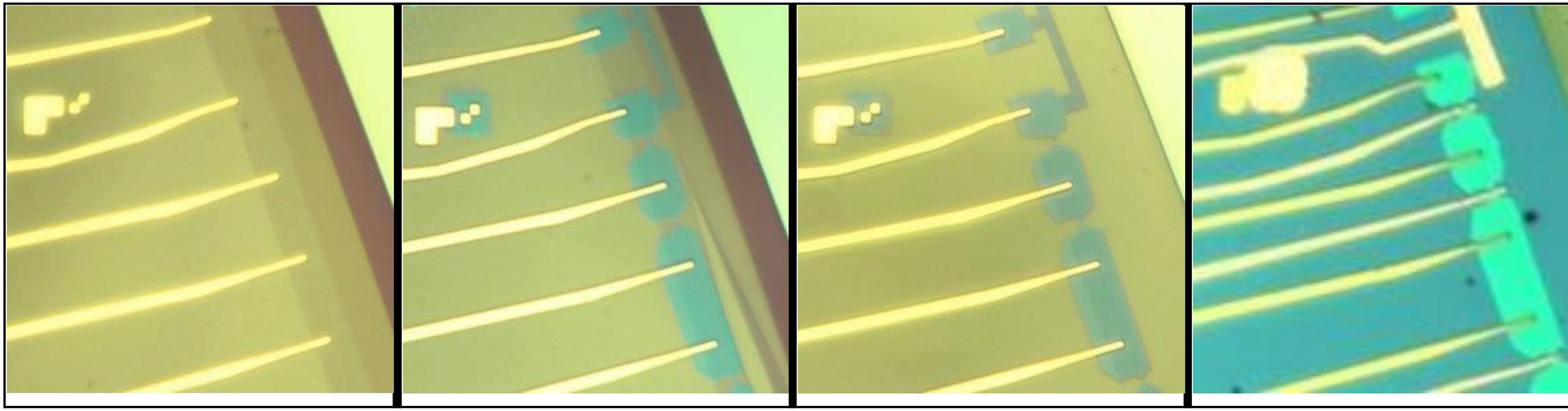


Fig. 4. (**A**) Electron Veselago lens and (**B** and **C**) prism-shaped focusing beam splitter in the ballistic *n-p-n* junction in graphene-based transistor.

From Graphene “Samples” To Graphene “Devices”



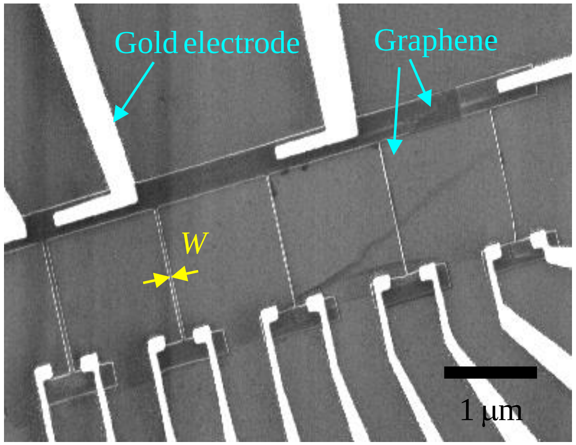
Contacts
:
PMMA
EBL
Evaporation

Graphene patterning:
HSQ
EBL
Development

Graphene etching:
Oxygen plasma

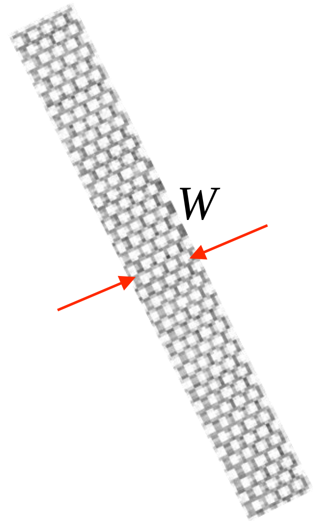
Local gates:
ALD HfO_2
EBL
Evaporation

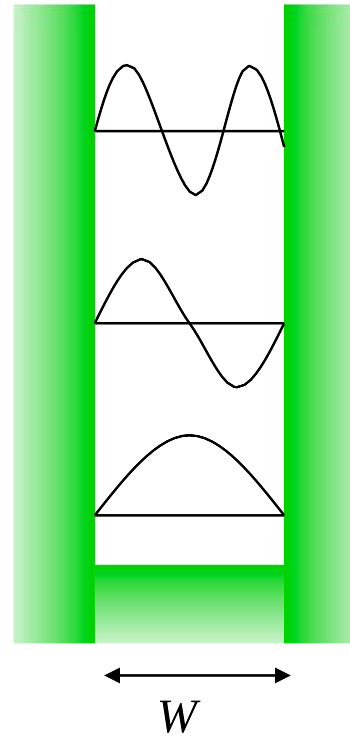
Graphene Nanoribbons: Confined Dirac Particles



10 nm < W < 100 nm

Dirac Particle Confinement





$$k_3 = \frac{3\cdot\pi}{W}$$

$$k_2 = \frac{2\cdot\pi}{W}$$

$$k_1 = \frac{1\cdot\pi}{W}$$

$$\Delta k - \frac{\pi}{W}$$

$$E_{gap} \sim \hbar v_F * k \sim h v_F / W$$

Graphene nanoribbon theory partial list

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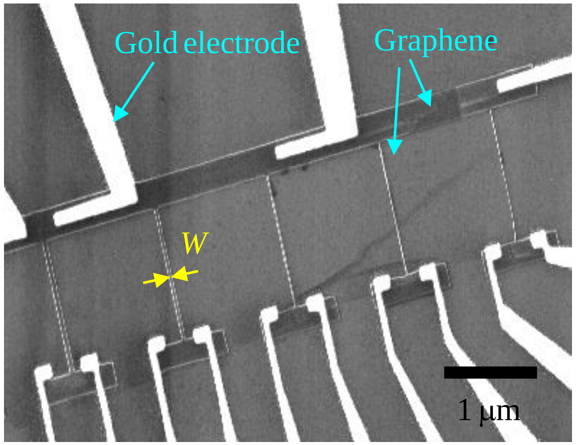
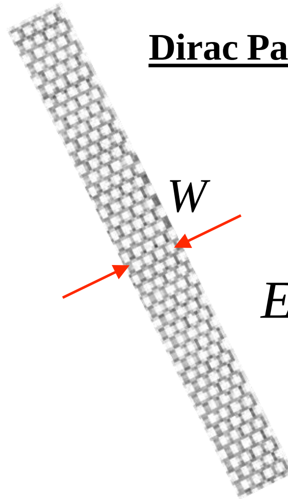
Graphene Ribbon Devices

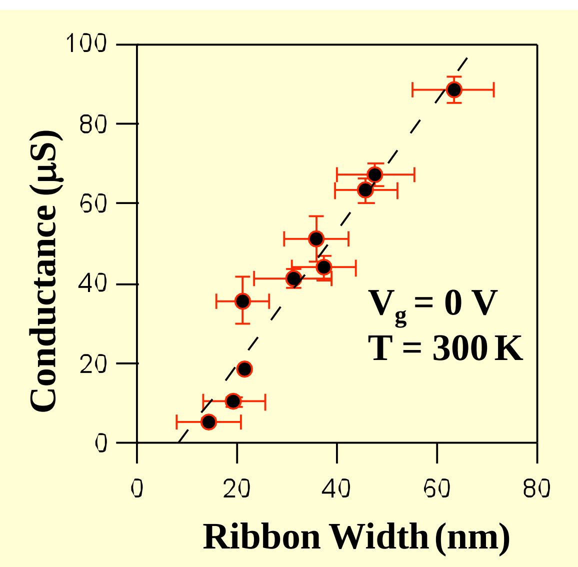


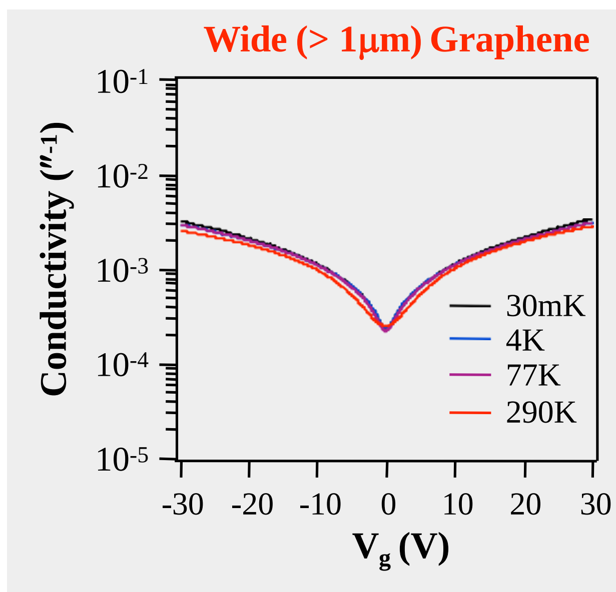
10 nm < W < 100 nm

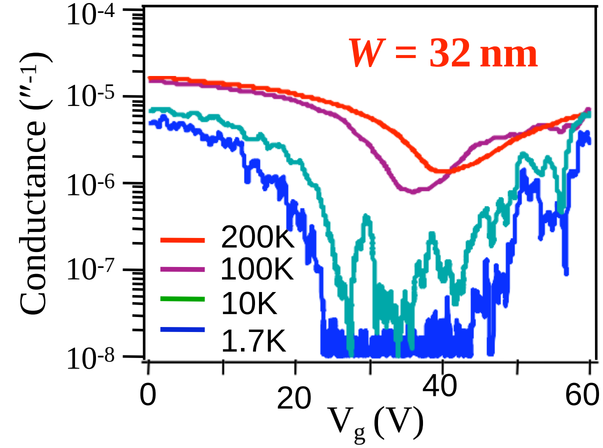


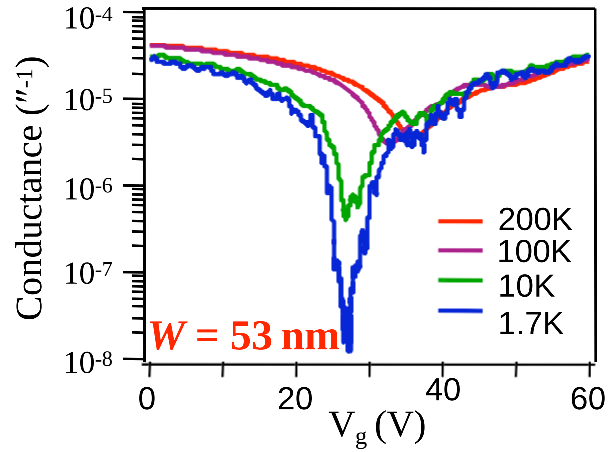
Dirac Particle Confinement

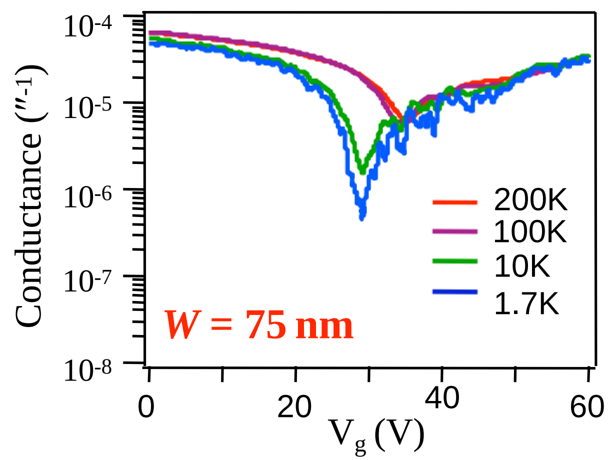
$$E_{gap} \sim \hbar v_F / W$$



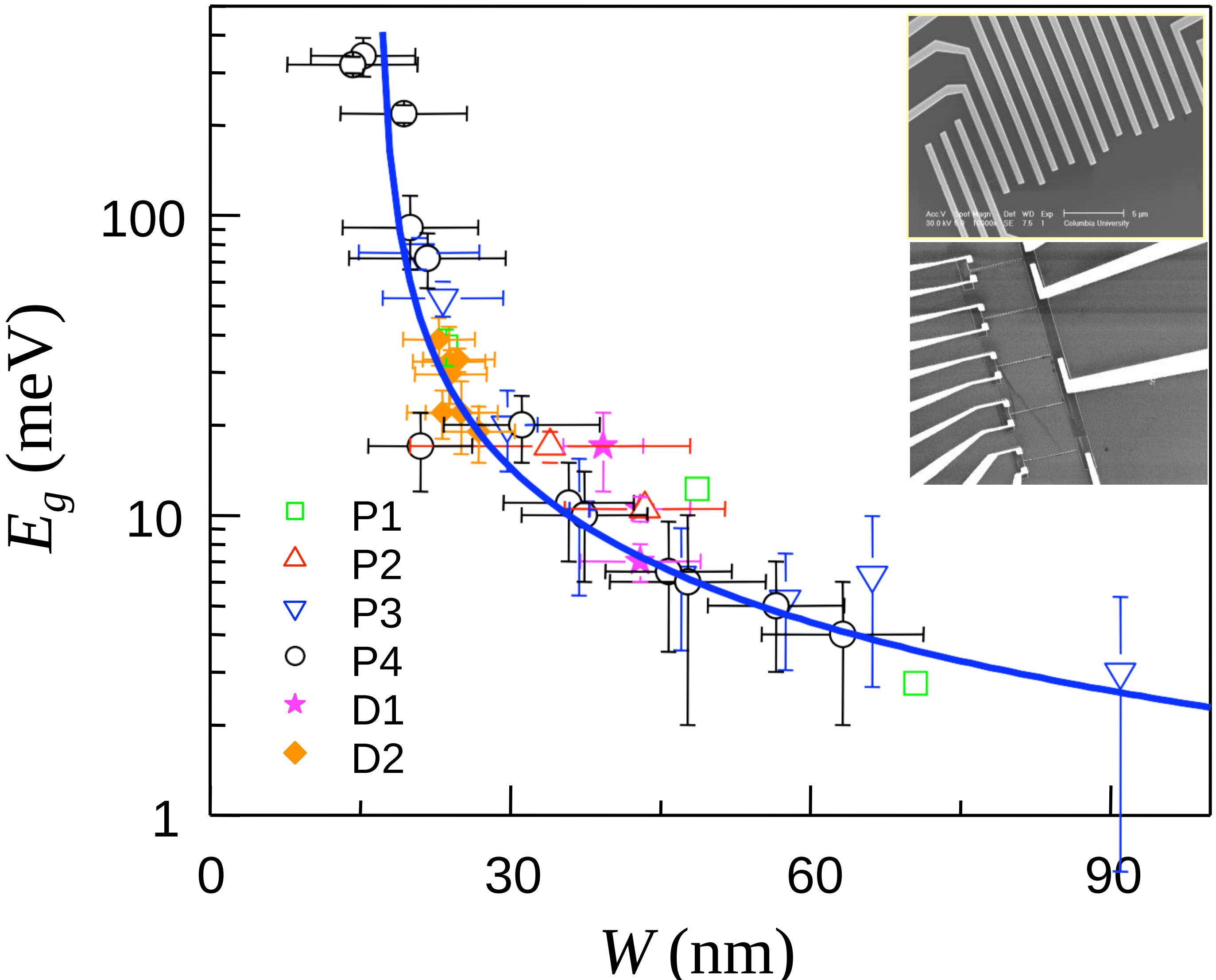








Scaling of Energy Gaps in Graphene Nanoribbons



$E_g = E_0/(W-W_0)$

Han, Oezyilmaz, Zhang and Kim PRL (2007)