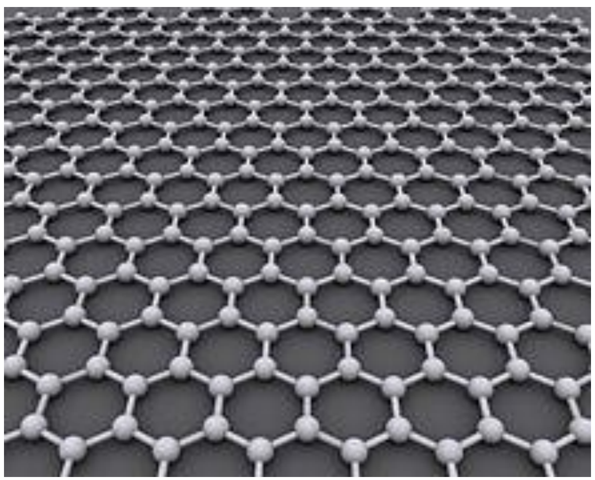
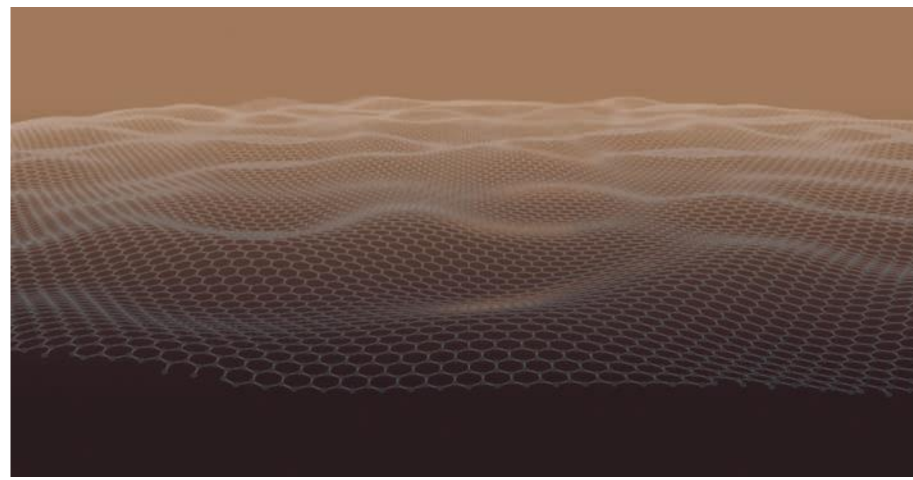
Emergent Properties of Two-Dimensional Materials

Flatlands beyond Graphene

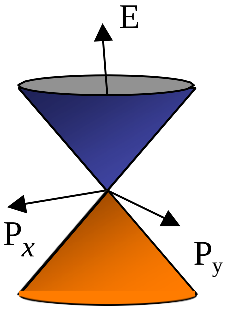




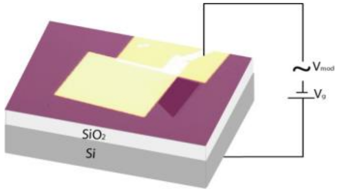
Prof. J. Raynien Kwo
Department of Physics,
National Tsing Hua University

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, anomalous quantum Hall effects, …



- **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

Andre Geim Konstantin Novoselov

Nobel Prize in Physics for 2010

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

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

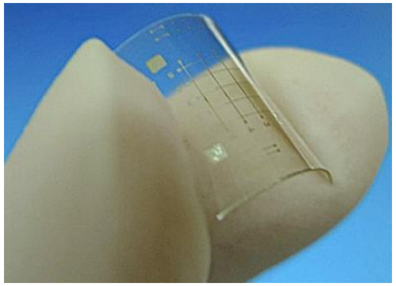
Aim to get graphene into industry and product development

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

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.

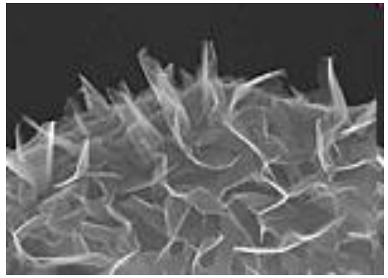
http://www.cambridgenetwork.co.uk/news/is-the-uk-set-to-miss-out-on-the-graphene-revolution/

Graphene's Applications



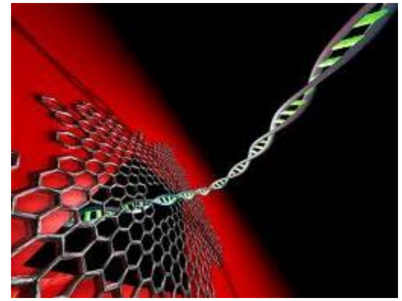
Flexible Memristors

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



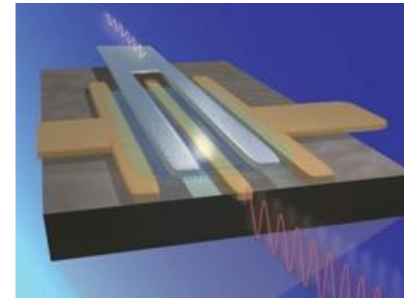
Ultracapacitor

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



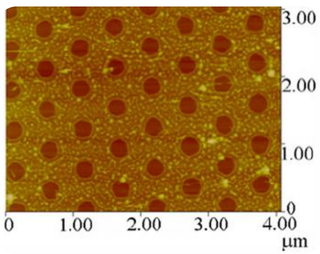
DNA graphene nanopore

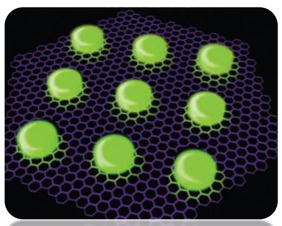
Nano Lett., ***10*** (8), 3163 (2010)
Nano Lett.,, ***10*** (8), 2915 (2010)
Nature **467**, 190–193 (2010)



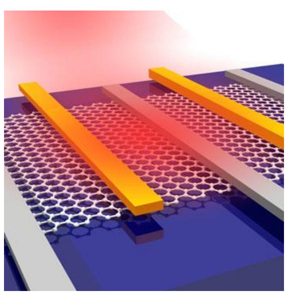
RF transistors

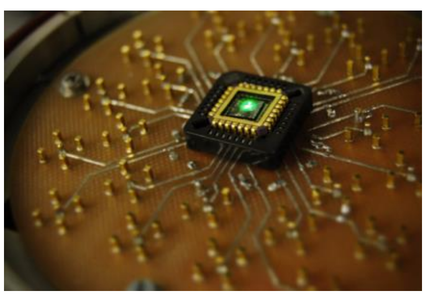
Nano Letters **9** (1), 422 (2009)
Nano Letters, **9** (12), 4474 (2009)
Science, **327**(5966), 662 (2010)
IEEE EDL, **31**(1), 68 (2010)
Nature **467**, 305–308 (2010)





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





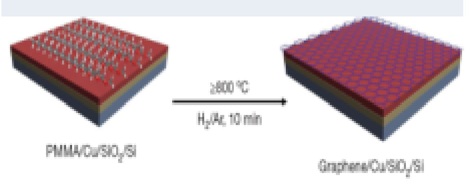
Graphene Photodetector
Nature Photonics **4**, 297 - 301 (2010)
Nature Nanotechnology **7**, 363–368 (2012)

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

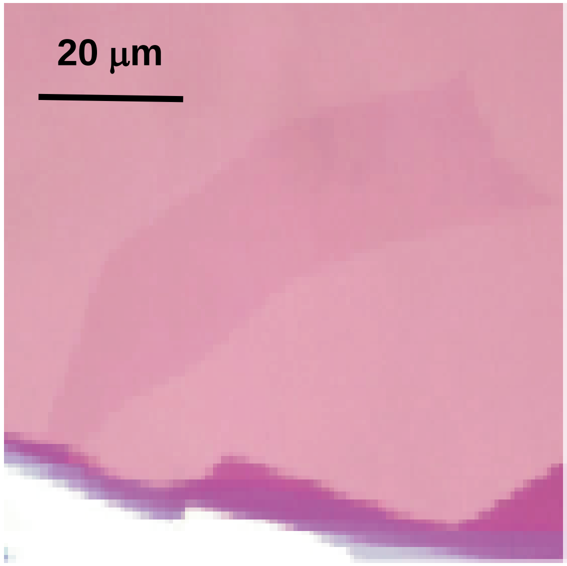
*http://www.nanowerk.com/news2/newsid=27702.php

Fabrication of graphene

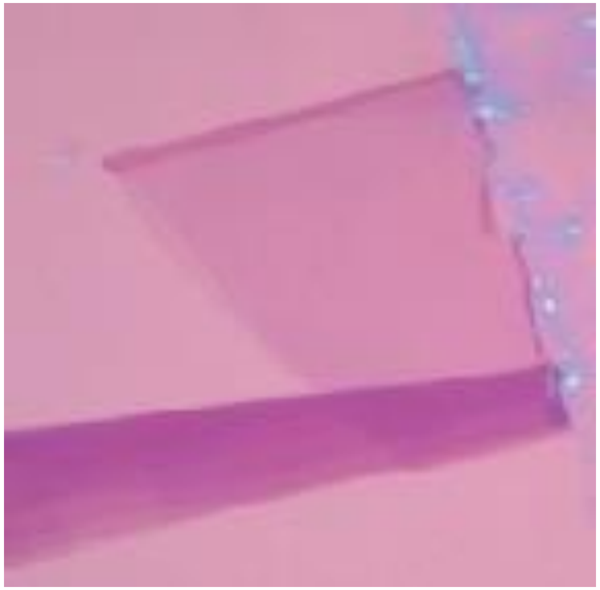
Method	Descriptions	Merits	References
Mechanical cleavage or exfoliation	Scotch Tape 	Minimal defects Intrinsic properties Small sizes	Science 306, 666 (2004)
Chemical oxidized process	Producing GO by the oxidation of graphite with acid	Large scale flakes Composite	Nature 442, 282 (2006)
Epitaxial growth 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



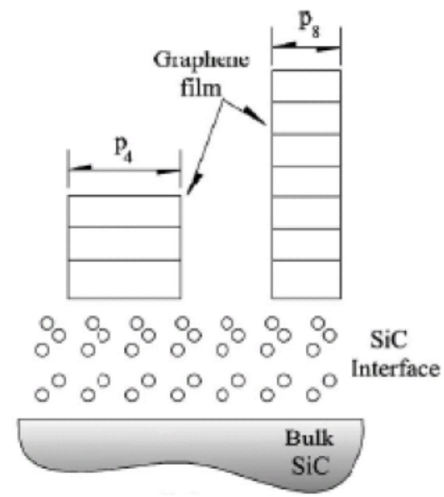
Bilayer

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

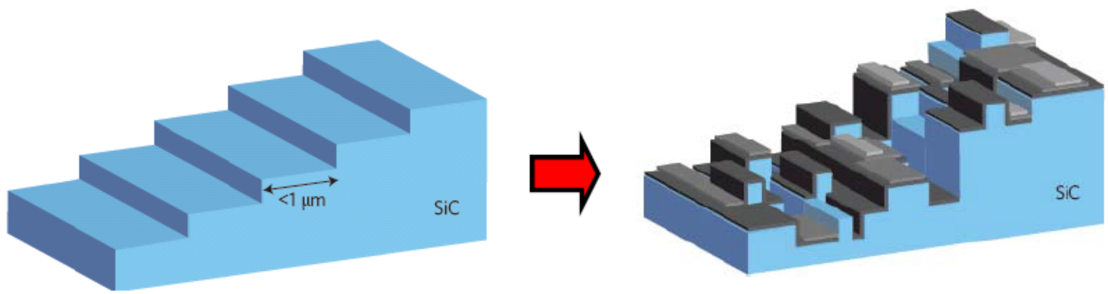
Epitaxial growth of graphene

Epitaxial graphene grown on SiC(0001) surfaces

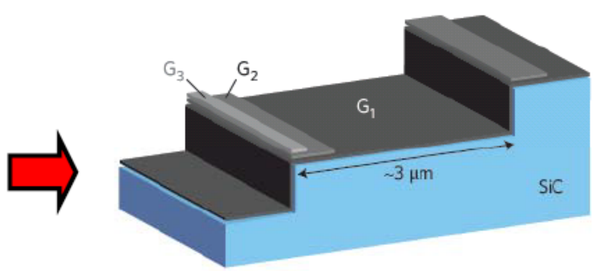
One often ends up with multi-layers of graphene with small grains 30nm-200nm



Recent progress:



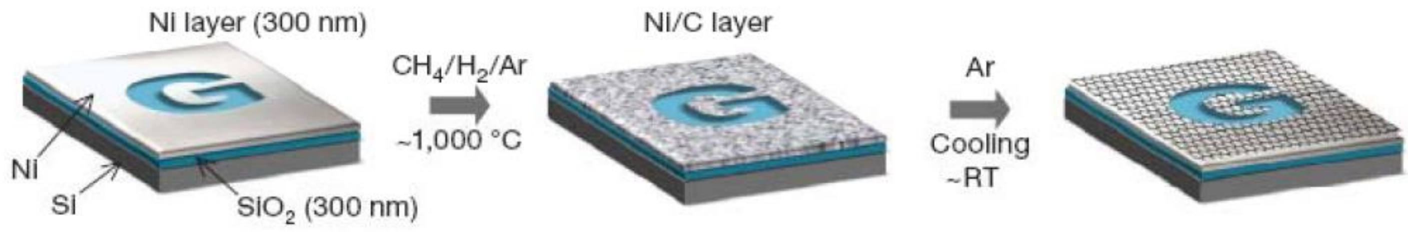
UHV



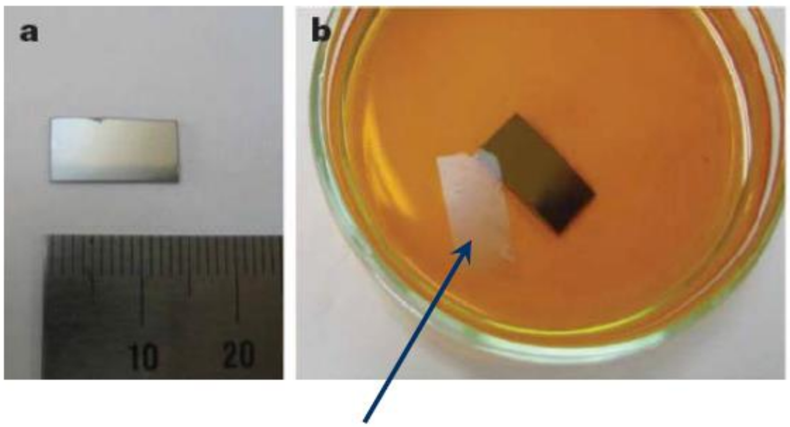
In the presence of pressurized Ar

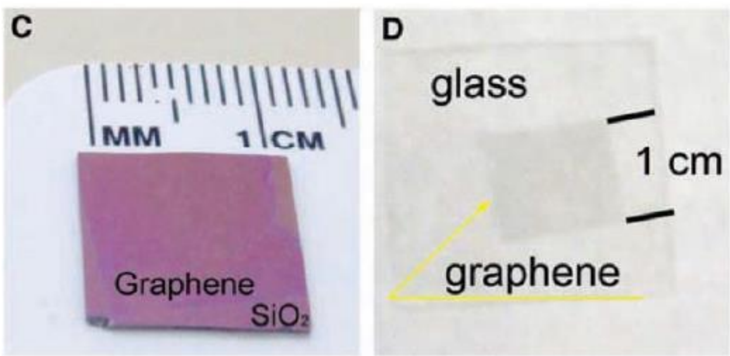
K.V. Emvsev et al., Nature Materials 8, 203 (2009)

CVD graphene on metal substrates



Etching and transfer



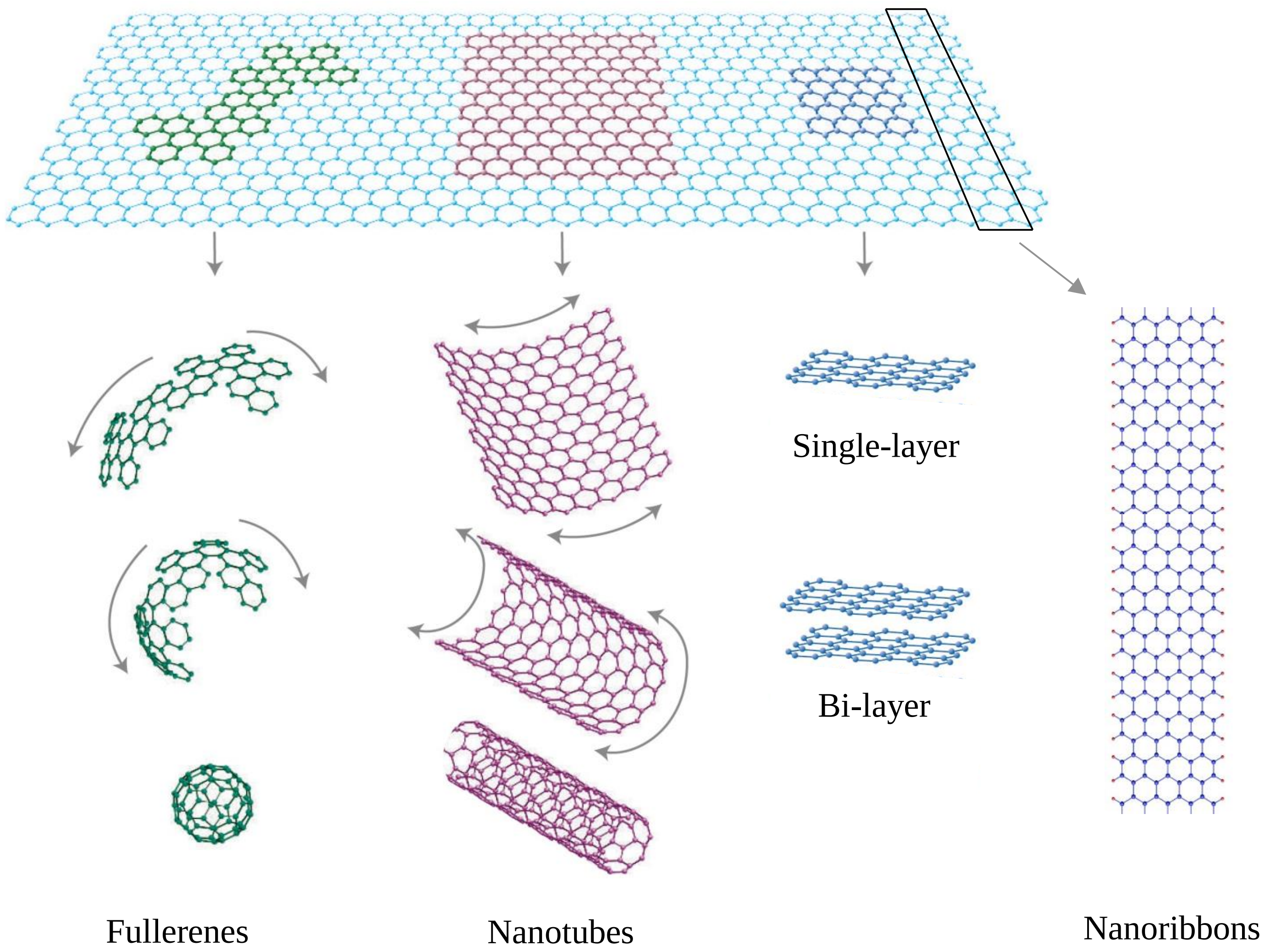


Cu: Li et al., Science 324, 1312 (2009)

Floating graphene after Ni being etched

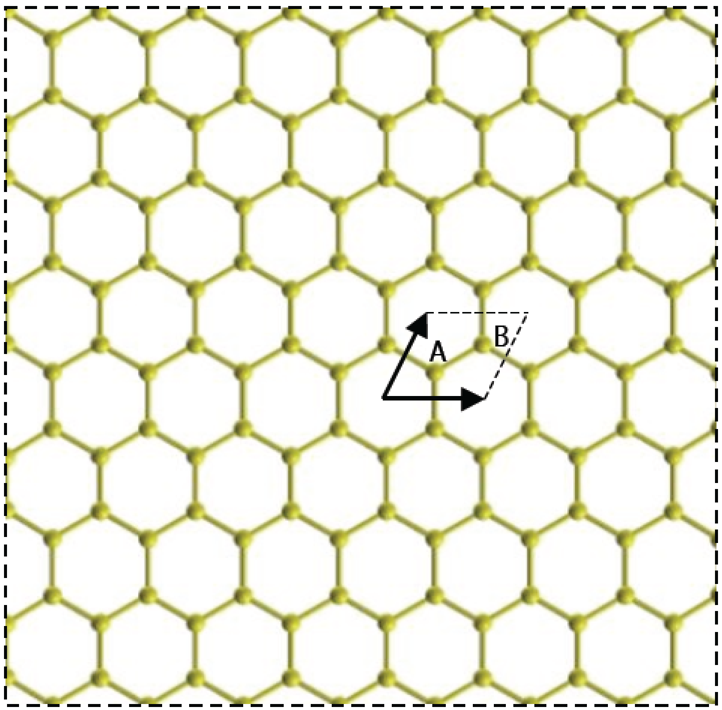
Ni: Kim et al., Nature 457, 706 (2009)

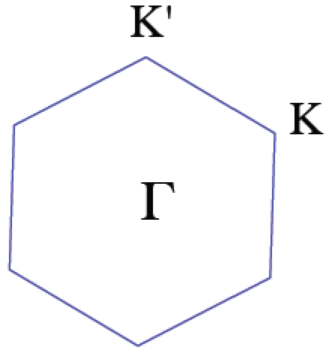
Graphene and Related Carbon sp^2-bonded Structures



Graphene

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

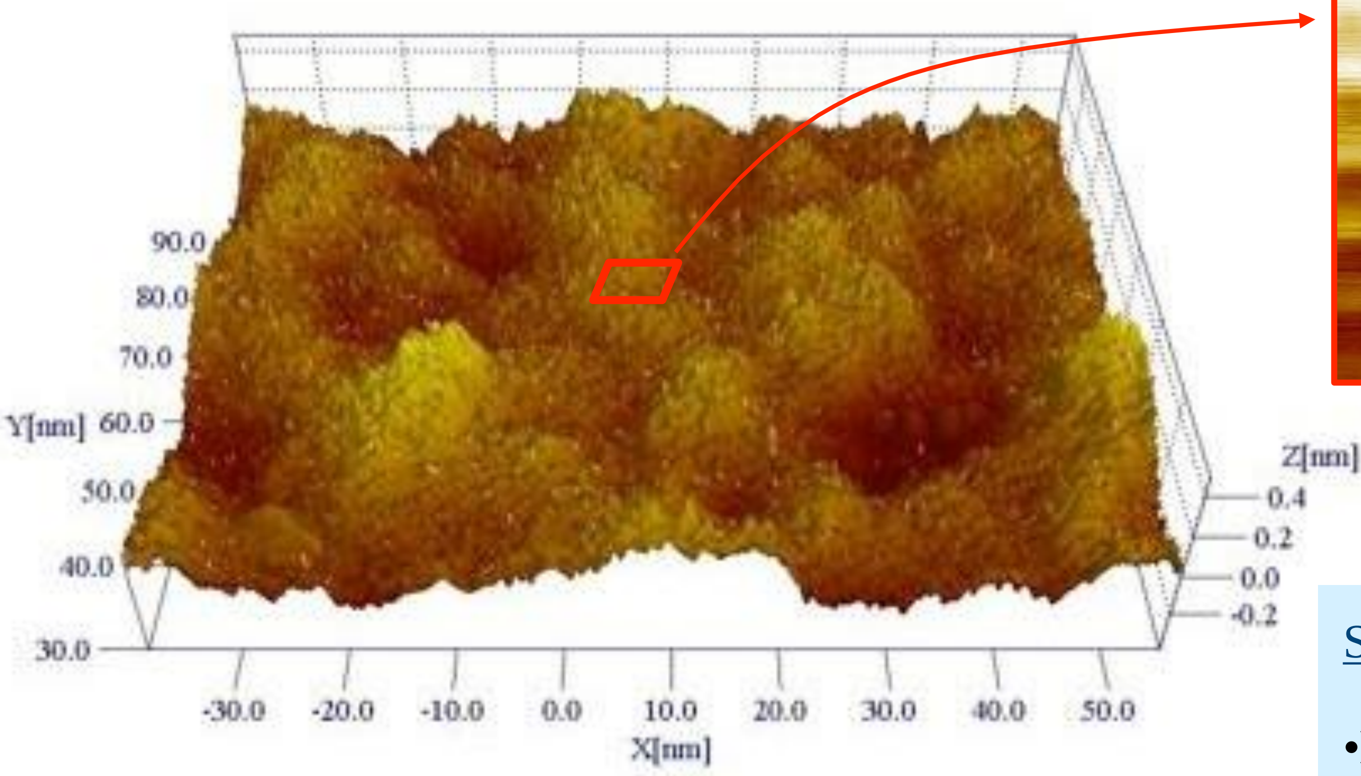




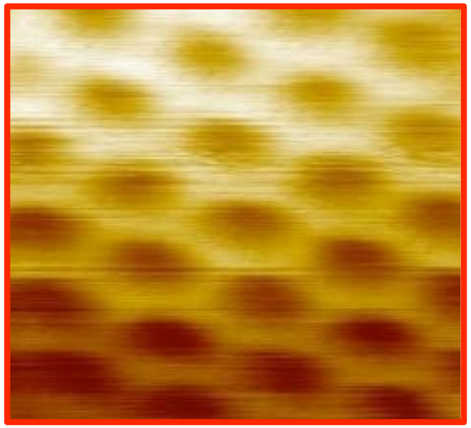
Brillouin zone

STM on Graphene

Ripples of graphene on a SiO_2 substrate



Atomic resolution



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

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

Scattering Mechanism?

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

Unique Properties of Graphene

- ❑ **Room-temperature electron mobility of $2.5x10^5$ cm^2V^{-1} s^{-1}**

  Nano Lett. 11, 2396–2399 (2011).

- ❑ **Young's modulus of 1 TPa and intrinsic strength of 130 GPa**

  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).

- ❑ **Optical absorption of 2.3%**

  Science 320, 1308 (2008).

- ❑ **No band gap for undoped graphene**

- ❑ Graphene shows a large and nonlinear **diamagnetism**,[4] greater than graphite and can be levitated by neodymium magnets.

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

Exotic Behaviors

- Quantum Hall effect

- Barry Phase

- Ballistic transport

- Klein's paradox

- Others

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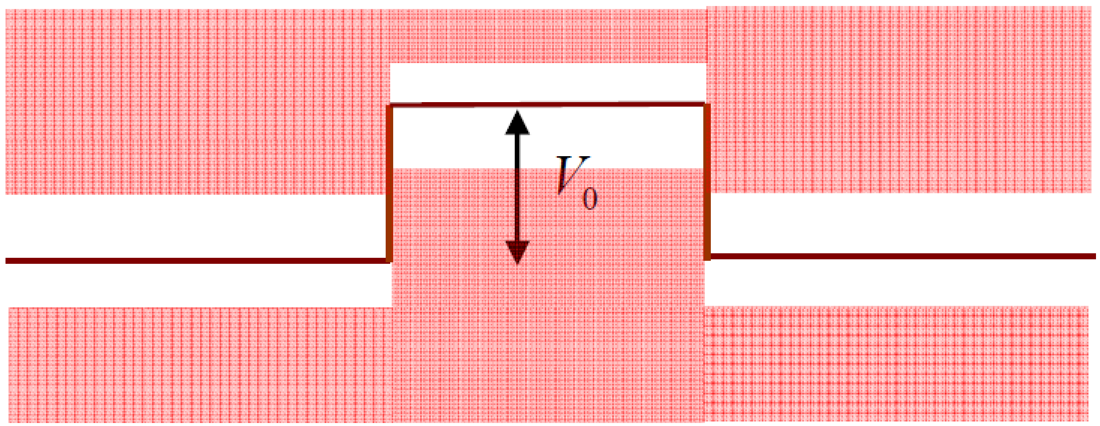
Electron scattering from a potential barrier

Potential complication: Klein Paradox (1929)



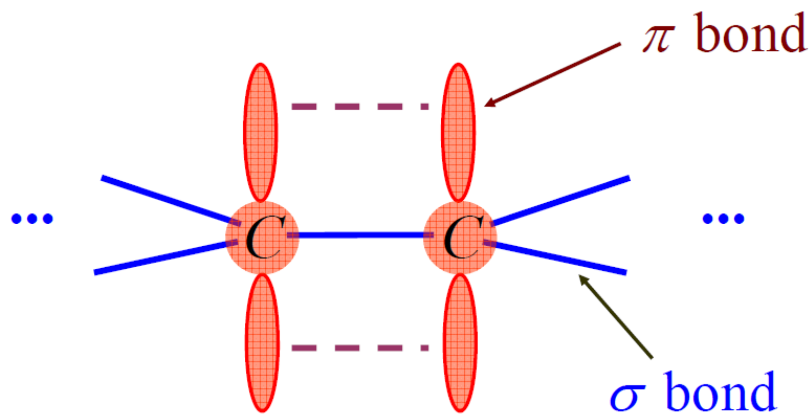
$$T \to 1 \text{ as } V_0 \Rightarrow m_0 c^2$$

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

No confinement for electrons

On/off ratio is reduced in graphene FET

Element of Carbon Network

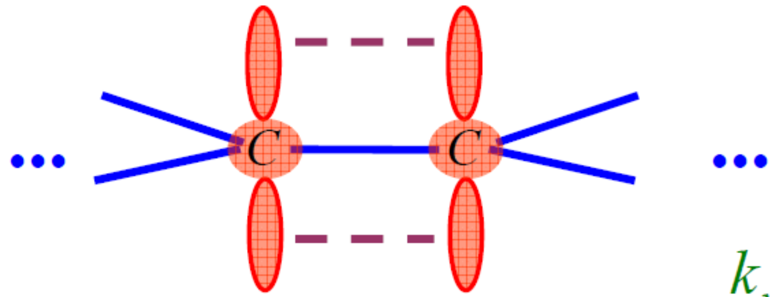


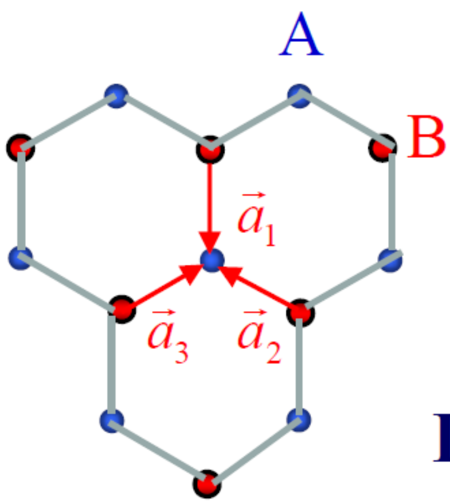
Carbon $1S^2 \underbrace{2S^2 2P^2}$

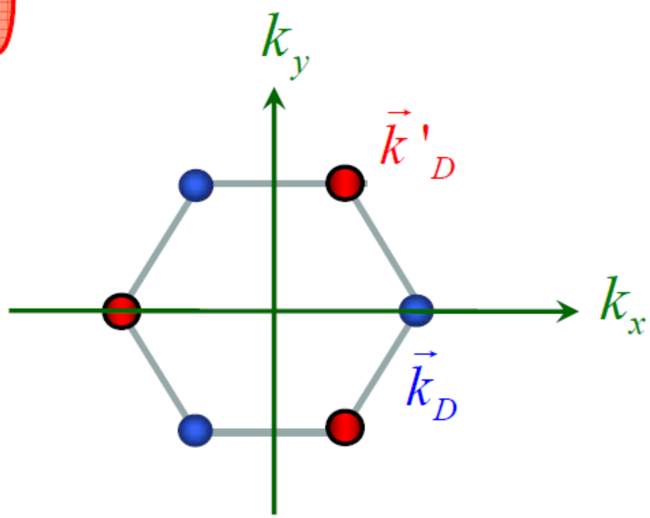
- Each atom has four bonds, one **σ bond** with each of its three neighbors, and one **π-bond** that is oriented out of plane. The atoms are about 1.42 A apart. Graphene's hexagonal lattice can be regarded as two interleaving triangular lattices. This perspective was used to calculate the band structure for a single graphite layer using a tight-binding approximation.
- Graphene's stability is due to its tightly packed carbon atoms and a sp^2 orbital hybridization

  – a combination of orbitals **s, p_x** and **p_y** that constitute the **σ-bond**.
- The final ***p_z*** electron makes up the **π-bond**. The π-bonds hybridize together to form the π-band and π∗-bands. These bands are responsible for most of graphene's notable electronic properties, via the half-filled band that permits free-moving electrons.

Parent spectrum
Two dimensional Dirac Fermions







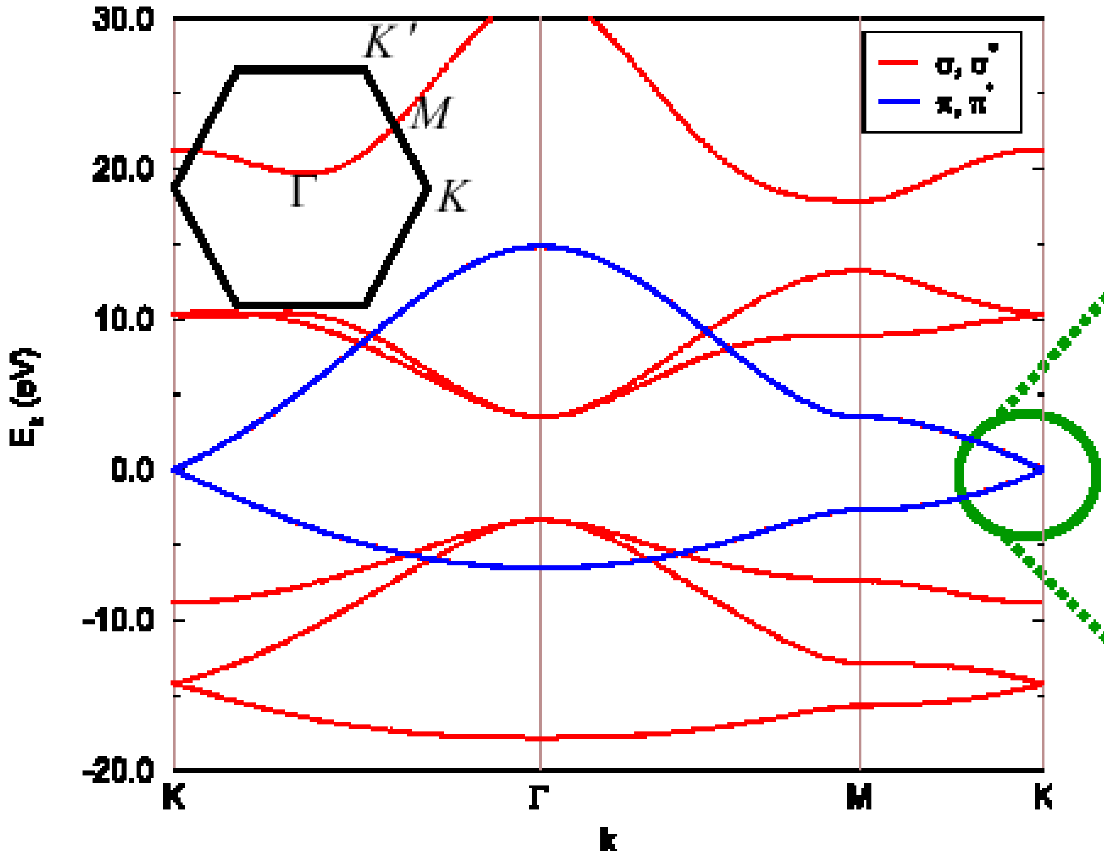
Dirac points

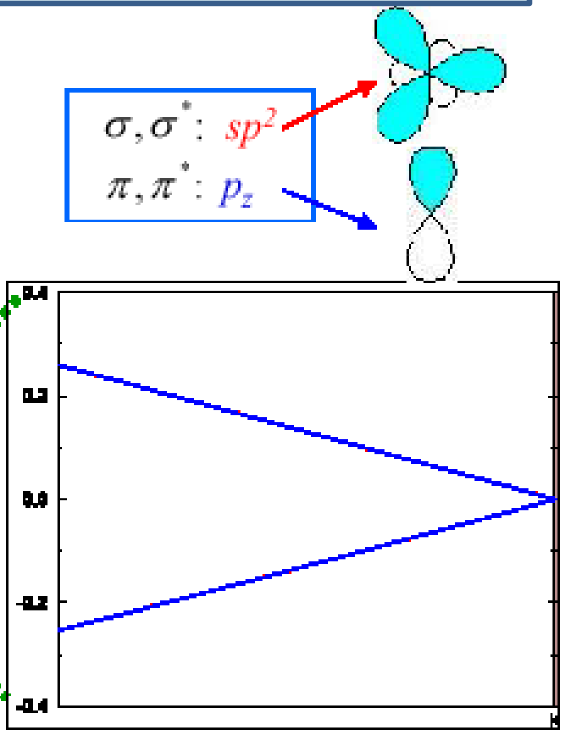
$$e^{i\vec{k}_D\cdot\vec{a}_n} = 1,\ e^{i2\pi/3},\ e^{i4\pi/3} \Leftrightarrow \sum_n e^{i\vec{k}_D\cdot\vec{a}_n} = 0$$

Electronic Structure of Graphene

Tight Binding Model

$$E = \pm\sqrt{\gamma_0^2\left(1 + 4\cos^2\frac{3k_y a}{2} + 4\cos\frac{3k_y a}{2}\cdot\cos\frac{k_x\sqrt{3}a}{2}\right)}$$





$\Rightarrow$ decoupled to $sp^2 + p_z$

Graphene electronic structure

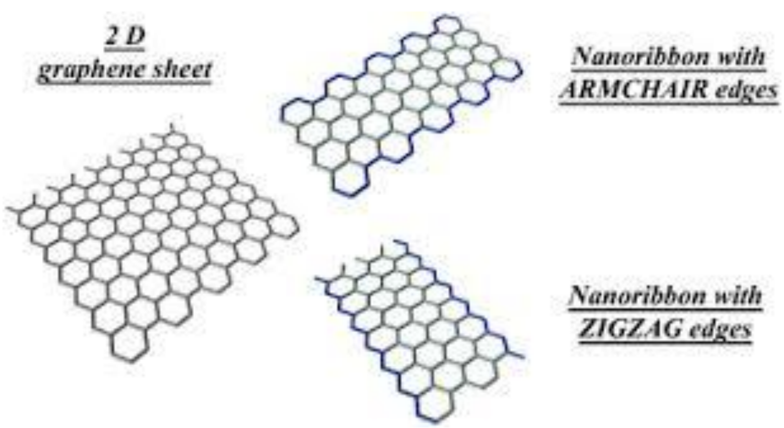
- Graphene is a zero-gap semiconductor, because its conduction and valence bands meet at the Dirac points.

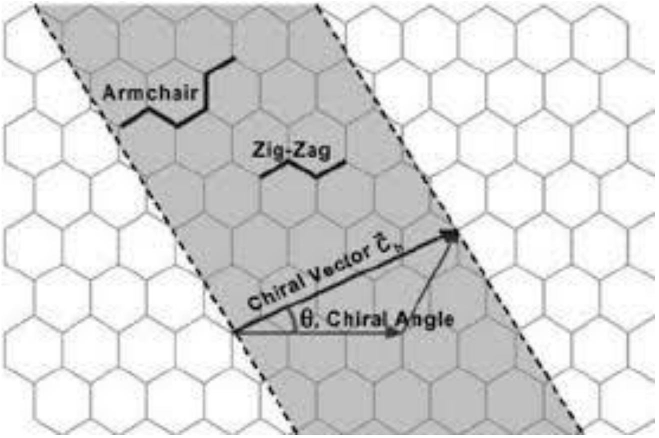
- The Dirac points are six locations in momentum space, on the edge of the Brillouin zone, divided into two non-equivalent sets of three points.

- The two sets are labeled **K** and **K**'. The sets give graphene a valley degeneracy of $g_v = 2$.

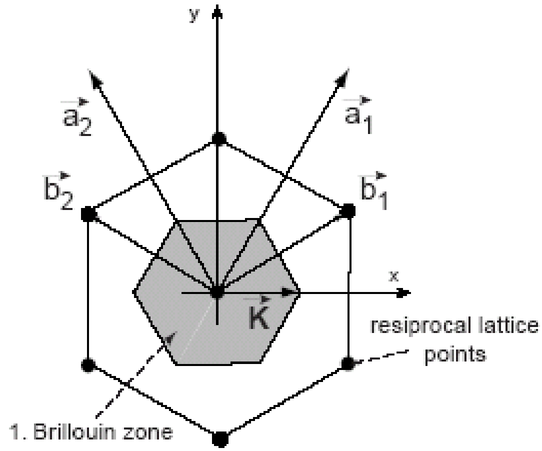
- However, if the in-plane direction is confined, in which case it is referred to as a nanoribbon, its electronic structure is different.

- If it is "zig-zag", the bandgap is zero. If it is "armchair", the bandgap is non-zero.





Graphene electronic structures



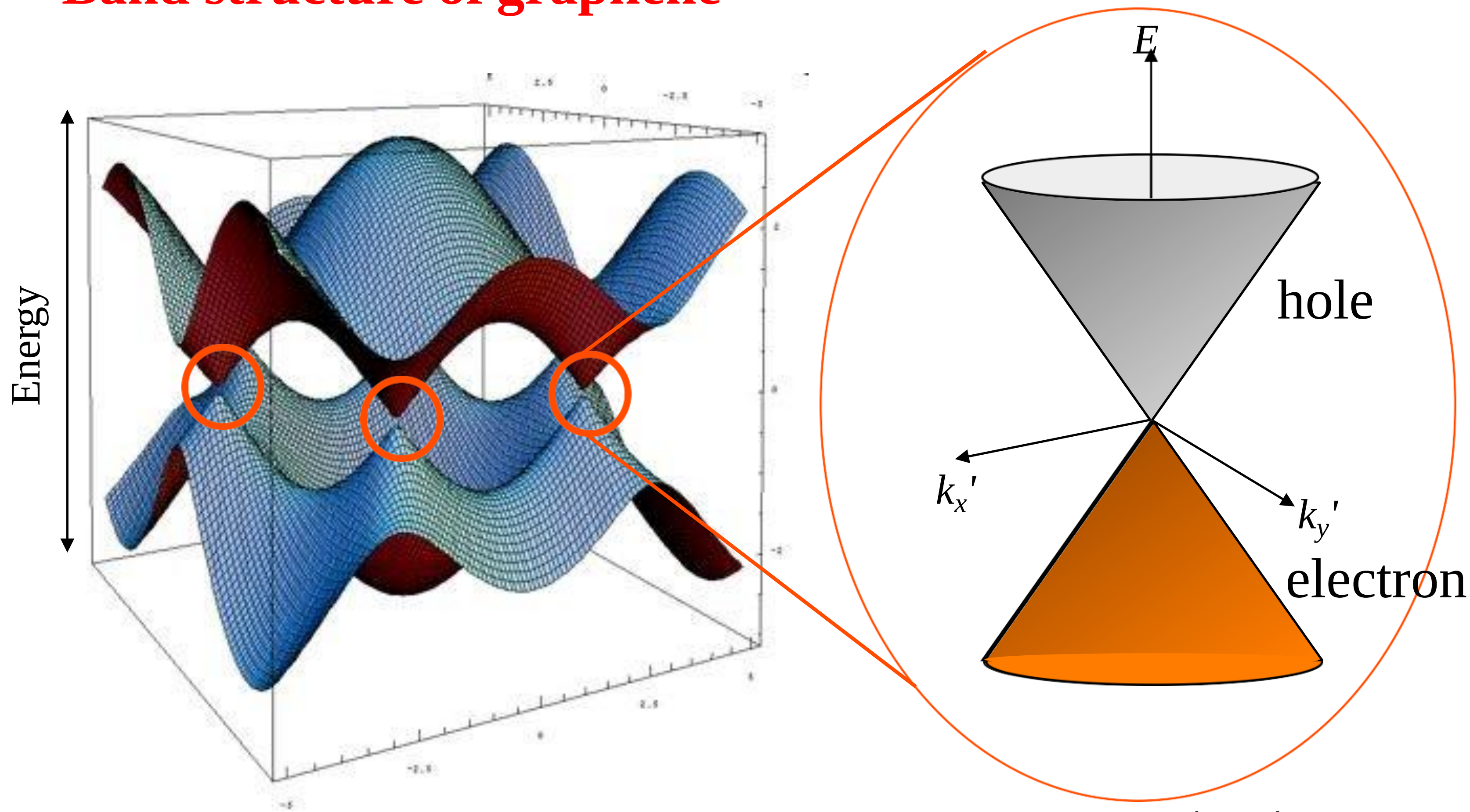
- E–K relation is linear for low energies near the six corners of the two-dimensional hexagonal Brillouin zone, leading to zero effective mass for electrons and holes.
- Due to this linear dispersion relation at low energies, electrons and holes near these six points, two of which are inequivalent, behave 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.

Graphene : 2-D Massless Dirac Fermions

Band structure of graphene

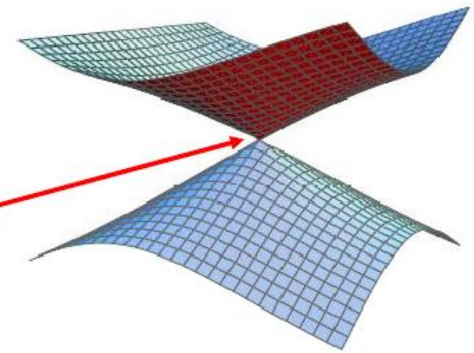


$$E \approx \hbar v_F \left| \vec{k}'_{\perp} \right|$$

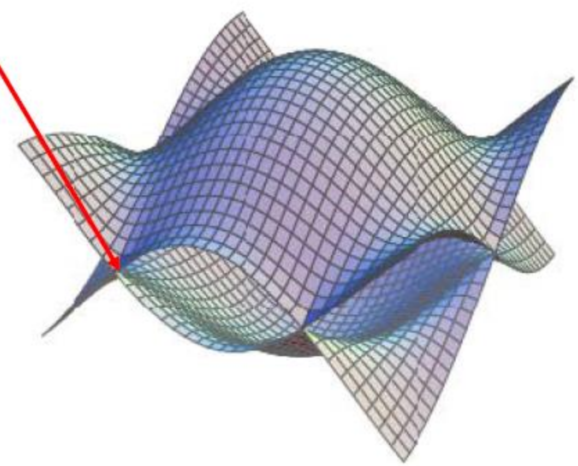
Zero effective mass particles moving with a constant speed v_F

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!

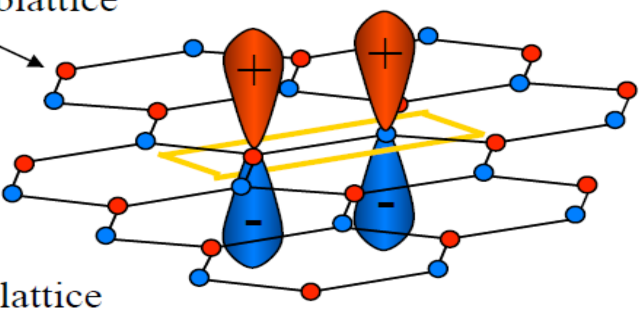
Pseudospin in Materials

- Although spin is the quantized intrinsic angular momentum of a particle, **many other physical quantities can act as an effective spin-1/2, which is referred to as pseudospin**.

This concept was first introduced by Heisenberg to describe the structure of the atomic nucleus as composed of neutrons and protons, modelled as two states of the same particle.

- **A pseudospin is a coherent superposition of two quantum states,** and is described in terms of Pauli matrices for spin -1/2, $\sigma = (\sigma x, \sigma y, \sigma z)$.
- In physics of Spin-orbit-coupled transport have identified new degrees of freedom, that can be accounted for within the pseudospin language.
- In hexagonal 2D diamonds, the pseudospin is composed of the sublattices,
- In TMDC it describes the valence and conduction bands of the transition metal.
- In van der Waals bilayers, when the layer index is a good quantum number, a layer pseudospin can also be identified.
- In cold-atom systems, the spin-1/2 pseudospin is defined by two hyperfine split states that can be, for example, coherently coupled by a laser.
- The concept of pseudospin is useful for predicting and interpreting the transport properties of the various systems, in particular when a Rashba-type pseudospin–orbit coupling is present.

Pseudo Spin in Graphene Lattice



Relative amplitude of sublattice wavefunctions

$p_z^{\mathbf{A}}(r) + e^{i\theta} p_z^{\mathbf{B}}(r)$ $\theta = 0$: bonding $\theta = \pi$: antibonding

½ Spinor

$$\begin{pmatrix} 1 \\ e^{i\theta} \end{pmatrix}$$

$p_z^{\mathbf{A}}(r)$

$p_z^{\mathbf{B}}(r)$

k•*p* perturbation theory

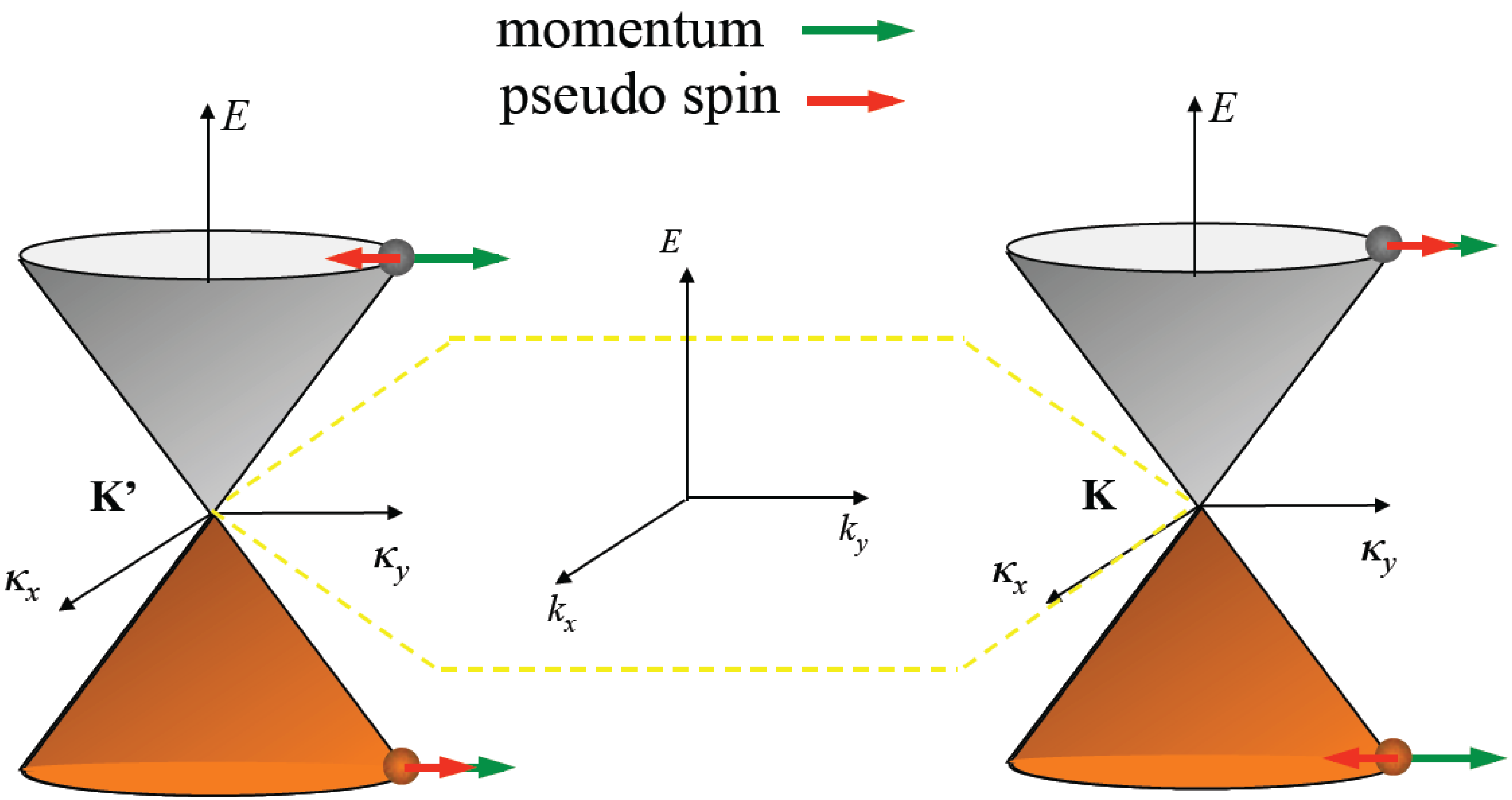
$$H_{eff} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_F \vec{\sigma} \cdot \vec{k}_\perp$$

$$|k_\perp\rangle = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ e^{i\theta_\kappa} \end{pmatrix}$$

$$\theta_k = \tan^{-1}(k_y / k_x)$$

DiVincenzo and Mele, PRB (1984); T. Ando, JPSJ (1998);McEuen at al, PRL (1999)

Dirac Fermions in Graphene : “Helicity”



σ is the vector of Pauli Matrices.

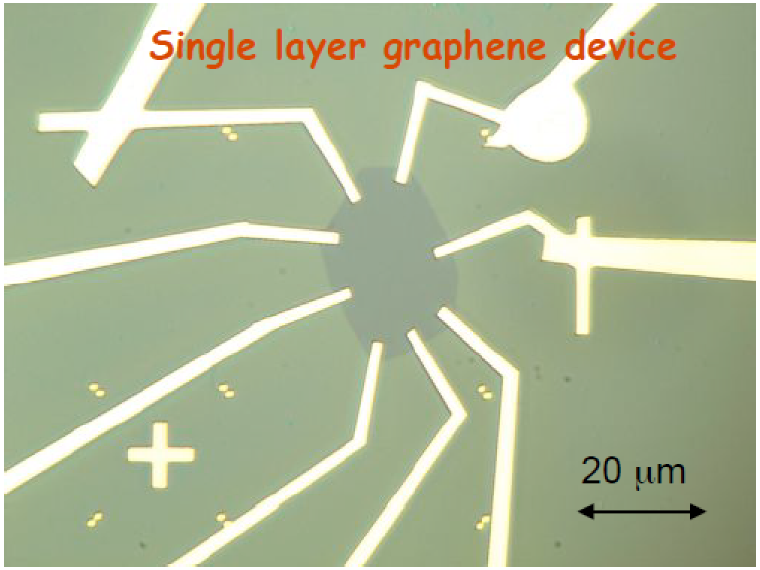
$$H_{eff} = \hbar v_F \vec{\sigma}^* \cdot \vec{k}_\perp$$

$$H_{eff} = \hbar v_F \vec{\sigma} \cdot \vec{k}_\perp$$

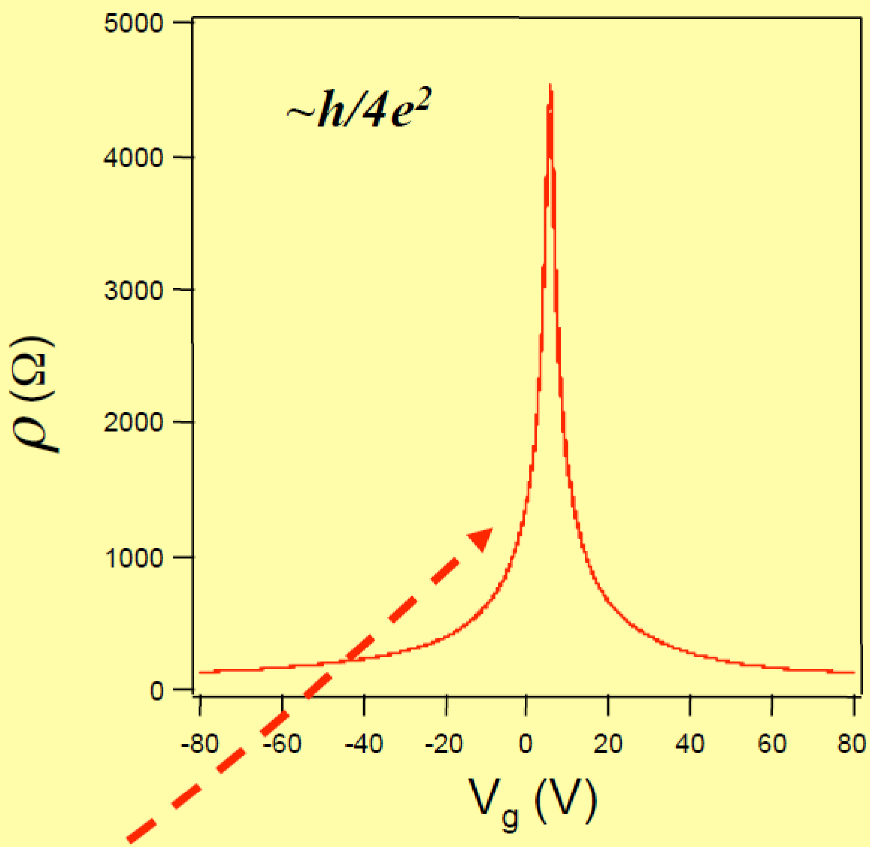
Quantum Hall effect in Graphene

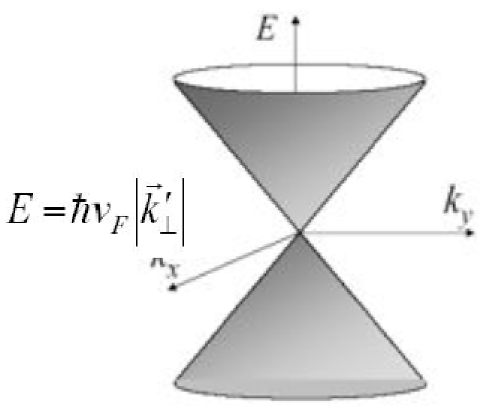
- The quantum Hall effect, a quantum mechanical version of the Hall effect, is the production of transverse conductivity in the presence of a magnetic field. The quantization of the Hall effect at integer multiples (the "Landau level") of the basic quantity. It can usually be observed only in very clean Si or GaAs solids 3K 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. In Graphene's Hall conductivity the double valley and double spin degeneracies give the factor of 4. at roughly 20 °C.
- This behavior is a direct result of graphene's massless Dirac electrons. These anomalies are present 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. 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.

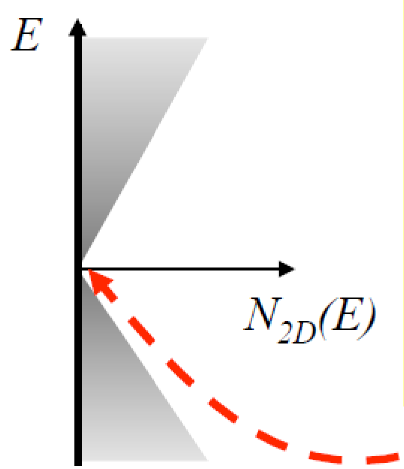
Transport Single Layer Graphene



Resistivity vs Gate Voltage





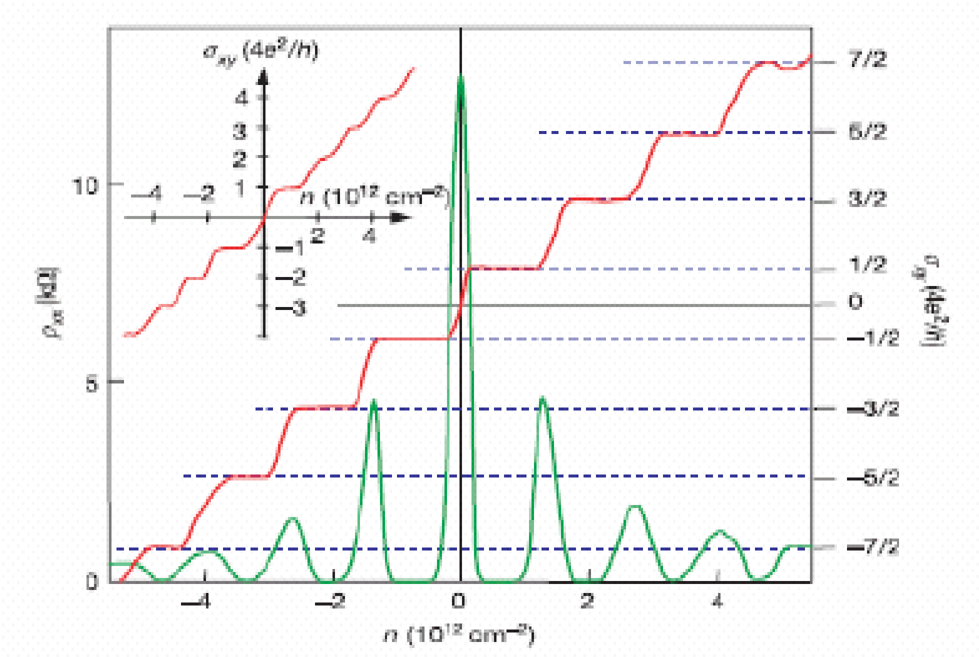


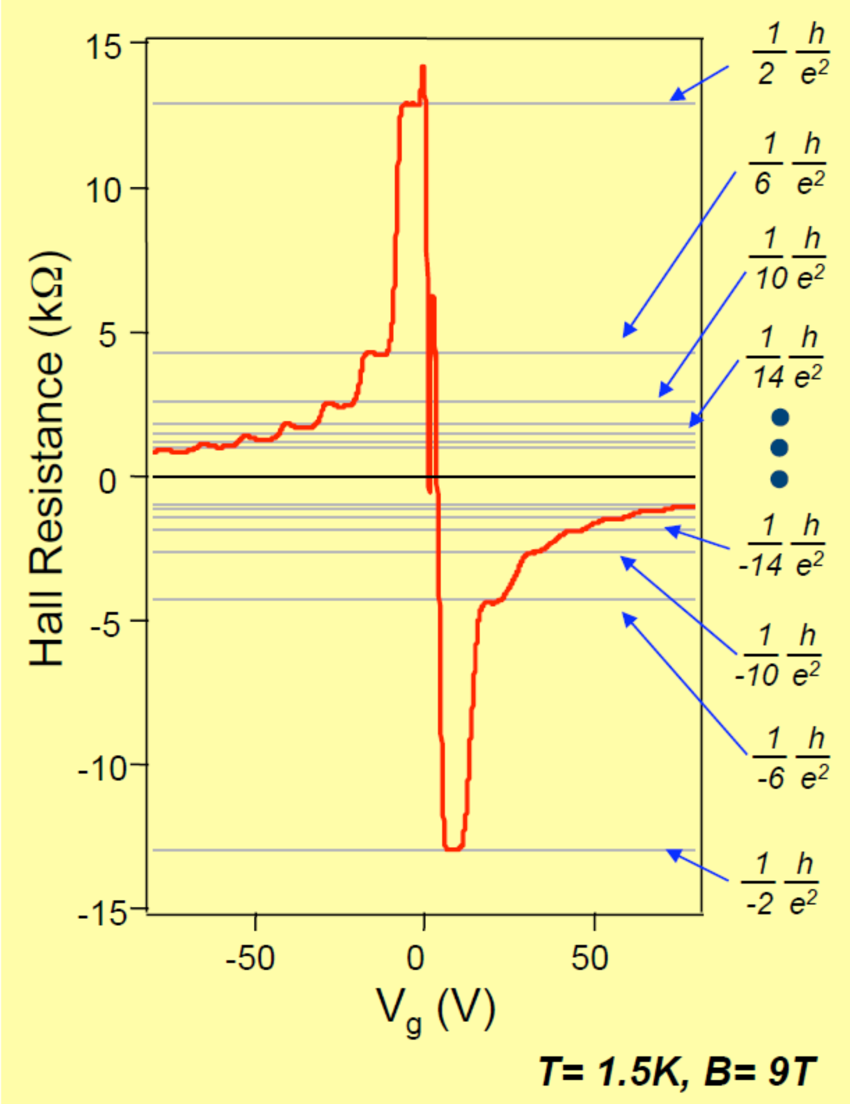
$$\rho^{-1} = e^2 v_F\, l_e\, N_{2D}$$

Quantum Hall Effect in Graphene

T = 3K

Novoselov et al ; Zhang et al (2005)



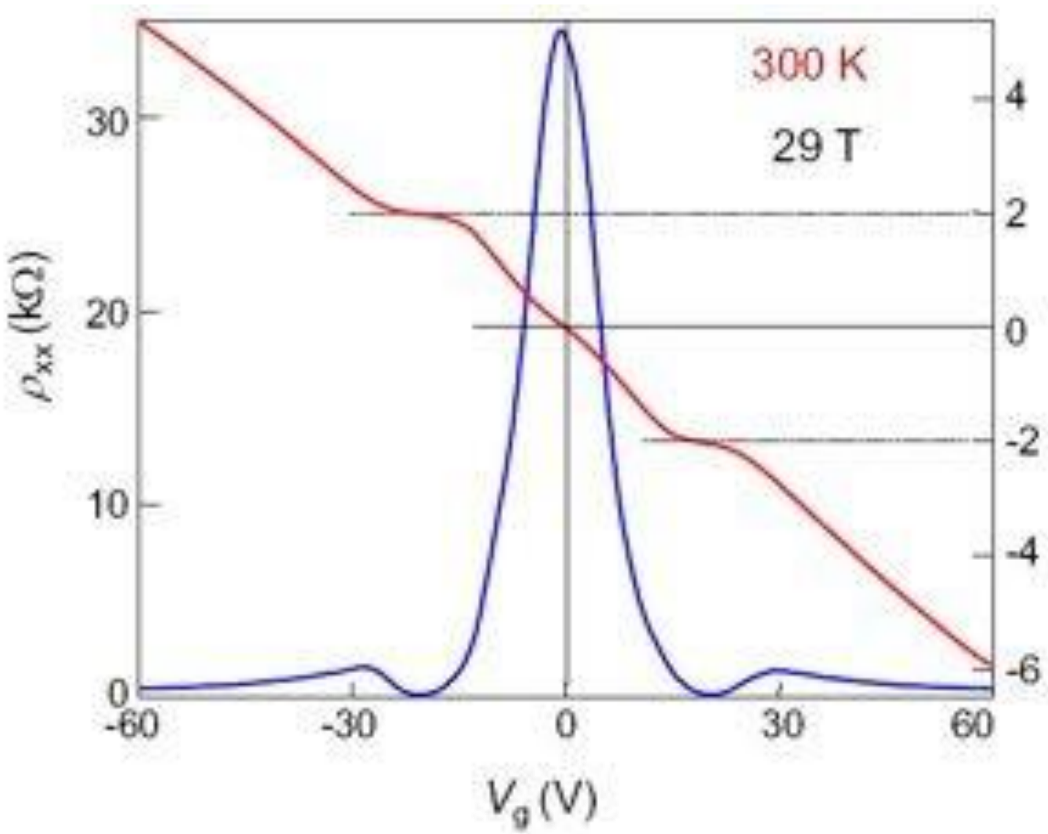


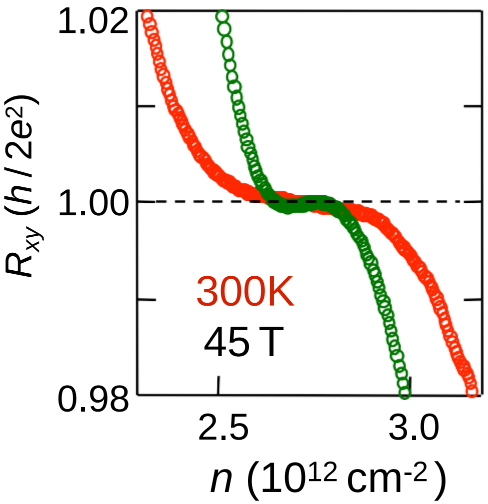
Conductivity Quantization:

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

Y. B. Zhang et al, *Nature* **438**, 201(2005)

Room Temperature Quantum Hall Effect





Deviation < 0.3%

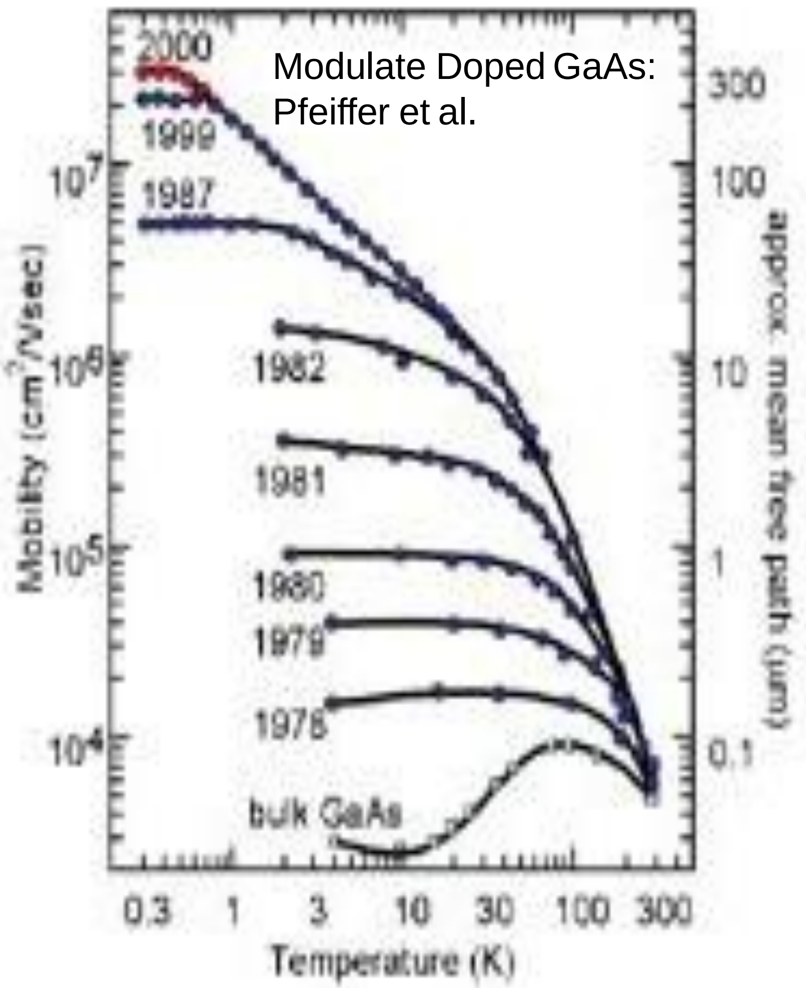
$$E_n = \pm\sqrt{2e\hbar v_F^2 |n| B}$$

E_1 ~ 100 meV @ 5 T

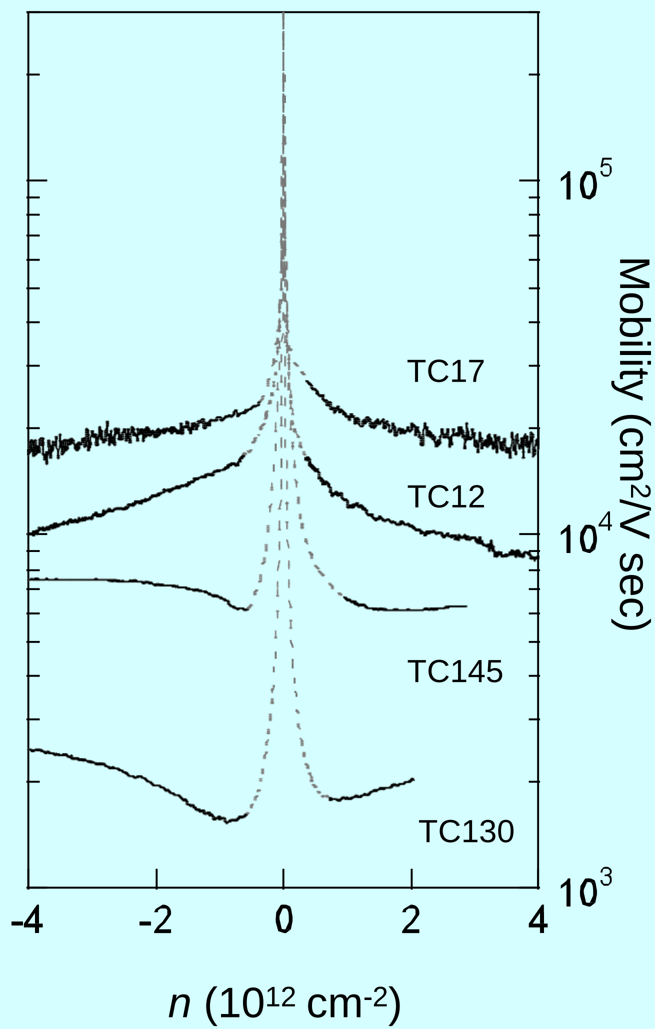
Novoselov, Jiang, Zhang, Morozov, Stormer, Zeitler, Maan, Boebinger, Kim, and Geim *Science* (2007)

Graphene Mobility

GaAs HEMT

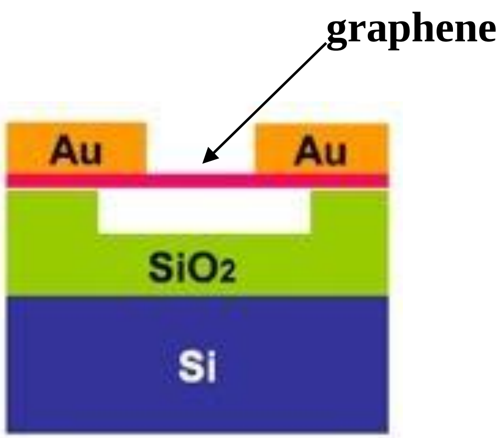


Graphene Mobility



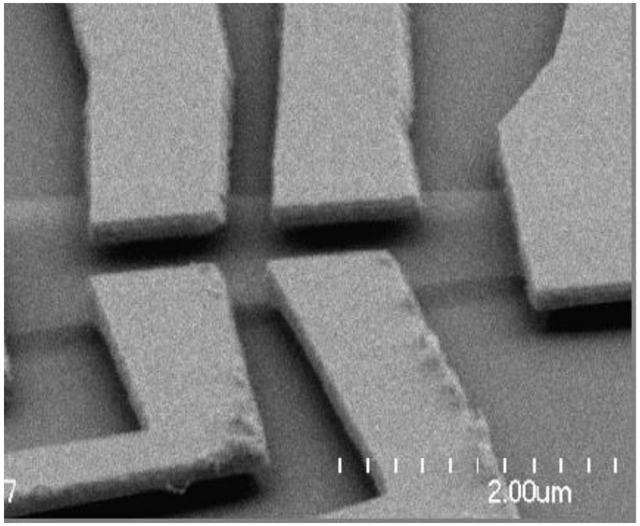
Tan al. PRL (2007)

Toward High Mobility: Suspending Samples



HF etching
-> critical pointing drying

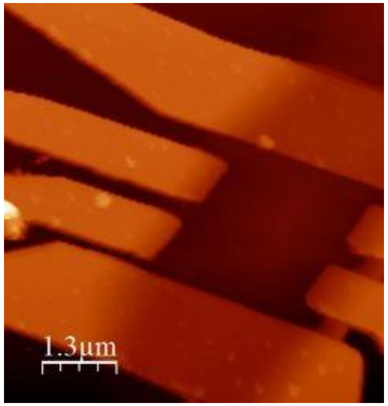
SEM image of suspended graphene

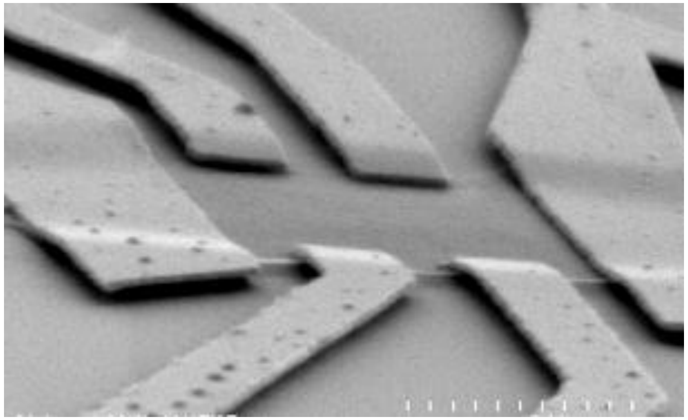


AFM image of suspended graphene

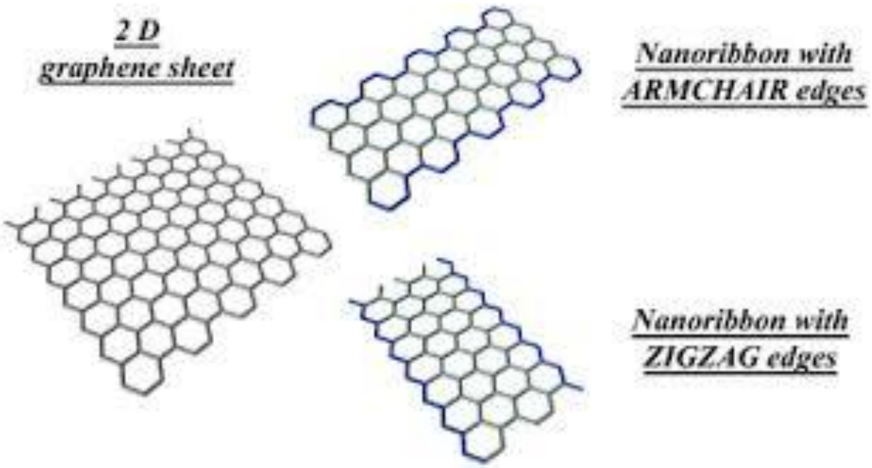
You should not apply to high gate voltage, otherwise…

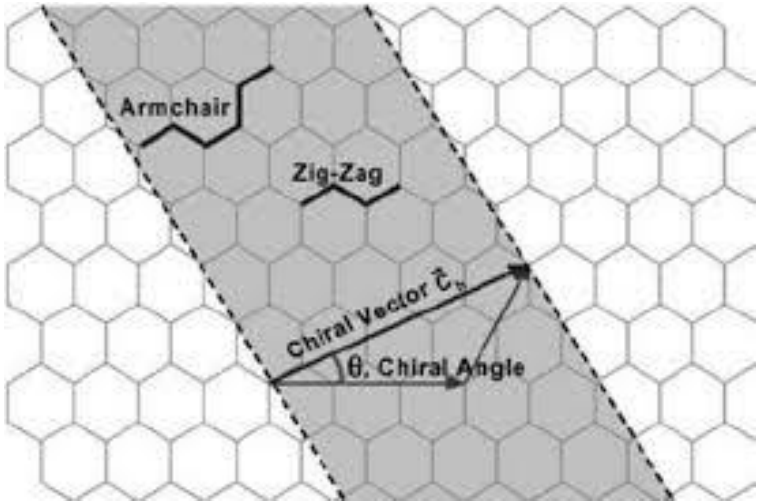
Collapsed graphene devices…





Edge State: Armchair vs Zigzag



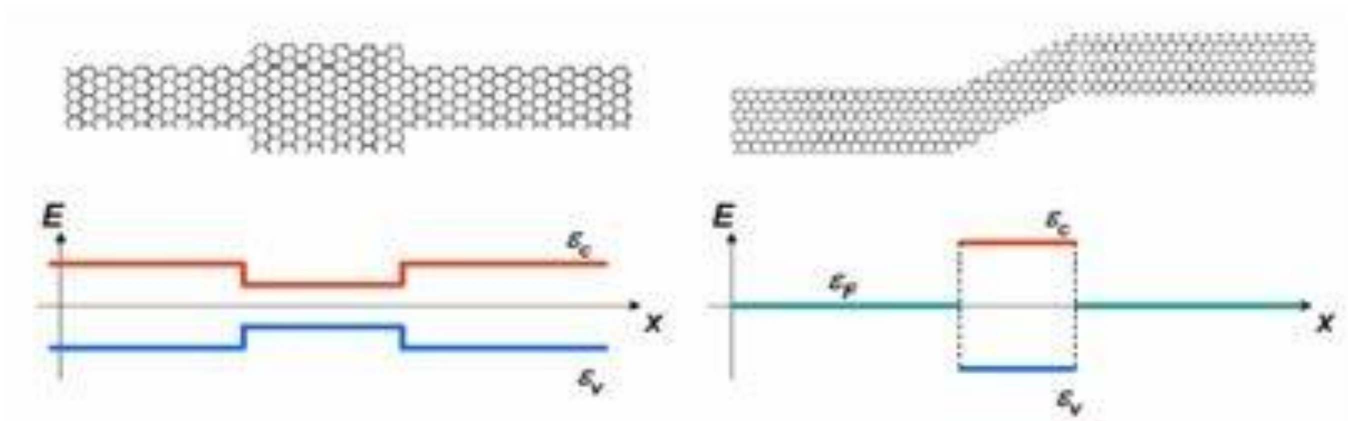


- Finite graphite systems having a zigzag edge exhibit a special **edge state**.
- The corresponding energy bands are almost flat at the Fermi level, and thereby give a sharp peak in the density of states.
- The charge density in the edge state is strongly localized on **the zigzag edge sites**.
- No such localized state appears in graphite systems having **an armchair edge**.
- By varying the width of the graphene ribbons, we find that the nanometer size effect is crucial for determining the relative importance of the edge state.
- We also have extended the graphene ribbon to have edges of a general shape, which is defined as a mixture of zigzag and armchair sites.

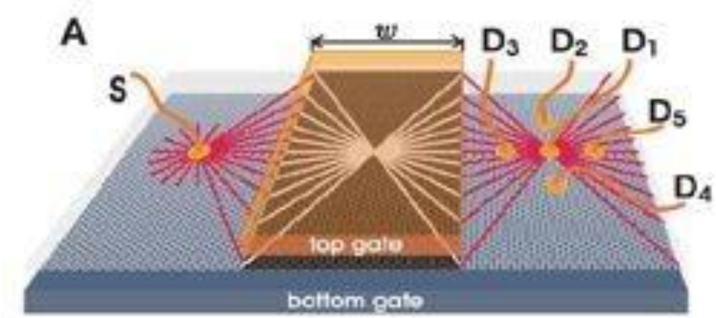
K. Nakada and M. Dresshaus, et al, PHYSICAL REVIEW B, **54**, NUMBER 24, 17954, (1996).

Graphene Electronics

Engineer Dreams

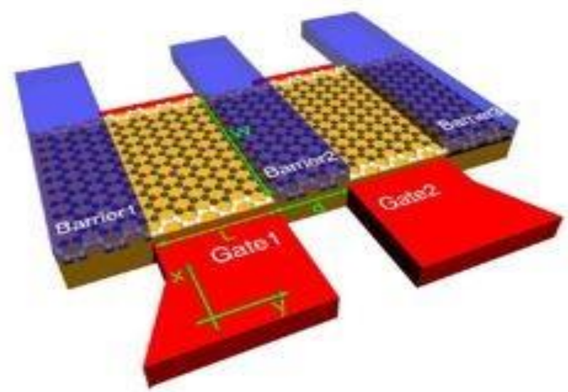


Theorist Dreams



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, **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.

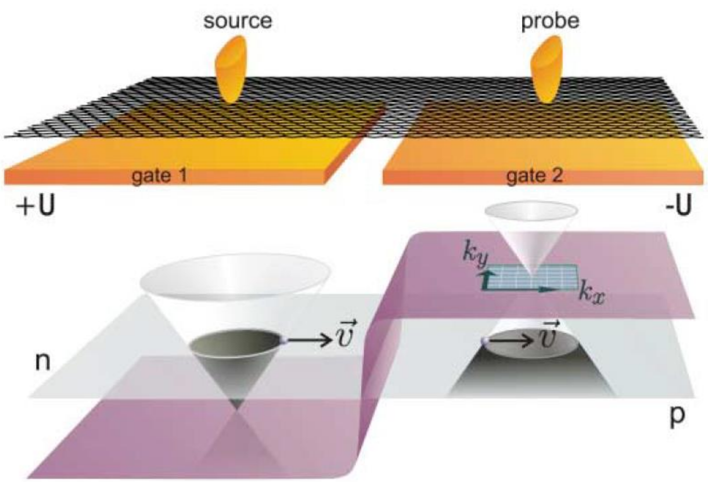


Fig. 1. Graphene *p-n* junction (PNJ). Monolayer of graphite is placed over the split gate, which is used to create *n*- (**left**) and *p*-doped (**right**) regions. The energy diagram shows the position of the Fermi level with respect to the touching point of the valence and the conduction bands.

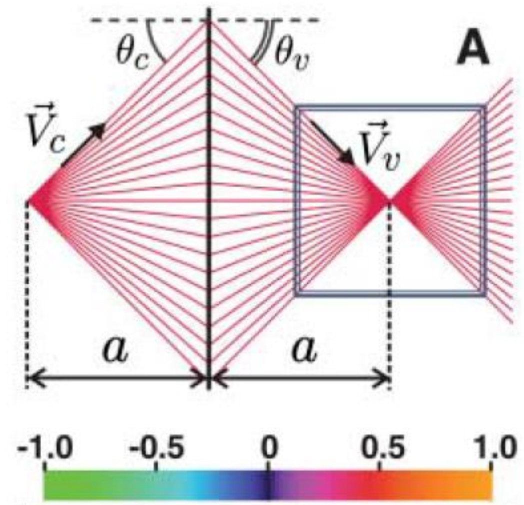


Fig. 2. Focusing of electrons by symmetric PNJ, $\rho_h = \rho_e$. (**A**) Classical trajectories of electrons diverging from a source at distance *a* from the junction become convergent after refraction. (**B**)

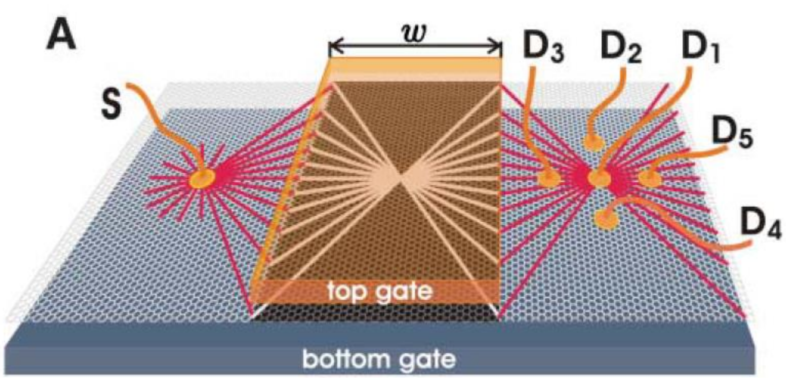
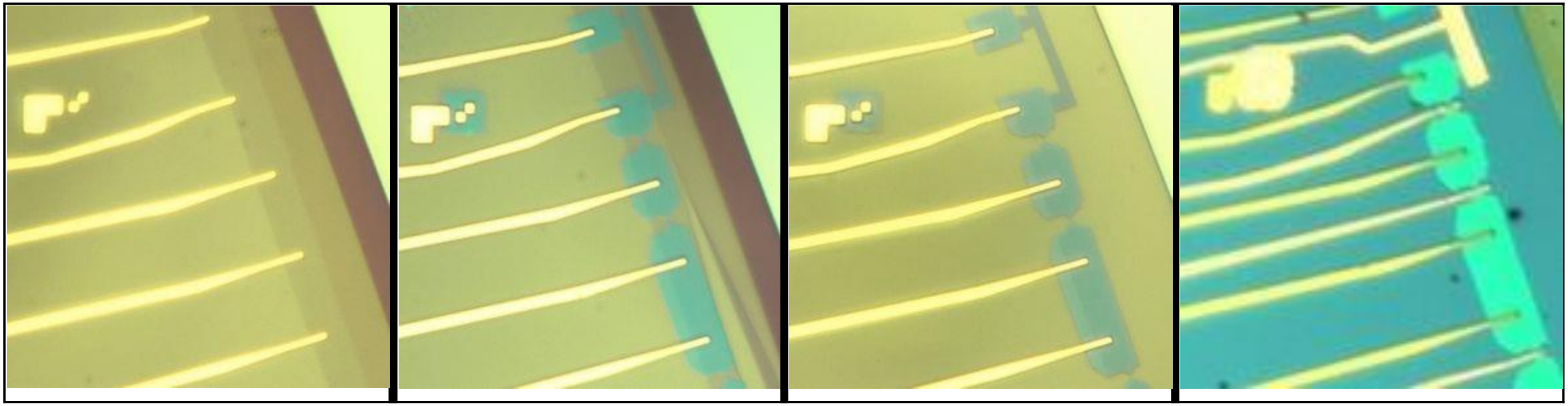


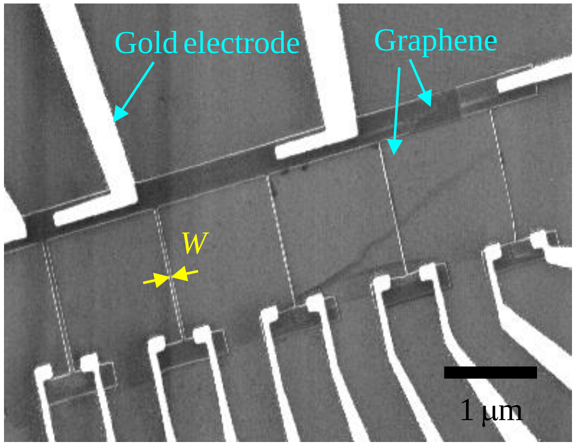
Fig. 4. (**A**) Electron Veselago lens and (**B** and **C**) prism-shaped focusing beam splitter in the ballistic *n-p-n* junction in graphene-based transistor.

From Graphene “Samples” To Graphene “Devices”



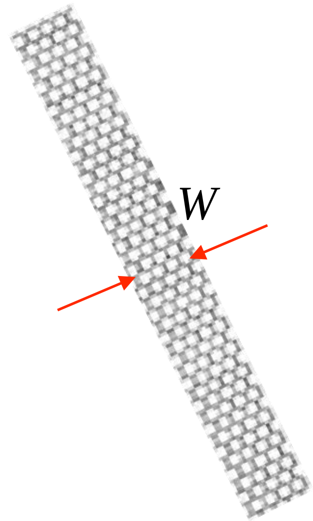
Contacts:	Graphene patterning:	Graphene etching:	Local gates:
PMMA EBL Evaporation	HSQ EBL Development	Oxygen plasma	ALD HfO_2 EBL Evaporation

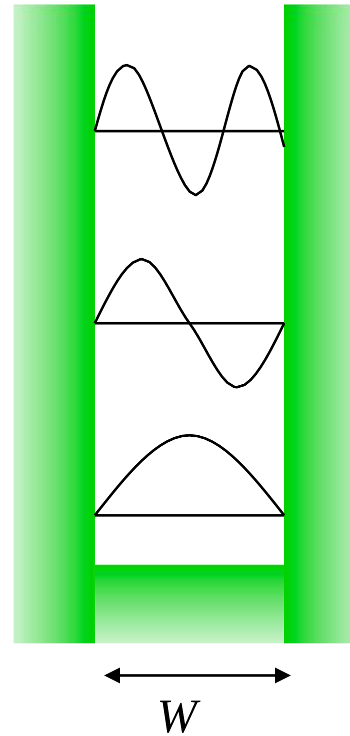
Graphene Nanoribbons: Confined Dirac Particles



10 nm < W < 100 nm

Dirac Particle Confinement





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

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

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

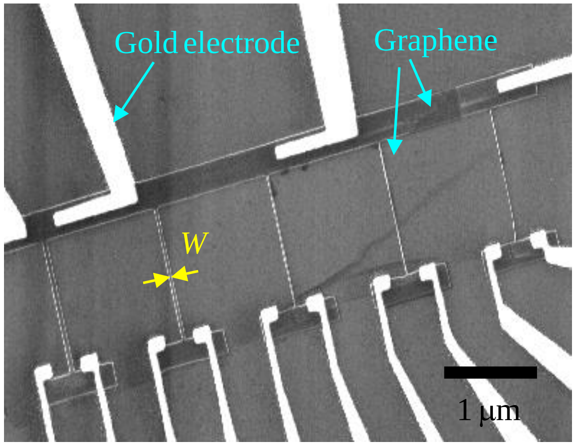
$$\Delta k - \frac{\pi}{W}$$

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

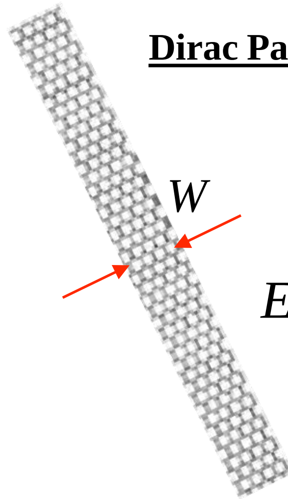
Graphene nanoribbon theory partial list

K. Nakada, M. Fujita, G. Dresselhaus, M. S. Dresselhaus, Phys. Rev. B **54**, 17954 (1996).
K. Wakabayashi, M. Fujita, H. Ajiki, M. Sigrist, Phys. Rev. B **59**, 8271 (1999).
Y. Miyamoto, K. Nakada, M. Fujita, Phys. Rev. B **59**, 9858 (1999).
M. Ezawa, Phys. Rev. B **73**, 045432 (2006).
N. M. R. Peres, A. H. Castro Neto, and F. Guinea, Phys. Rev. B **73**, 195411 (2006)
L. Brey and H. A. Fertig, Phys. Rev. B **73**, 235411 (2006).
Y. Ouyang, Y. Yoon, J. K. Fodor, and J. Guo, Appl. Phys. Lett. **89**, 203107 (2006).
Y.-W. Son, M. L. Cohen, S. G. Louie, Nature **444**, 347 (2006)
Y.-W. Son, M. L. Cohen, S. G. Louie, Phys. Rev. Lett. **97**, 216803 (2006).
V. Barone, O. Hod, G. E. Scuseria, Nano Lett **6** 2748 (2006).
D. A. Areshkin, D. Gunlycke, C. T. White, Nano Lett. **7**, 204 (2007).
• • •

Graphene Ribbon Devices

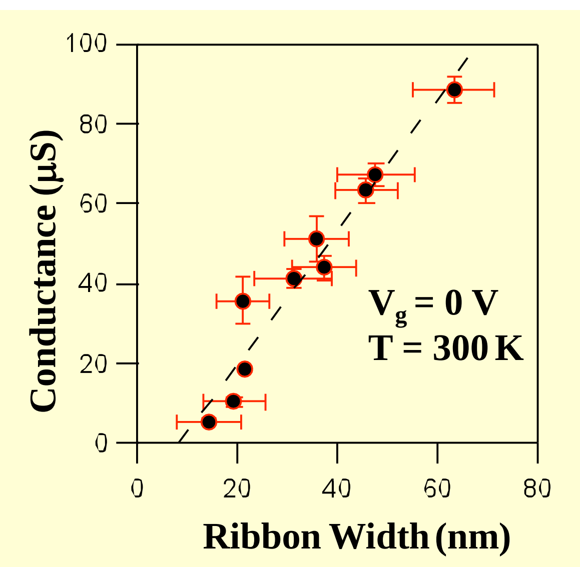


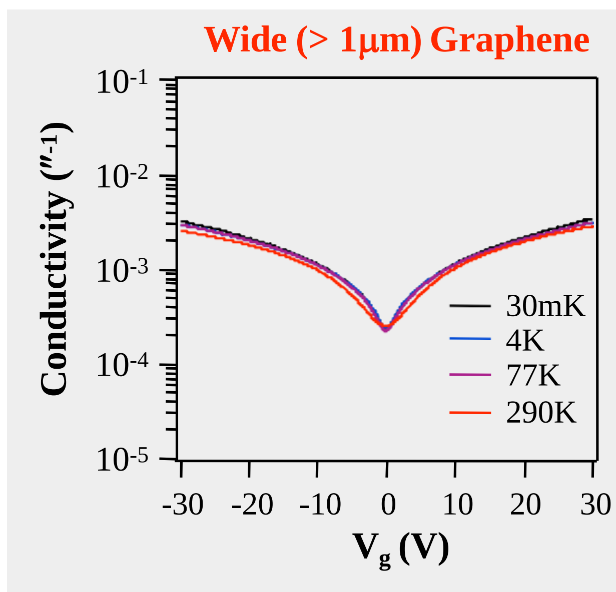
10 nm < W < 100 nm

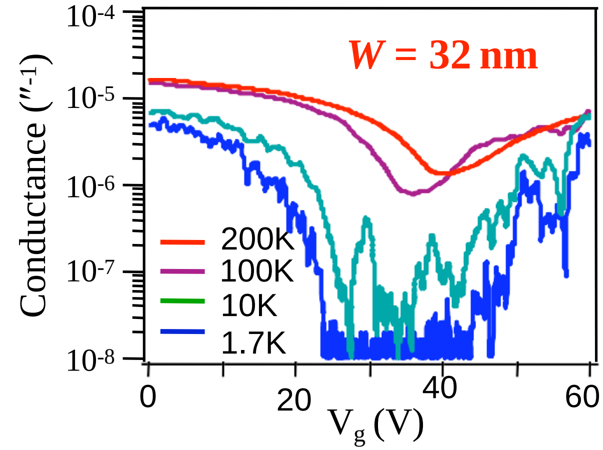


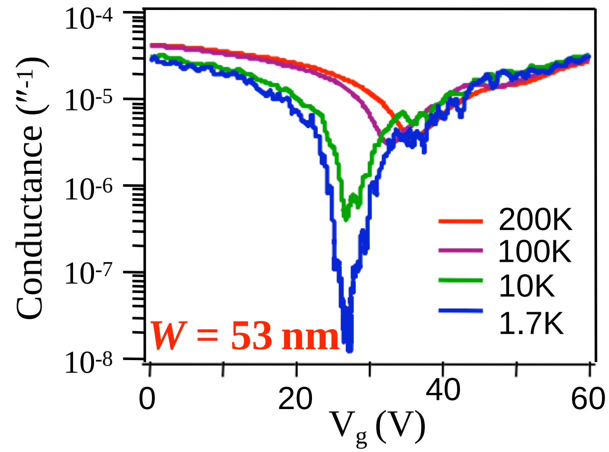
Dirac Particle Confinement

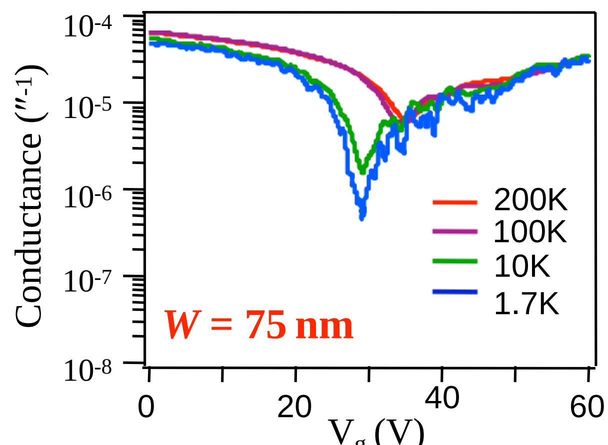
$$E_{gap} \sim \hbar v_F / W$$



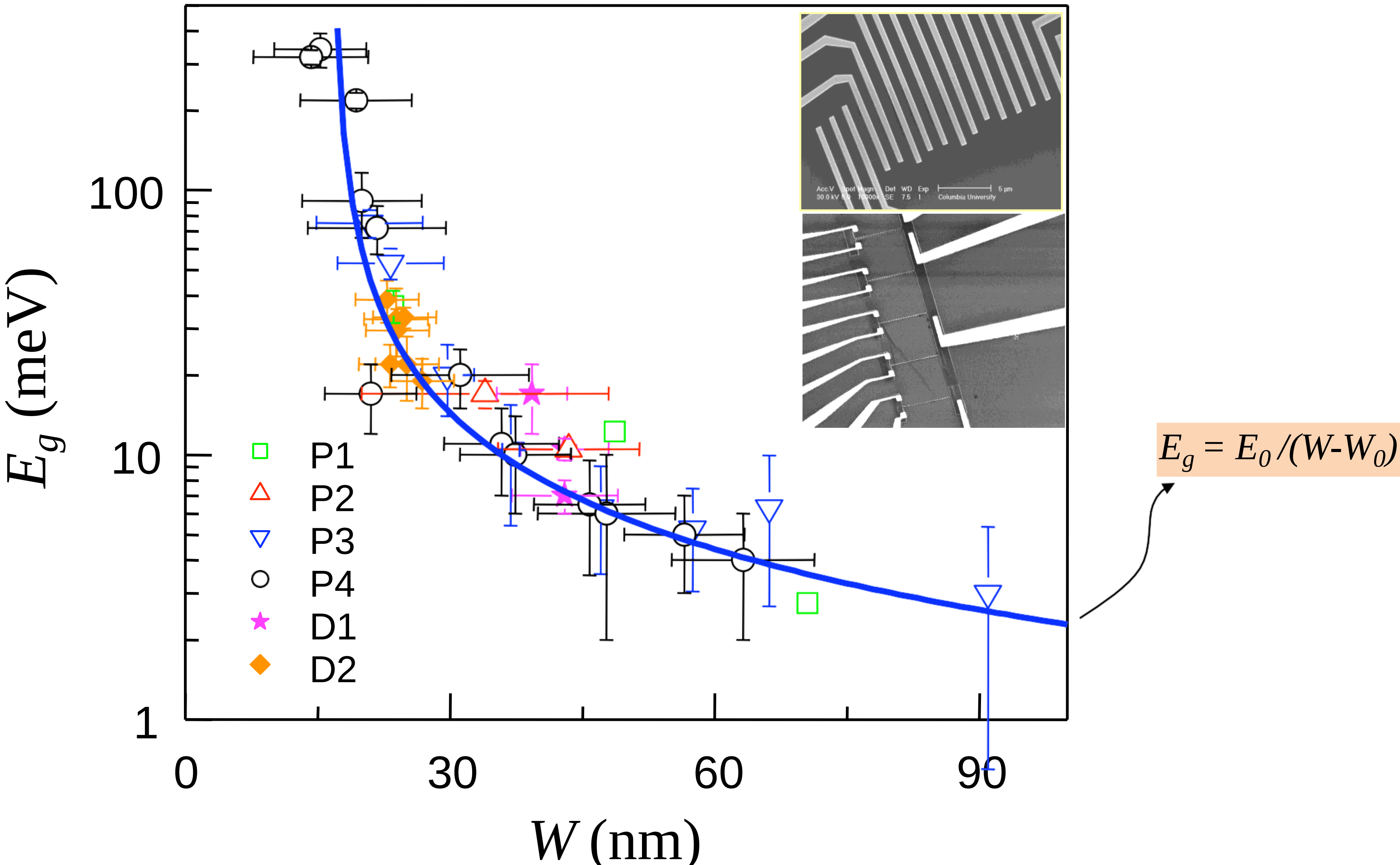








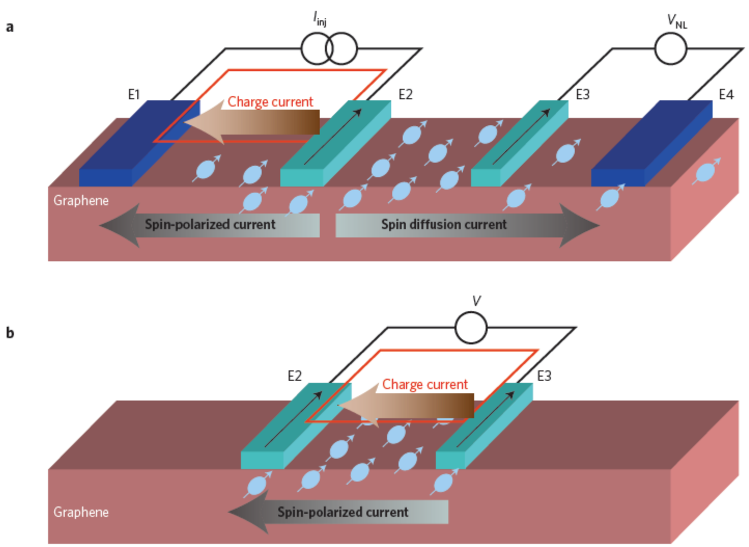
Scaling of Energy Gaps in Graphene Nanoribbons

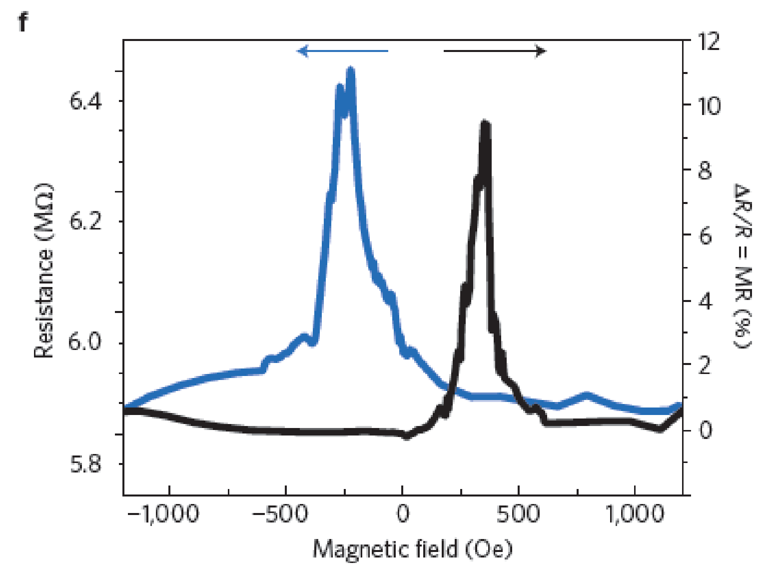


Han, Oezyilmaz, Zhang and Kim PRL (2007)

Graphene Spintronics

- Graphene is claimed to be an ideal material for spintronics due to its small spin-orbit interaction, and the near absence of nuclear magnetic moments in carbon.
- Very low spin flip scattering rate, and very long spin diffusion length λ ~ 1 micrometer at RT.
- Electrical spin current injection and detection has been demonstrated up to RT.
- control of the spin current polarity with an electrical gate was observed at low temperature

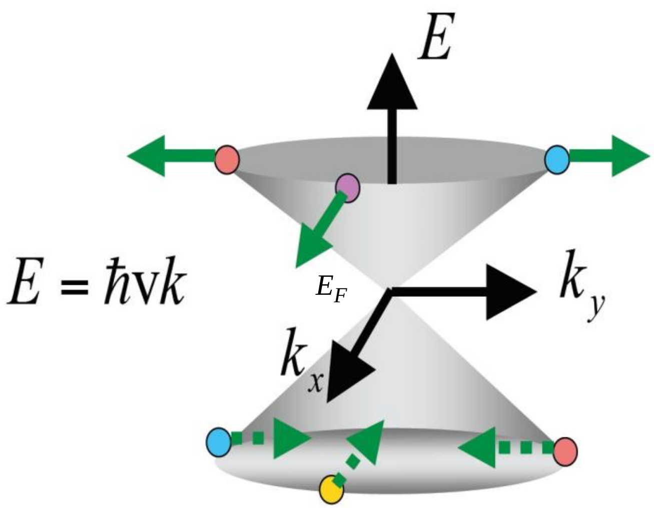


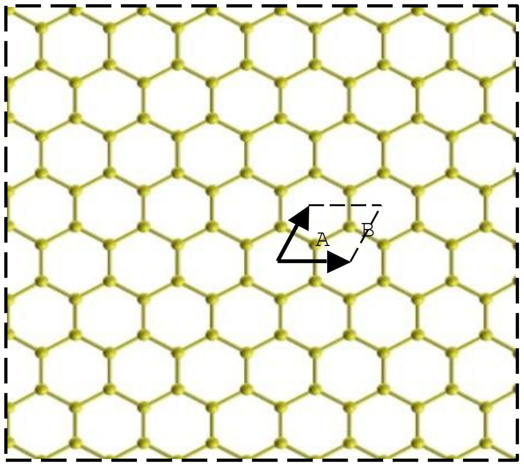


NATURE NANOTECHNOLOGY VOL 9, 794 (2014)

Spin injection and transport in graphene **spin valves**:
(a) Non-local , and local spin transport measurement geometries

Electronic Structure and Pseudospin Physics in Graphene





- Energy dispersion of the electron in graphene near the Fermi surface looks like that of ***light***, i.e., a cone.

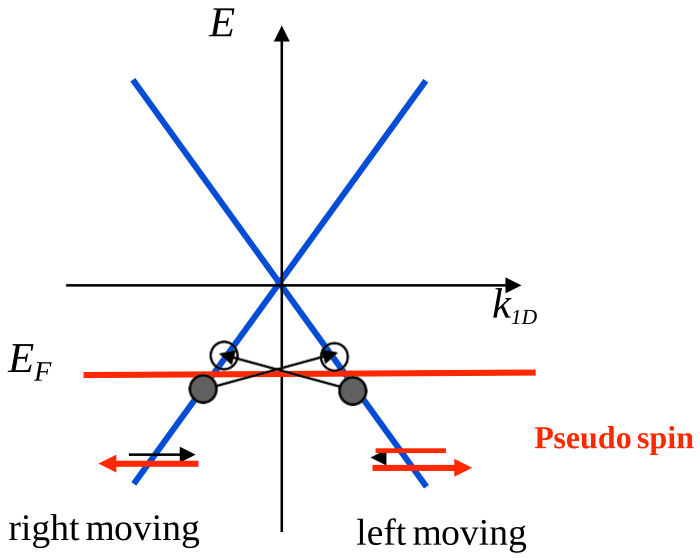
- A pseudospin pointing along **k** associated with each state, describing the bonding character between the neighboring carbon atoms in the two sublattices.

- The ***chirality*** of graphene wavefunctions near the Dirac point suppresses backscattering events.

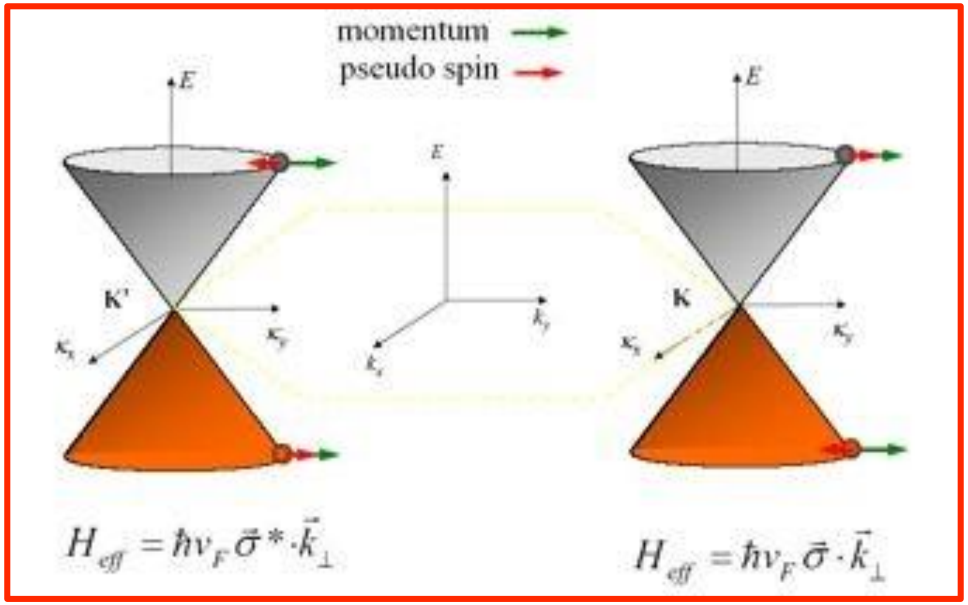
T. Ando, et al (1998); McEuen, Louie, et al (1999)

Extremely Long Mean Free Path: Hidden Symmetry ?

1D band structure of nanotubes



Low energy band structure of graphene

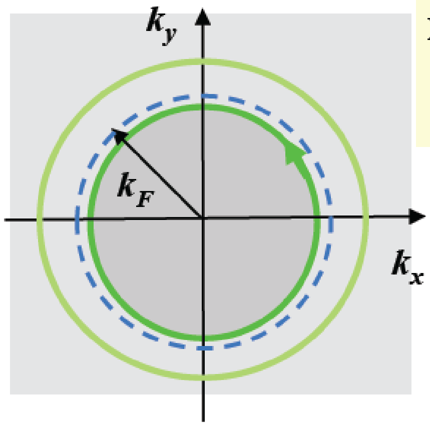


- Small momentum transfer backward scattering becomes inefficient, since it requires pseudo spin flipping.

T. Ando, JPSJ (1998); McEuen at al, PRL (1999)

Berry's Phase and Magnetoresistance Oscillations

Landau orbit near the Fermi level



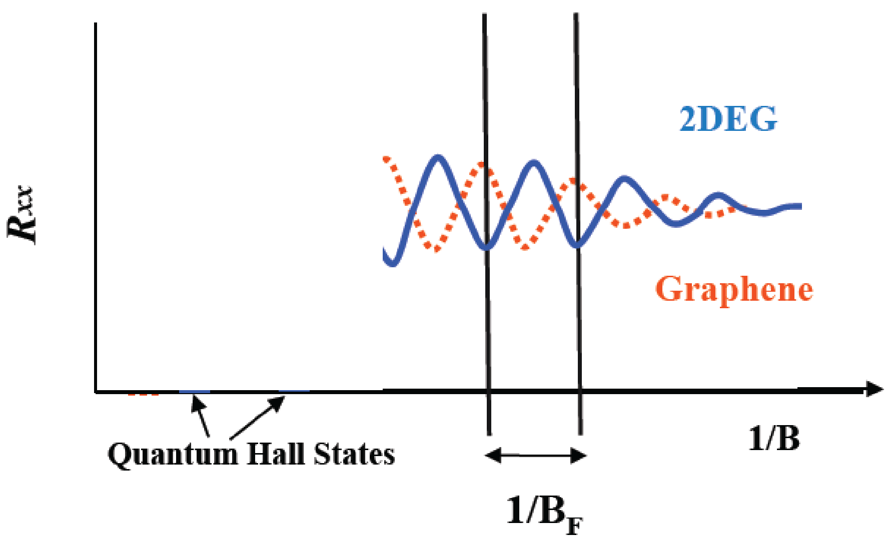
Magnetic flux in cyclotron orbit

$$\Phi_B = \Phi_o \, B_F / B$$

$$\Phi_o = h/e$$

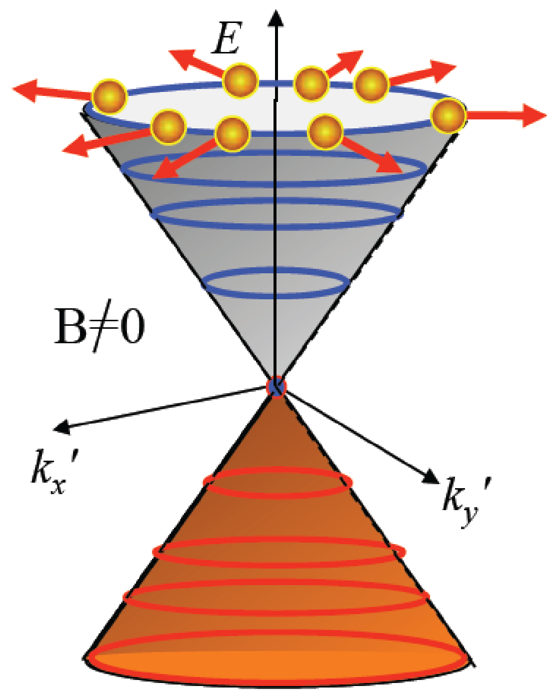
$$B_F = \Phi_o \, k_F^2 / 4\pi$$

$$\psi \sim \psi_o \; \exp[2\pi(\Phi_B/\Phi_o)]$$



Graphene: $H_{eff} = \hbar v_F \vec{\sigma} \cdot \vec{k}'_{\perp}$

Pseudo Spin

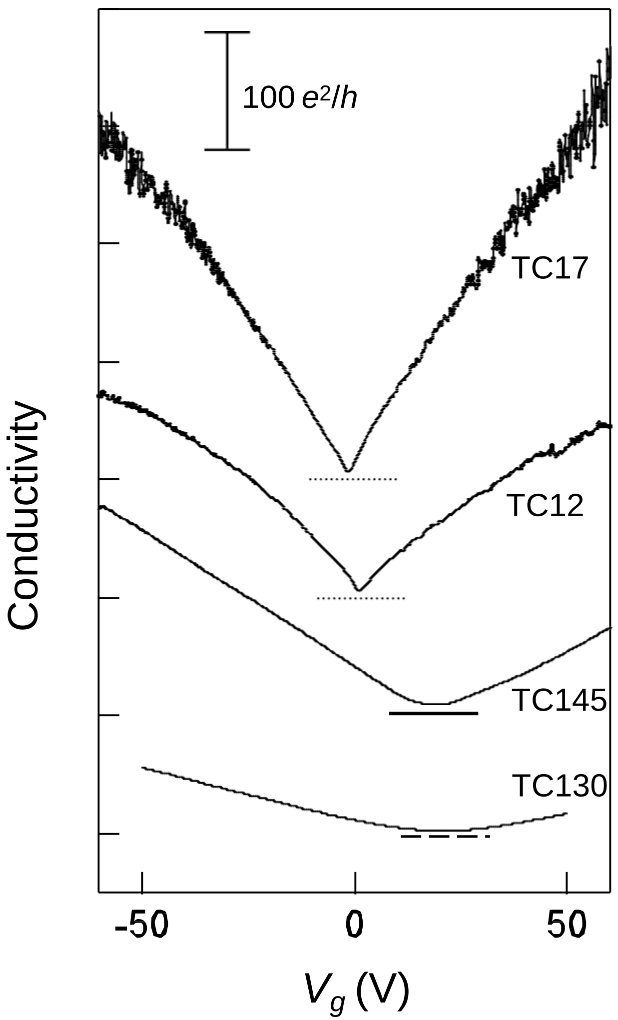


$S = \hbar/2$
$\theta = 2\pi$

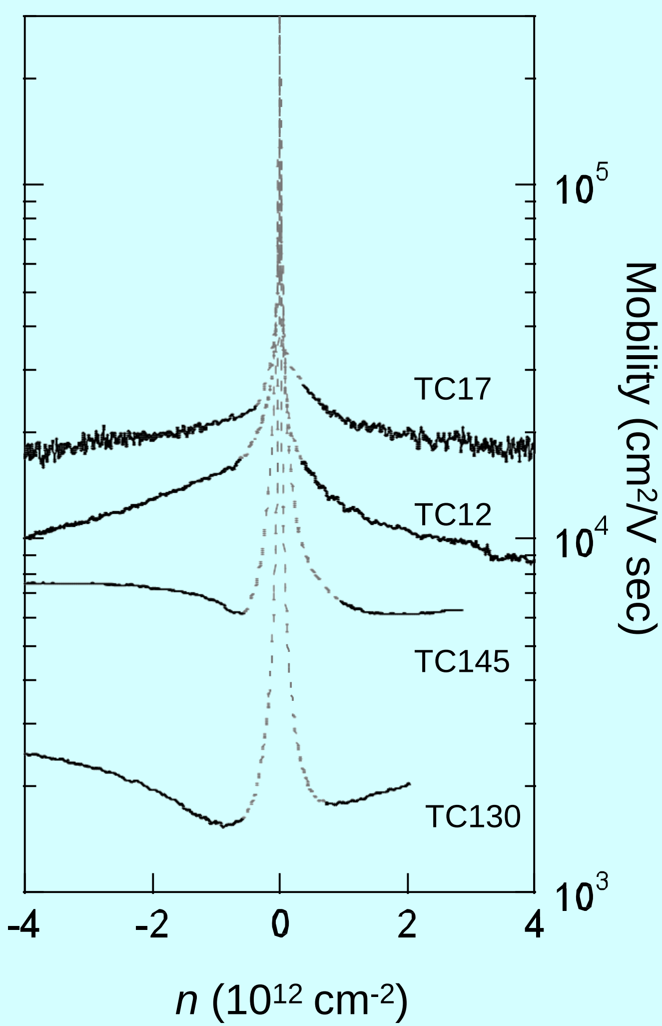
$$\psi \sim \psi_o \; \exp[2\pi(\Phi_B/\Phi_o) - \underbrace{S\theta/\hbar}_{\pi}]$$

Conductivity, Mobility, & Mean Free Path

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



Mobility



Mean free path