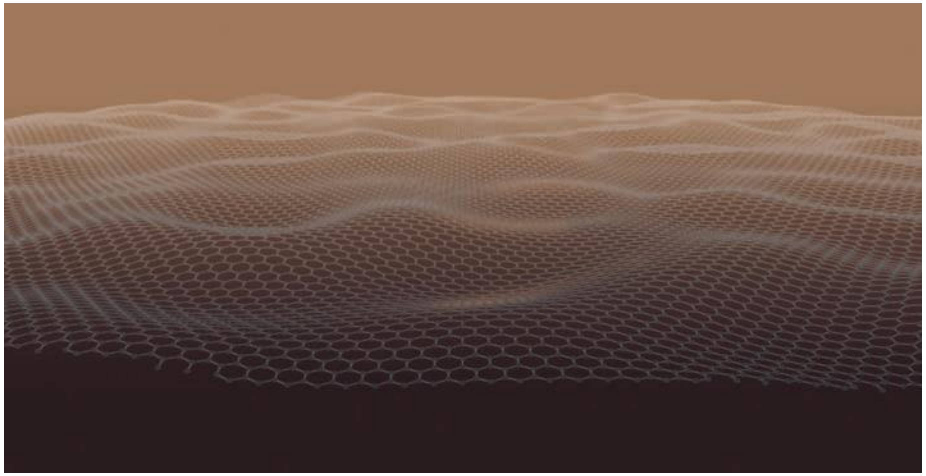
Emergent Properties of Two-Dimensional Materials

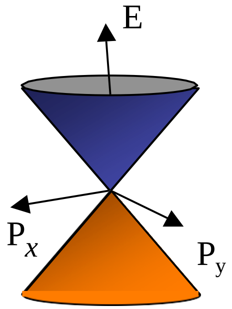
Flatlands beyond Graphene



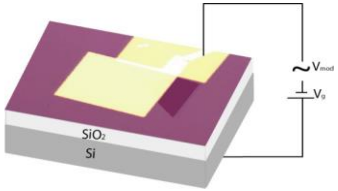
Prof. J. Raynien Kwo
Department of Physics,
National Tsing Hua University

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)

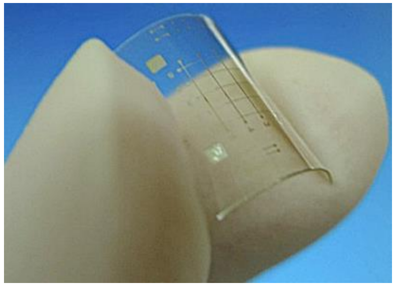
Aim to get graphene into industry and product development

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.

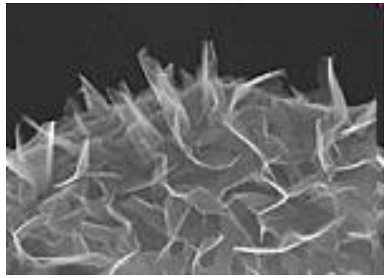
http://www.cambridgenetwork.co.uk/news/is-the-uk-set-to-miss-out-on-the-graphene-revolution/

Graphene's Applications



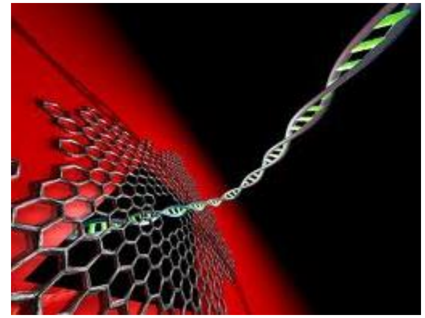
Flexible Memristors

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



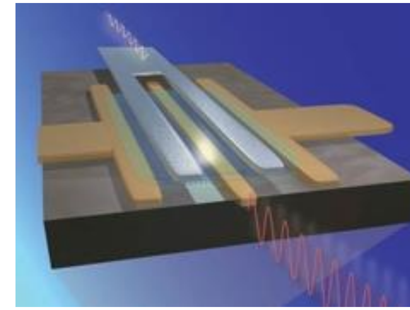
Ultracapacitor

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



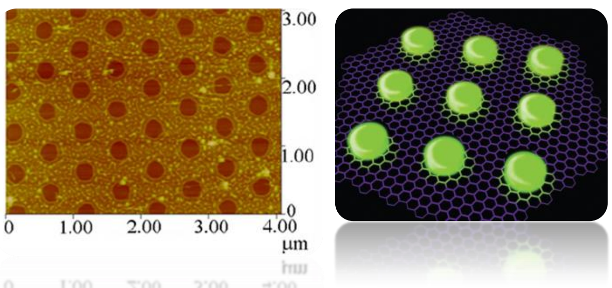
DNA graphene nanopore

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

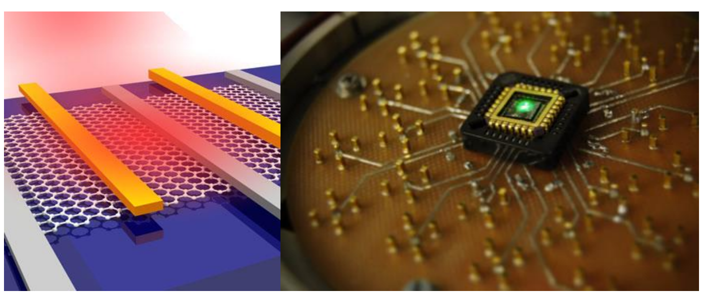


RF transistors

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)



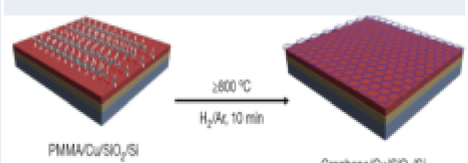
Graphene Photodetector
Nature Photonics **4**, 297 - 301 (2010)
Nature Nanotechnology **7**, 363–368 (2012)

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

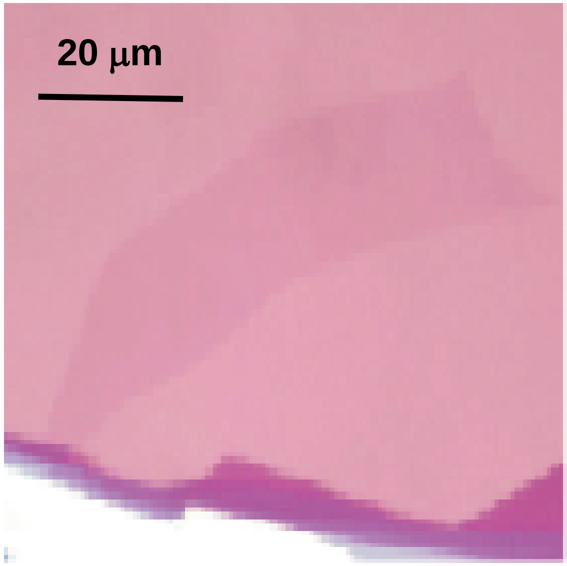
*http://www.nanowerk.com/news2/newsid=27702.php

Fabrication of graphene

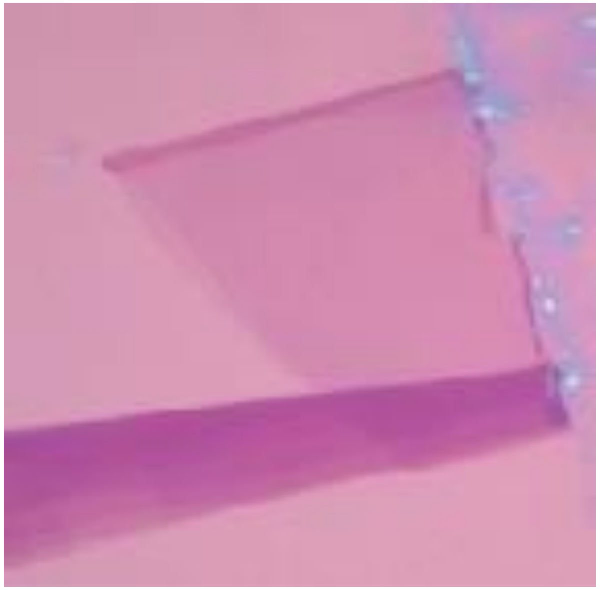
Method	Descriptions	Merits	References
Mechanical cleavage or exfoliation	Scotch Tape 	Minimal defects Intrinsic properties Small sizes	Science 306, 666 (2004)
Chemical oxidized process	Producing GO by the oxidation of graphite with acid	Large scale flakes Composite	Nature 442, 282 (2006)
Epitaxial growth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



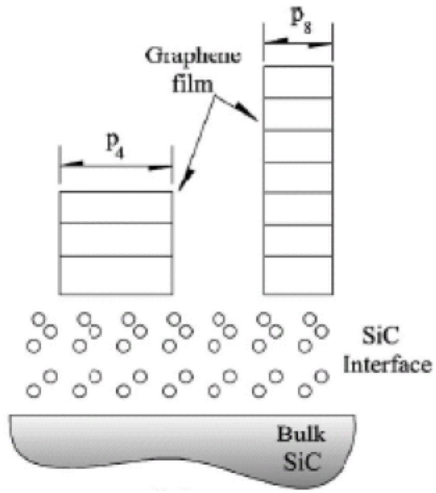
Bilayer

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

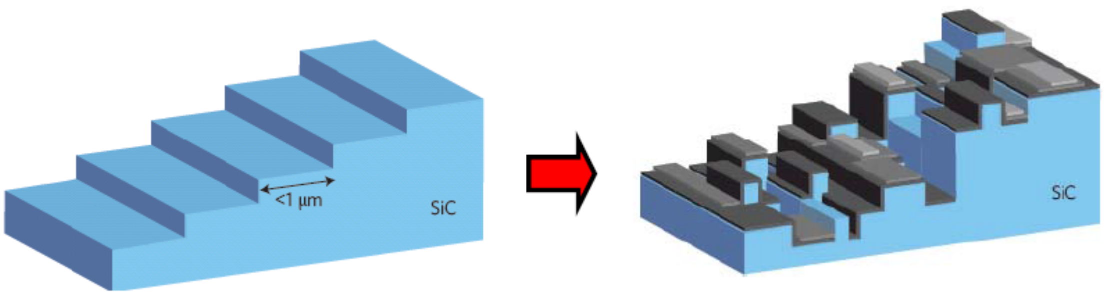
Epitaxial growth of graphene

Epitaxial graphene grown on SiC(0001) surfaces

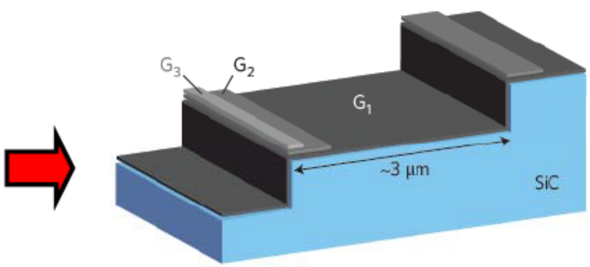
One often ends up with multi-layers of graphene with small grains 30nm-200nm



Recent progress:

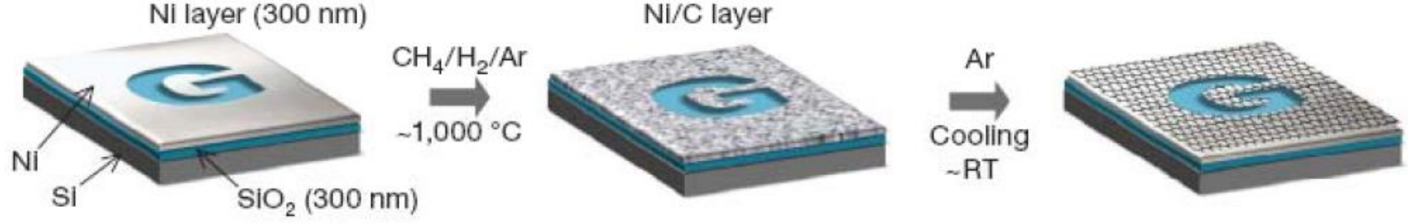


UHV

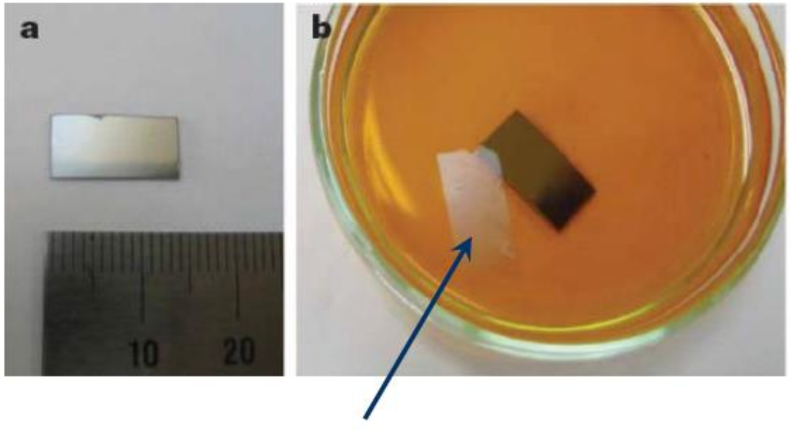


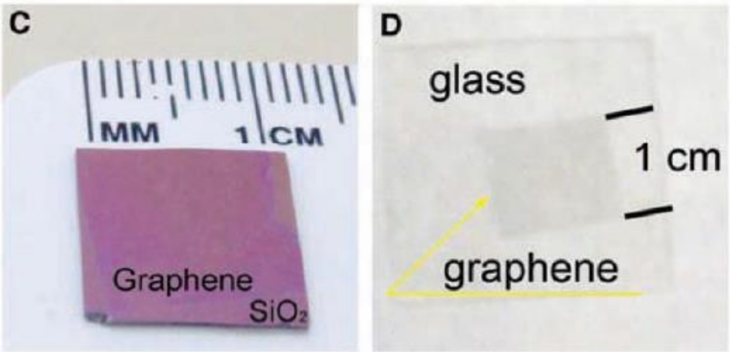
In the presence of pressurized Ar
K.V. Emvsev et al., Nature Materials 8, 203 (2009)

CVD graphene on metal substrates



Etching and transfer

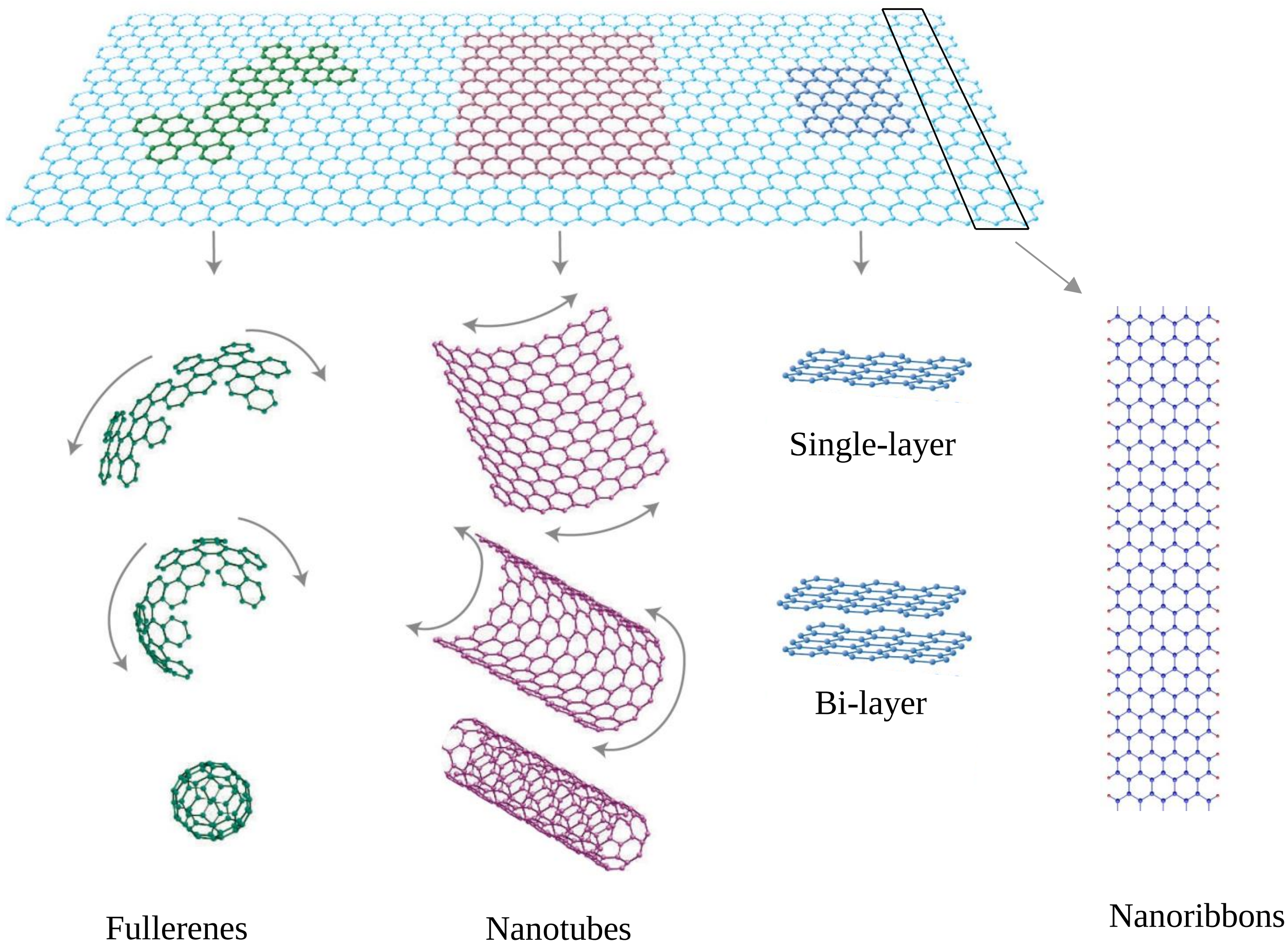




Floating graphene after Ni being etched
Ni: Kim et al., Nature 457, 706 (2009)

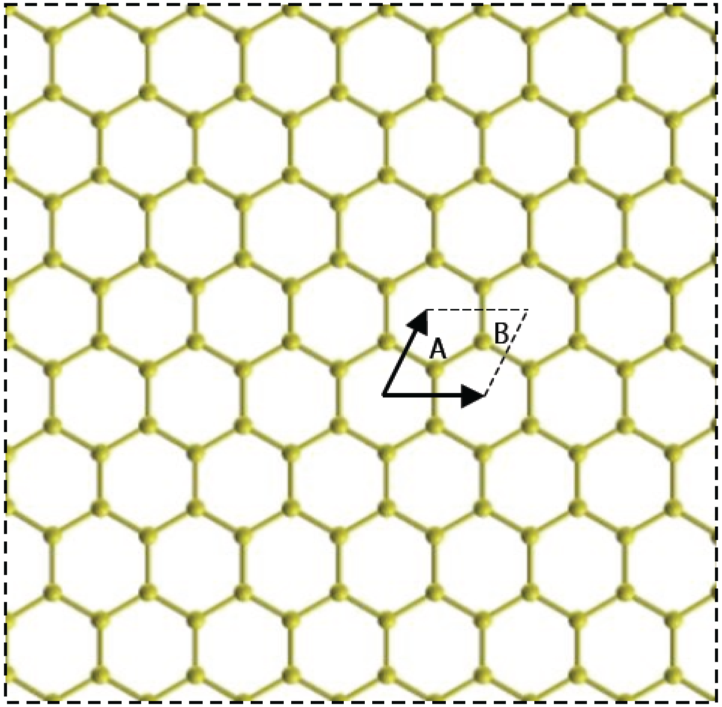
Cu: Li et al., Science 324, 1312 (2009)

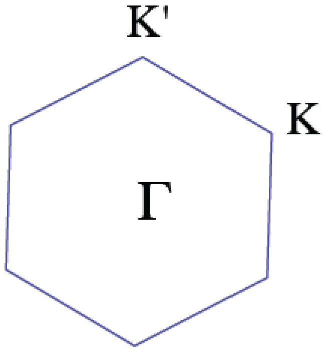
Graphene and Related Carbon sp^2-bonded Structures



Graphene

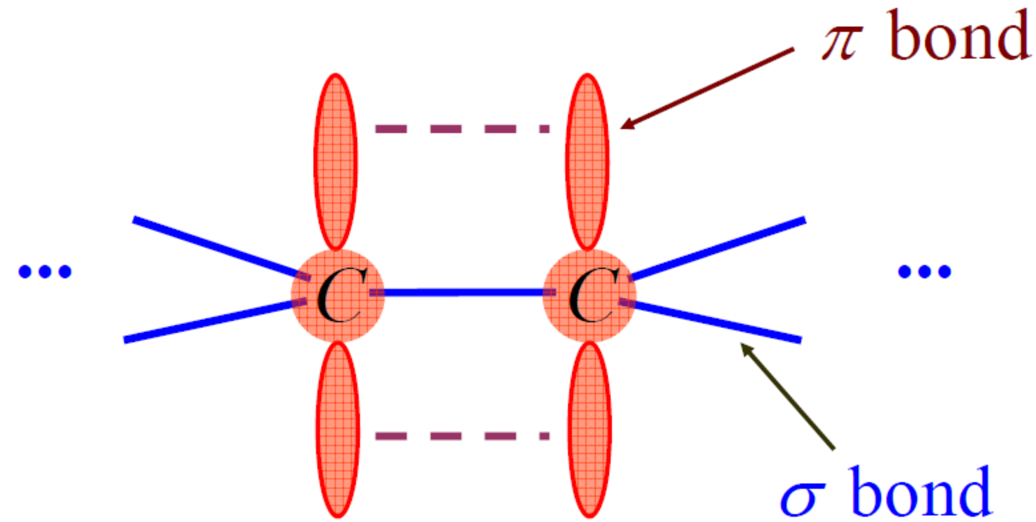
Single layer of graphite
Two carbon atoms per unit cell
in a honeycomb structure





Brillouin zone

Element of Carbon Network

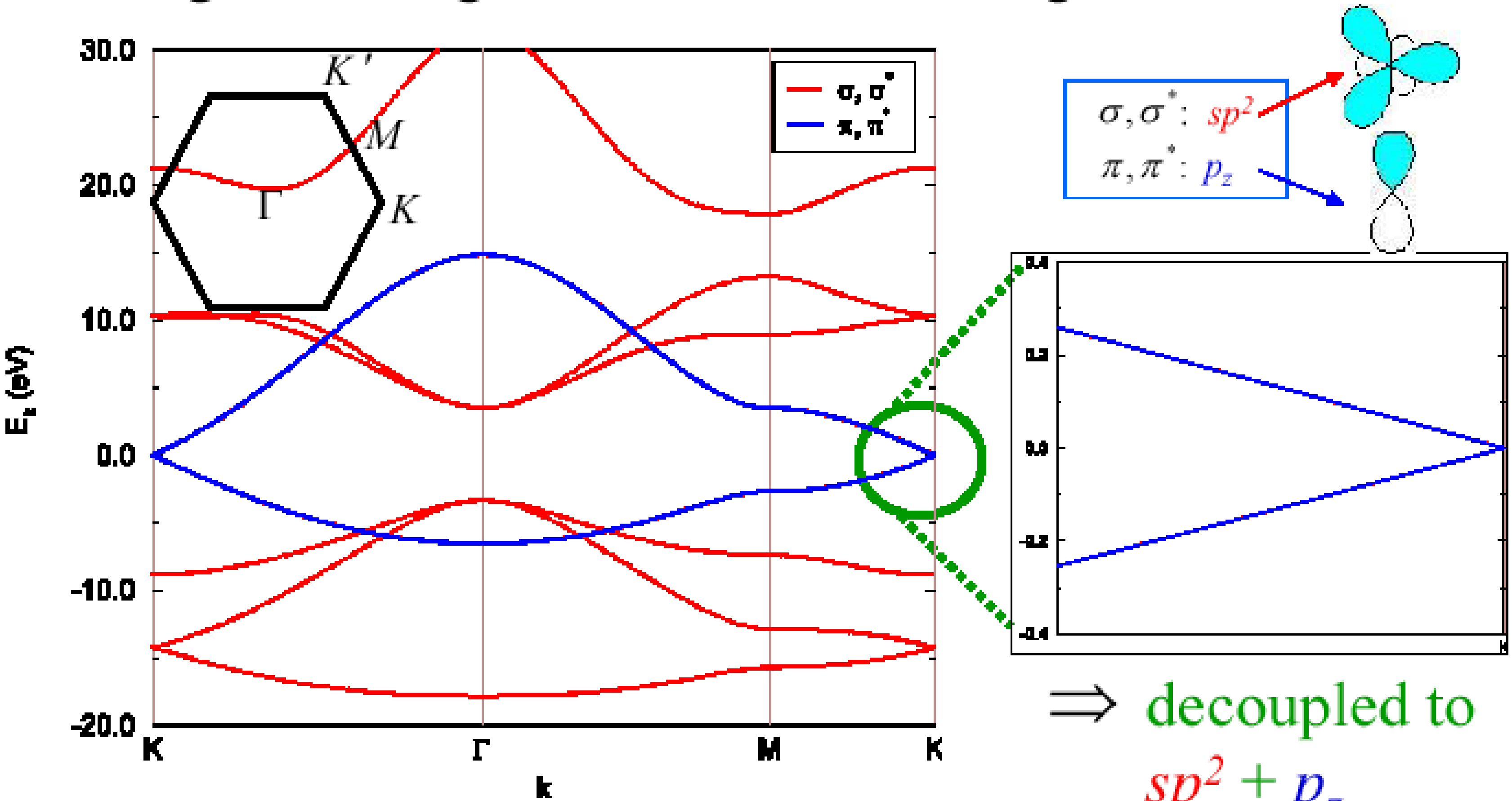


Carbon $1S^2 \underbrace{2S^2 2P^2}$

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

3) Band structure

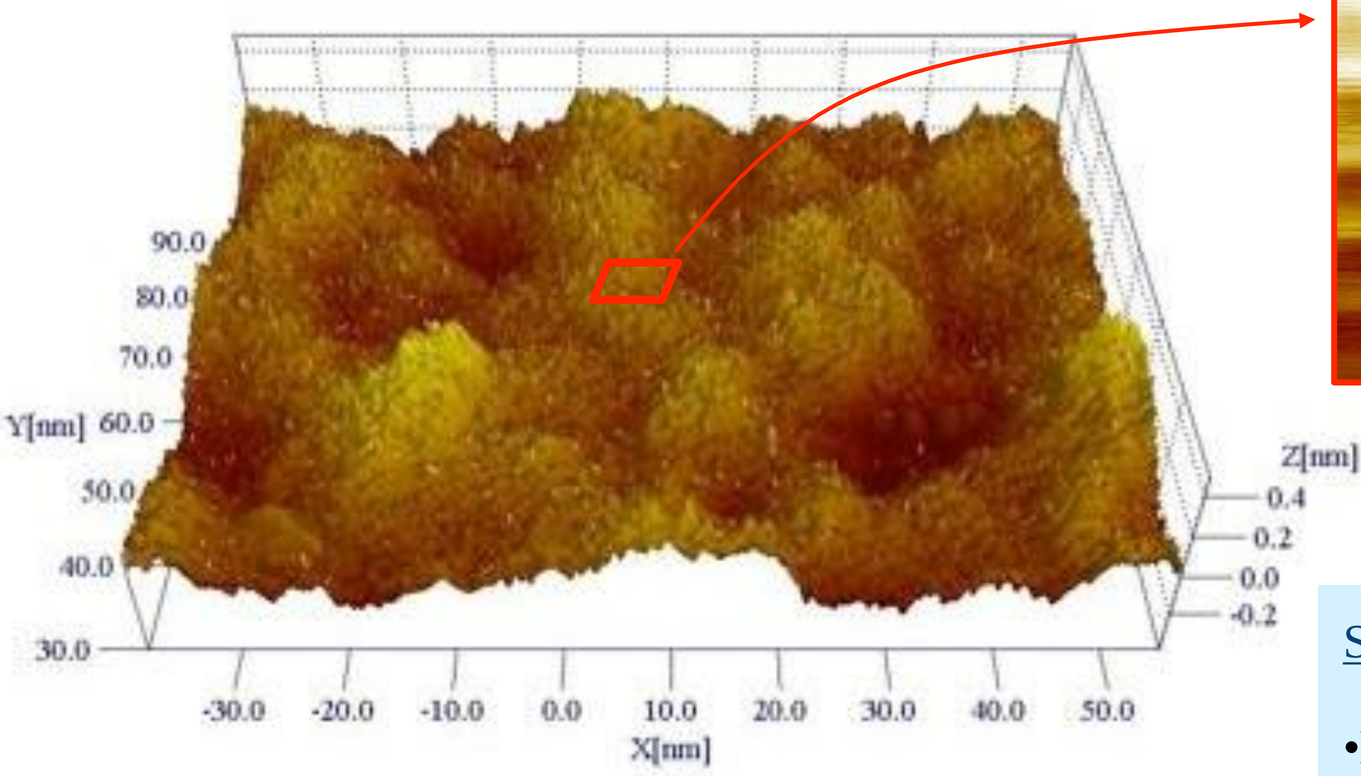
- Tight-binding model with nonorthogonal orbitals



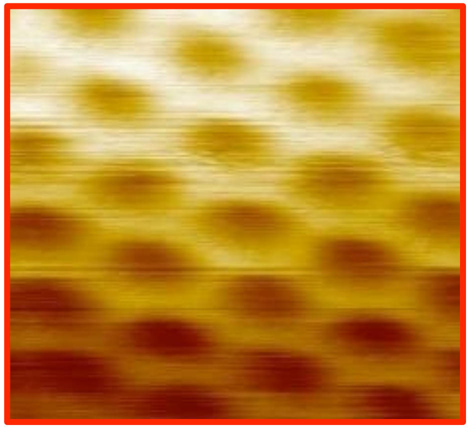
$\Rightarrow$ decoupled to $sp^2 + p_z$

STM on Graphene

Ripples of graphene on a SiO_2 substrate



Atomic resolution



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)

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

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)

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

Exotic Behaviors

-Quantum Hall effect

-Barry Phase

-Ballistic transport

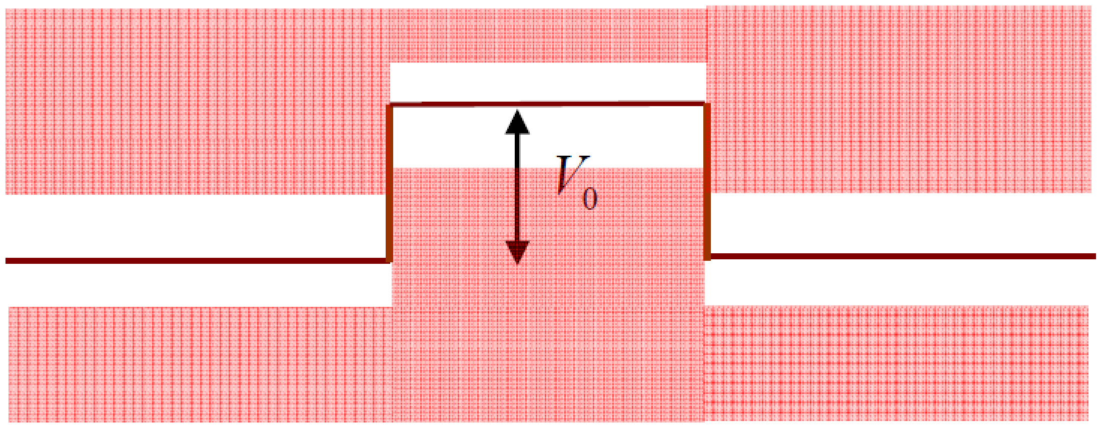
-Klein's paradox

-Others

-
-

Electron scattering from a potential barrier

Potential complication: Klein Paradox (1929)



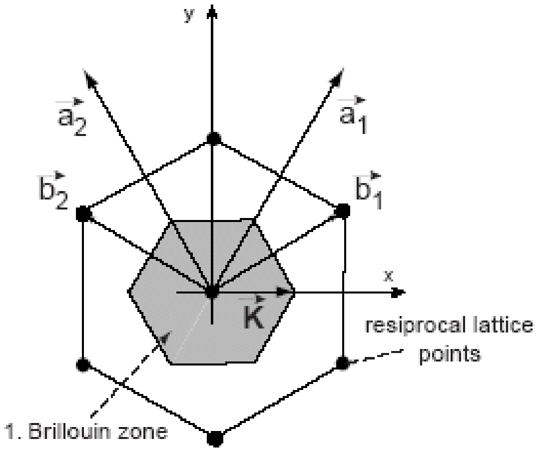
$$T \rightarrow 1 \text{ as } V_0 \Rightarrow m_0c^2$$

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

No confinement for electrons

On/off ratio is reduced in graphene FET

Graphene electronic structures

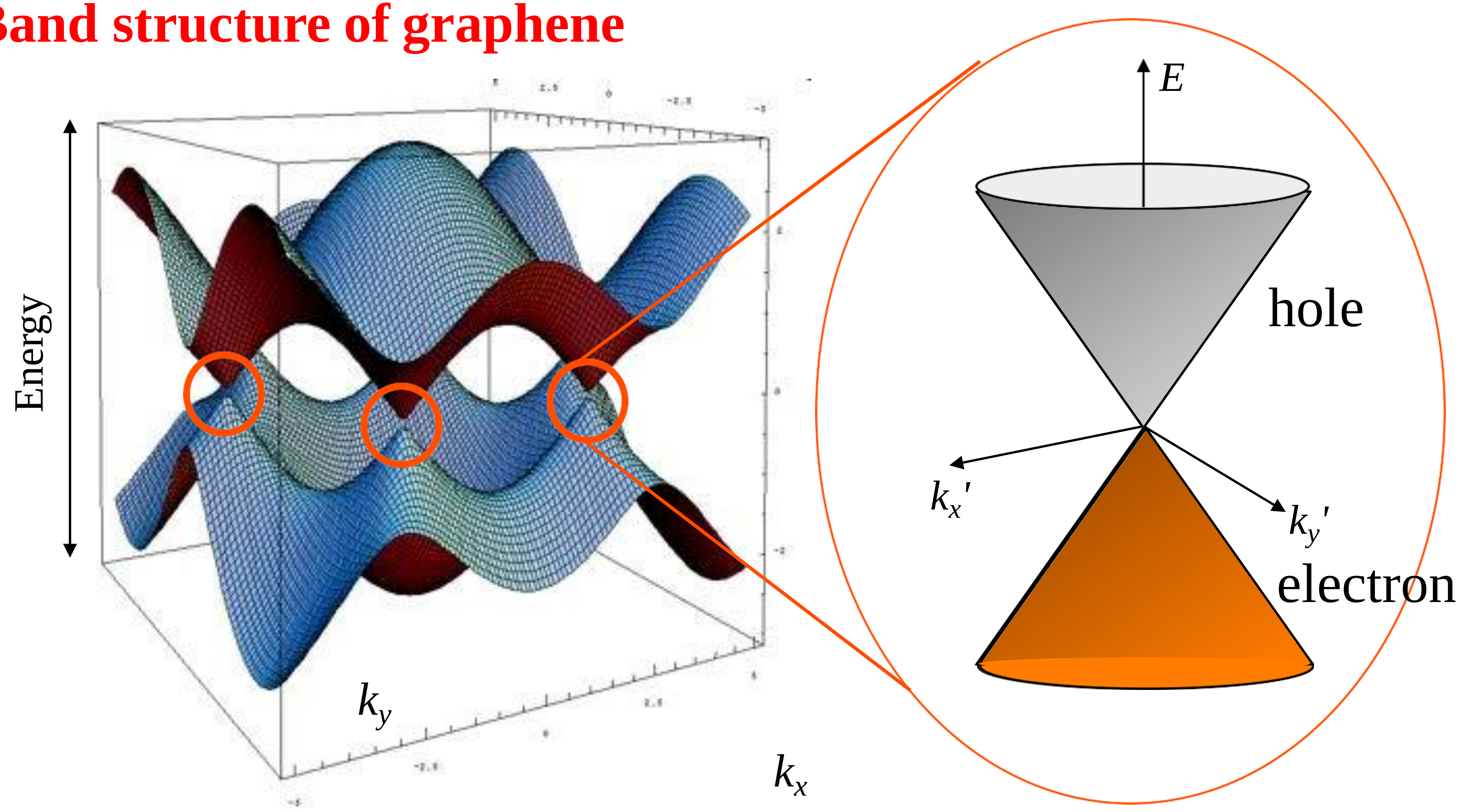


- E–k relation is linear for low energies near the six corners of the two-dimensional hexagonal Brillouin zone, leading to zero effective mass for electrons and holes.
- Due to this linear dispersion relation at low energies, electrons and holes near these six points, two of which are inequivalent, behave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

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

Graphene : 2-D Massless Dirac Fermions

Band structure of graphene

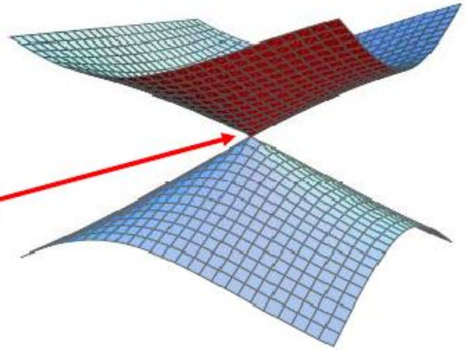


$$E \approx \hbar v_F \left| \vec{k}_{\perp}' \right|$$

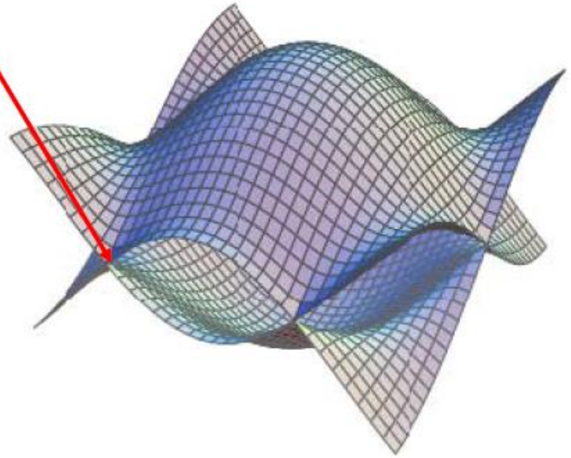
Zero effective mass particles moving with a constant speed v_F

Quasi-Dirac Fermions

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



Dirac points



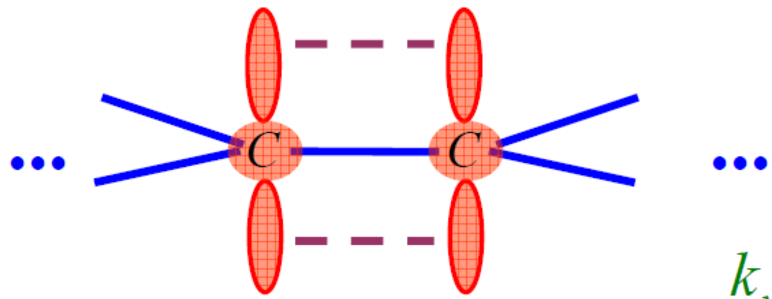
New playground for testing relativistic QM and QED!

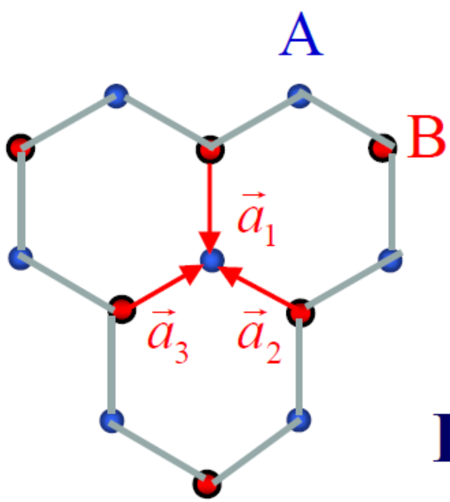
Not exactly Dirac Fermions

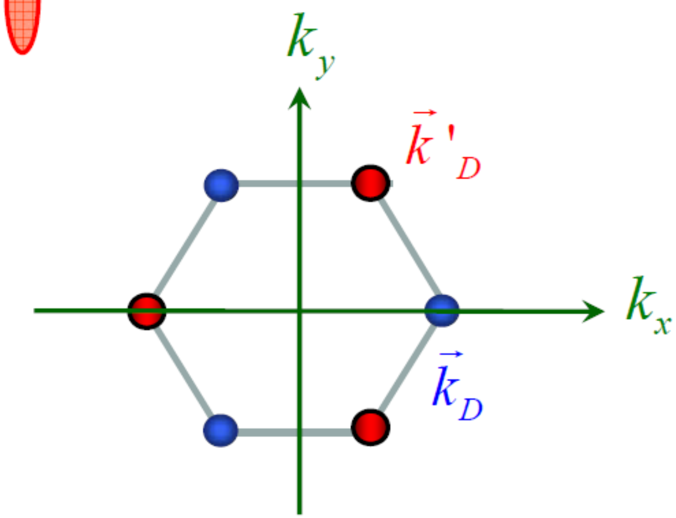
$\upsilon \approx c / 300$

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

Parent spectrum
Two dimensional Dirac Fermions



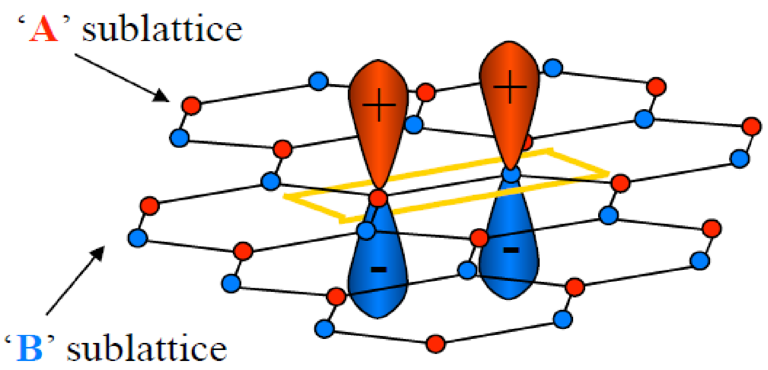




Dirac points

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

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

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

$1 \leftarrow p_z^{\mathbf{A}}(r)$

$e^{i\theta} \leftarrow p_z^{\mathbf{B}}(r)$

k•p perturbation theory

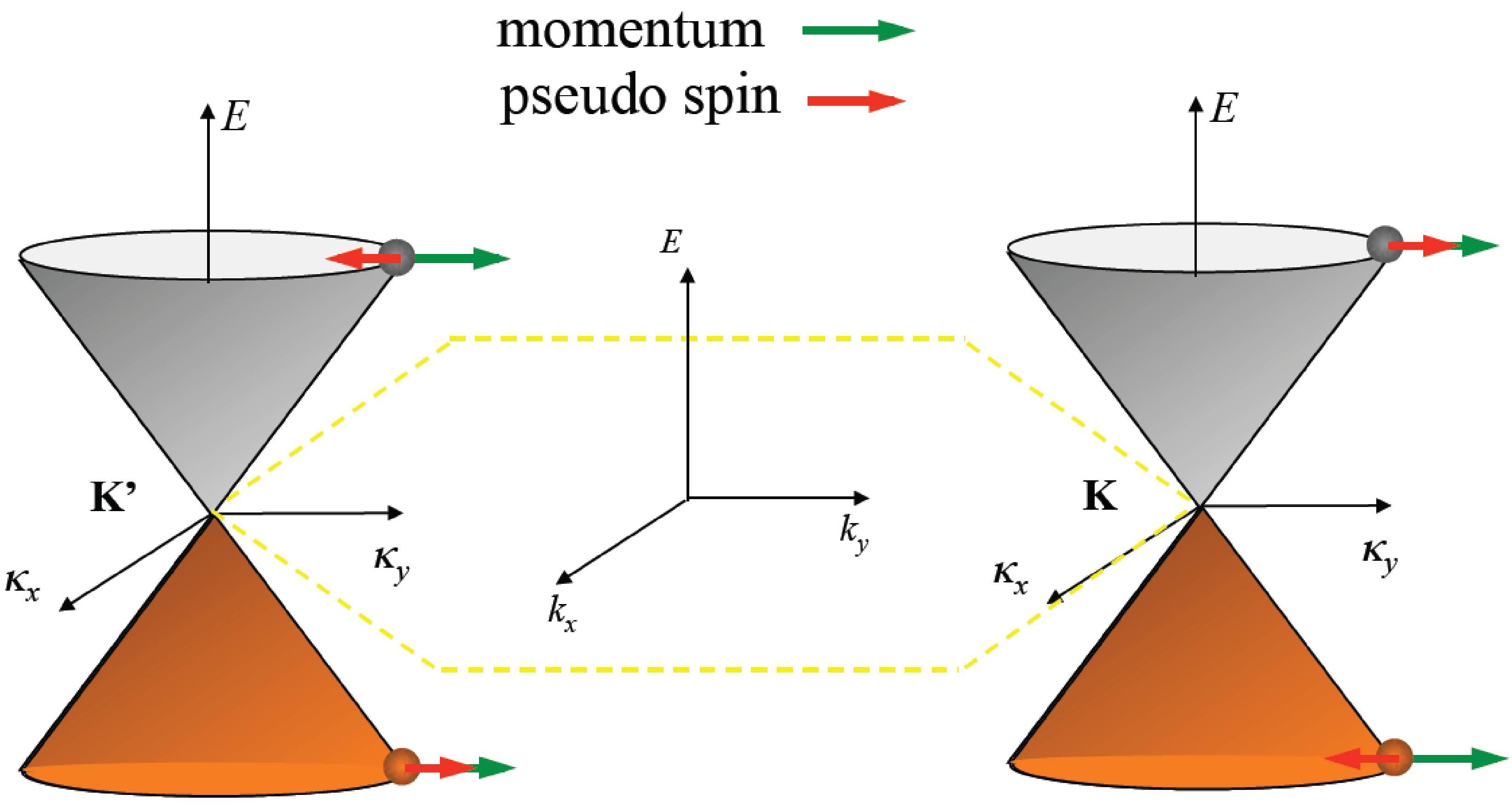
$$H_{eff} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_F \vec{\sigma} \cdot \vec{k}_\perp$$

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

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

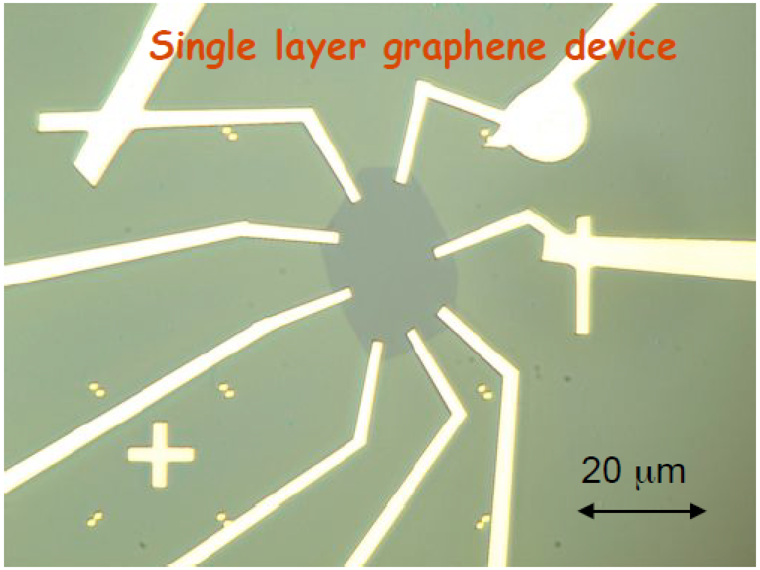
DiVincenzo and Mele, PRB (1984); T. Ando, JPSJ (1998);McEuen at al, PRL (1999)

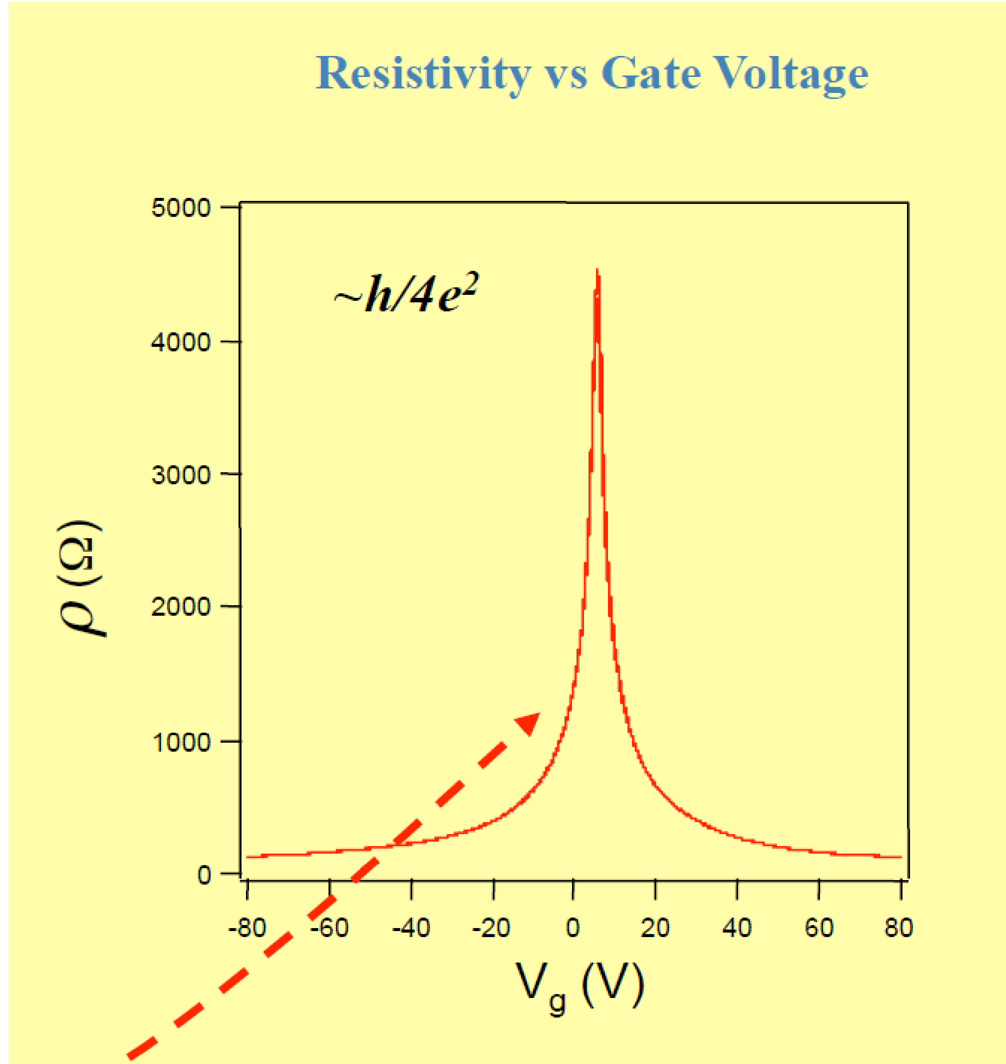
Dirac Fermions in Graphene : "Helicity"

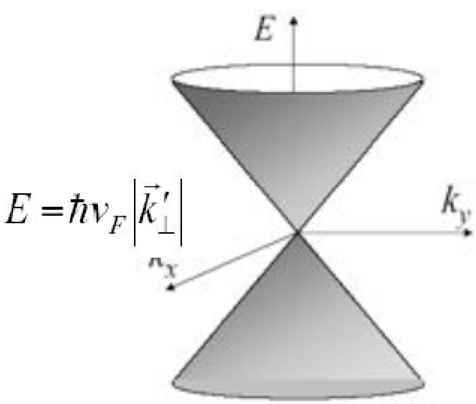


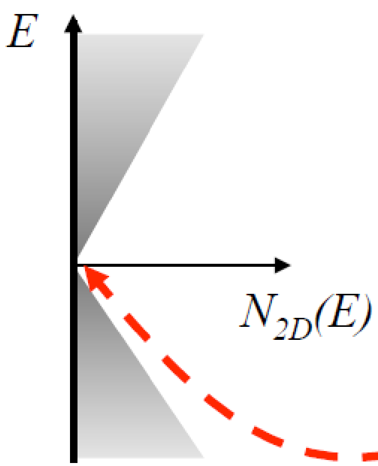
$$H_{eff} = \hbar v_F \vec{\sigma}^* \cdot \vec{k}_\perp \qquad H_{eff} = \hbar v_F \vec{\sigma} \cdot \vec{k}_\perp$$

Transport Single Layer Graphene







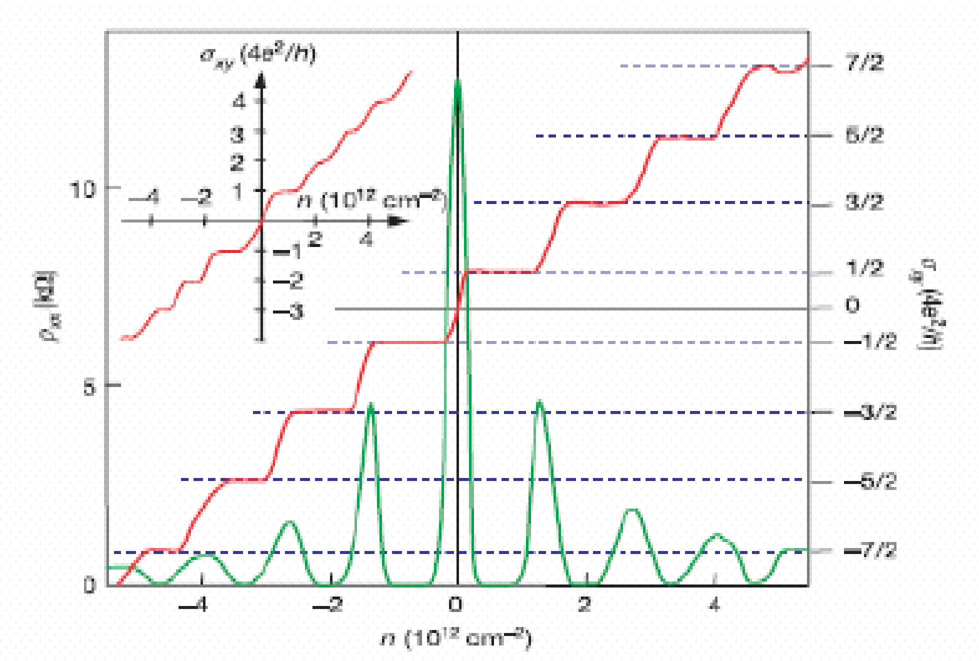


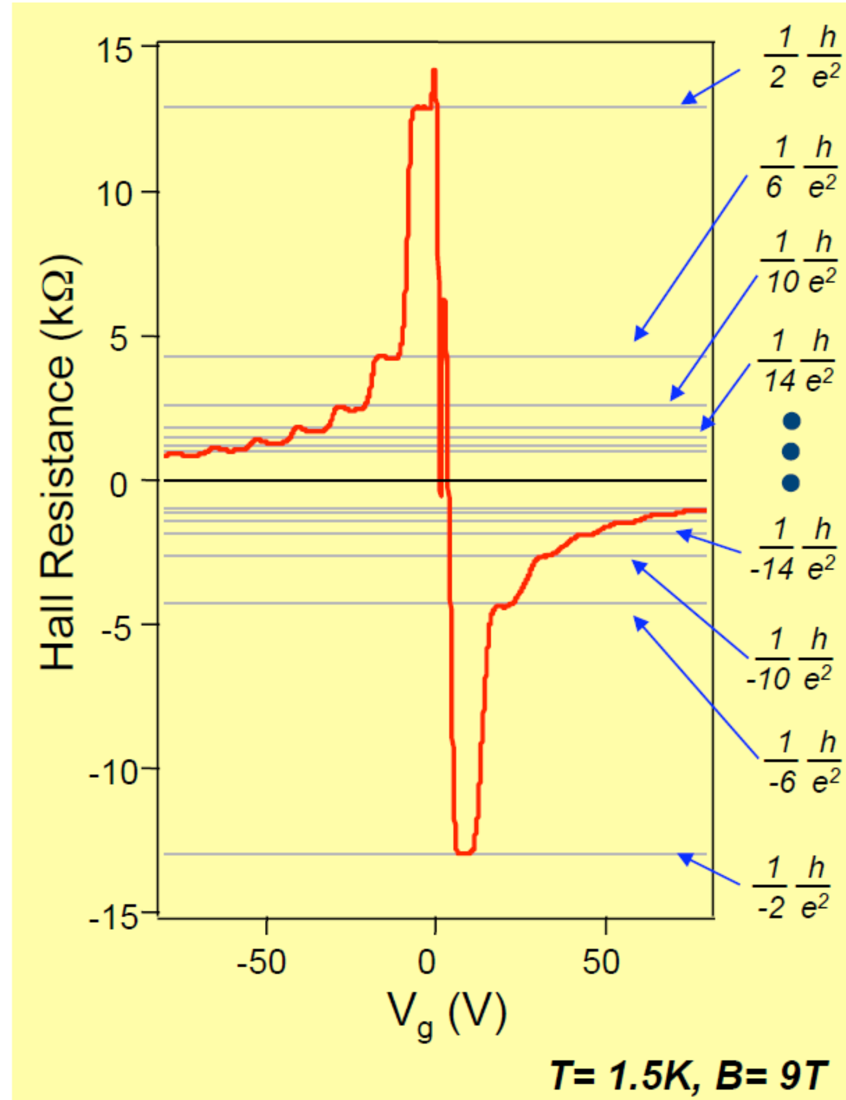
$$\rho^{-1} = e^2 v_F\, l_e\, N_{2D}$$

Quantum Hall Effect in Graphene

T = 3K

Novoselov et al ; Zhang et al (2005)



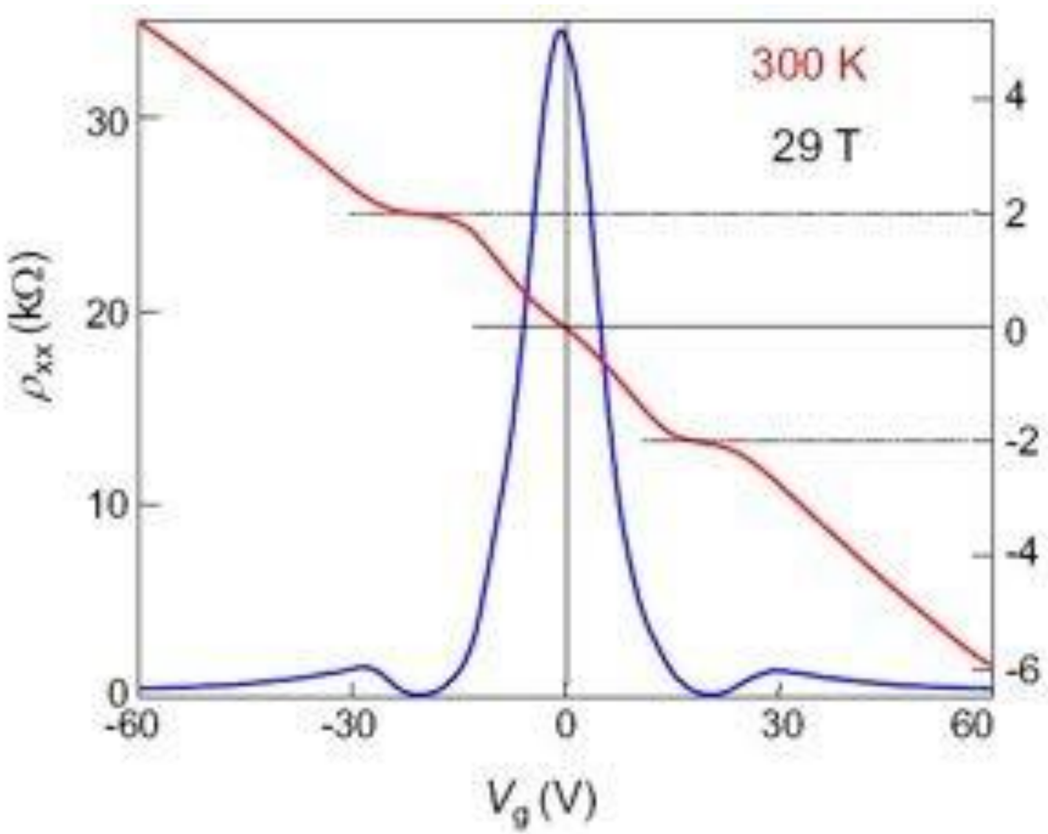


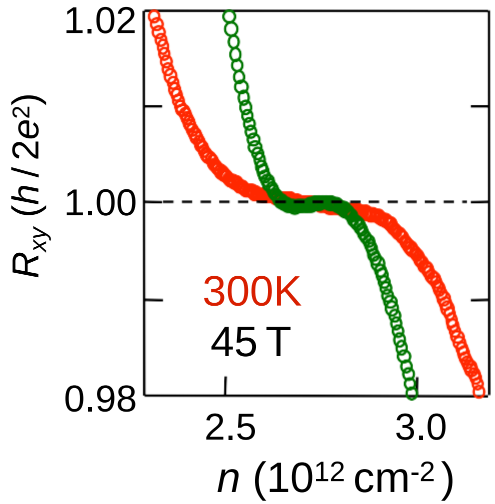
Y. B. Zhang et al, *Nature* **438**, 201(2005)

Quantization:

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

Room Temperature Quantum Hall Effect





Deviation < 0.3%

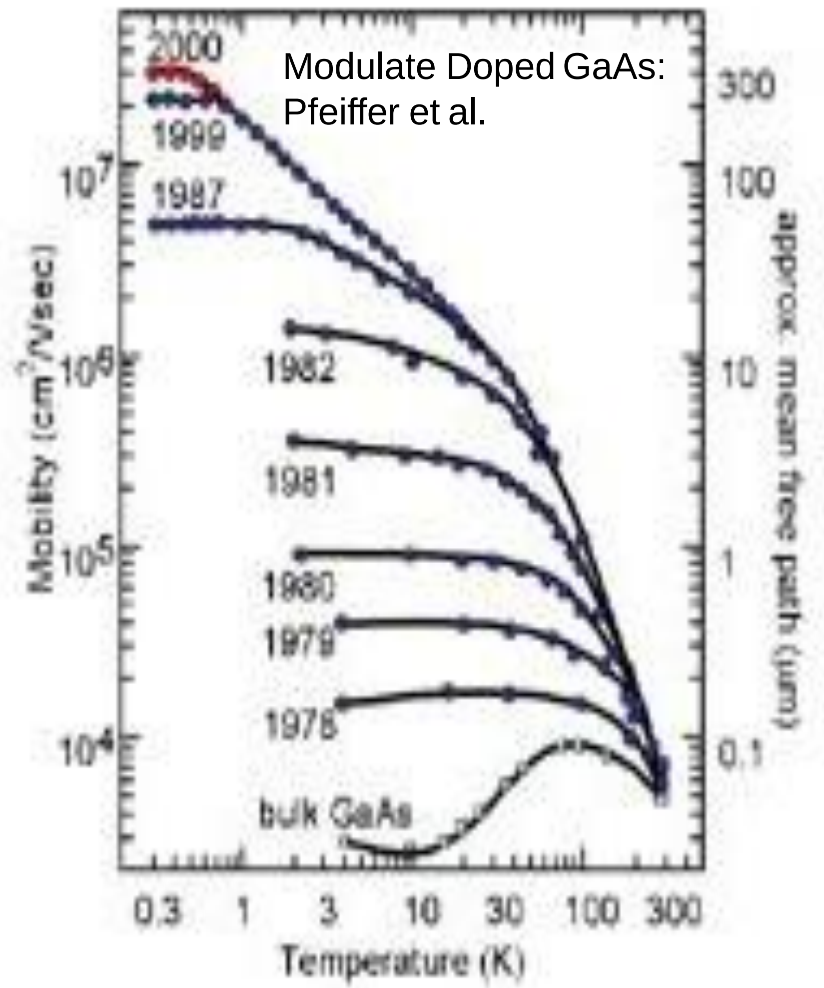
$$E_n = \pm\sqrt{2e\hbar v_F^2 |n| B}$$

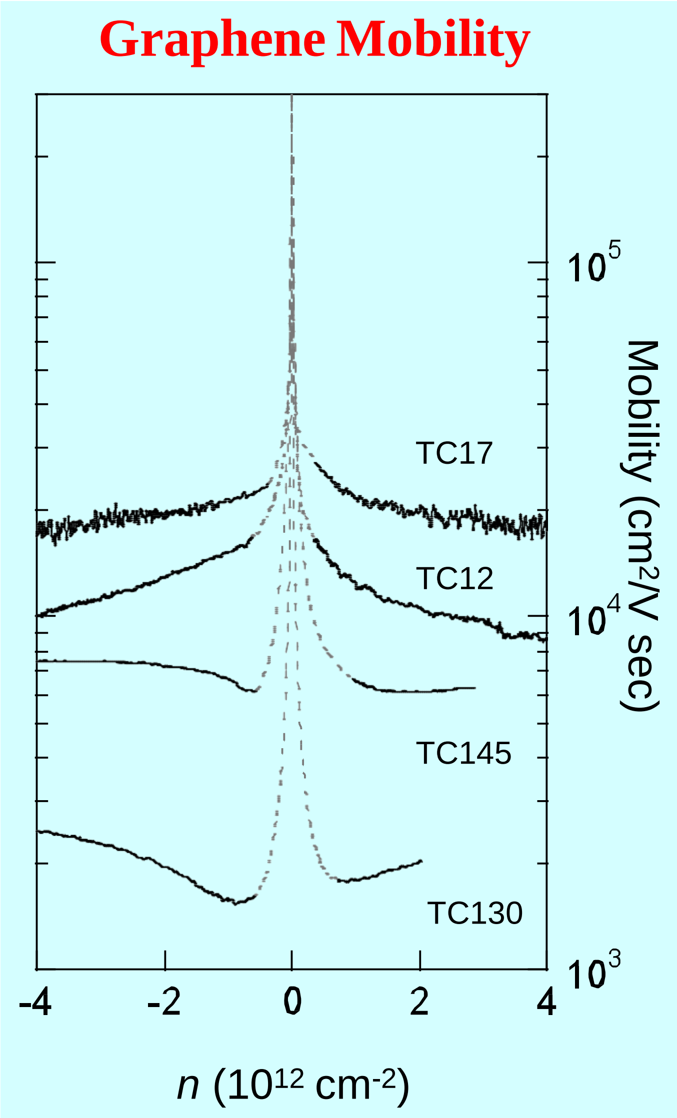
E_1 ~ 100 meV @ 5 T

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

Graphene Mobility

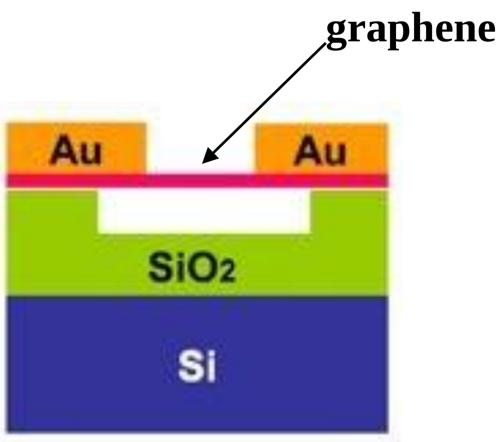
GaAs HEMT





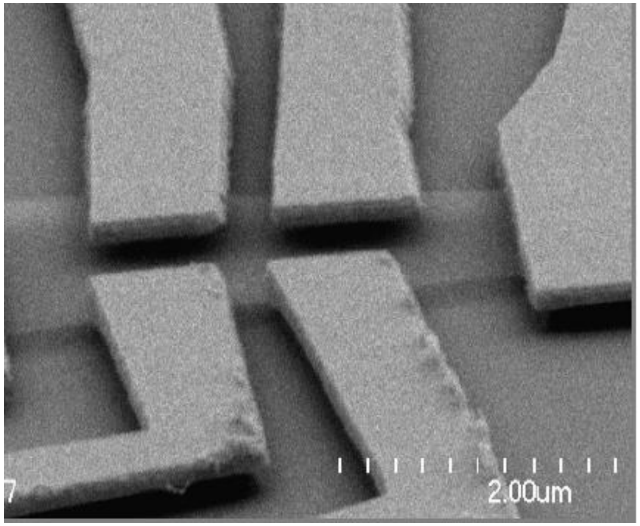
Tan al. PRL (2007)

Toward High Mobility: Suspending Samples



HF etching
-> critical pointing drying

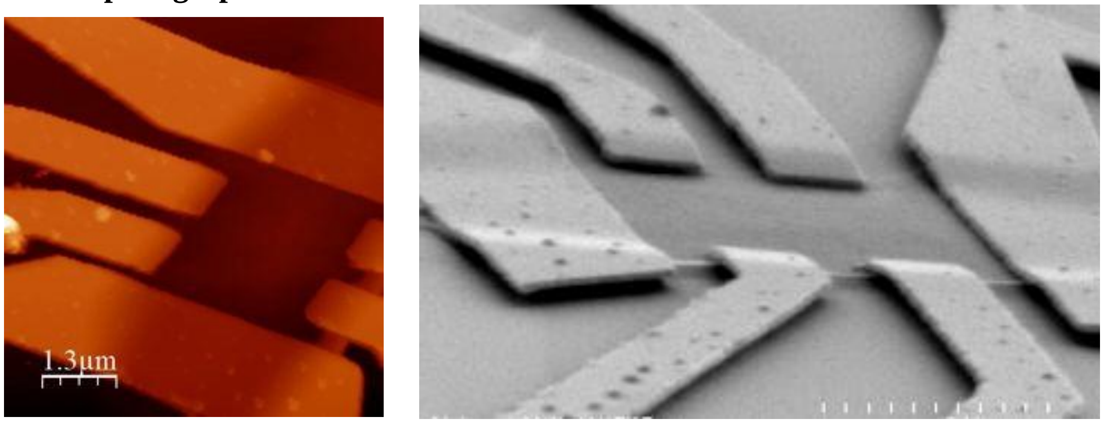
SEM image of suspended graphene



AFM image of suspended graphene

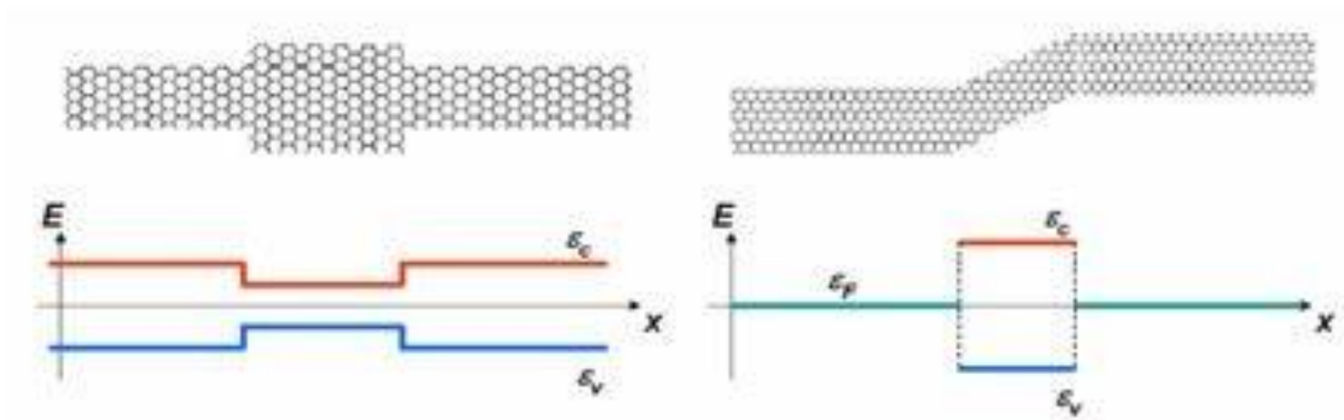
You should not apply to high gate voltage, otherwise…

Collapsed graphene devices…

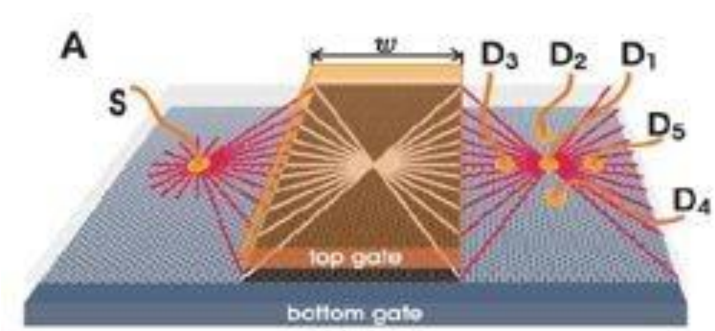


Graphene Electronics

Engineer Dreams

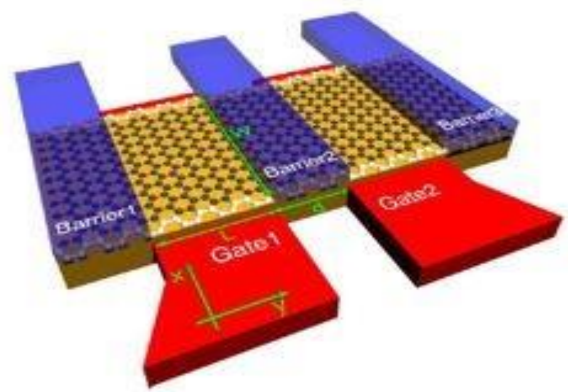


Theorist Dreams



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.

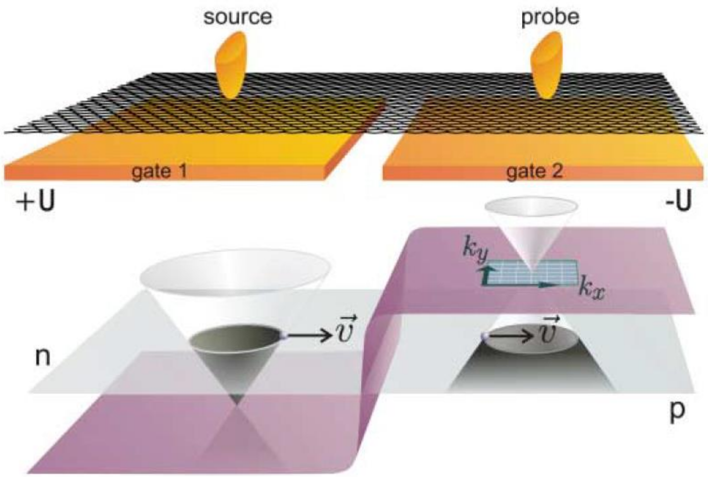


Fig. 1. Graphene *p-n* junction (PNJ). Monolayer of graphite is placed over the split gate, which is used to create *n-* (**left**) and *p*-doped (**right**) regions. The energy diagram shows the position of the Fermi level with respect to the touching point of the valence and the conduction bands.

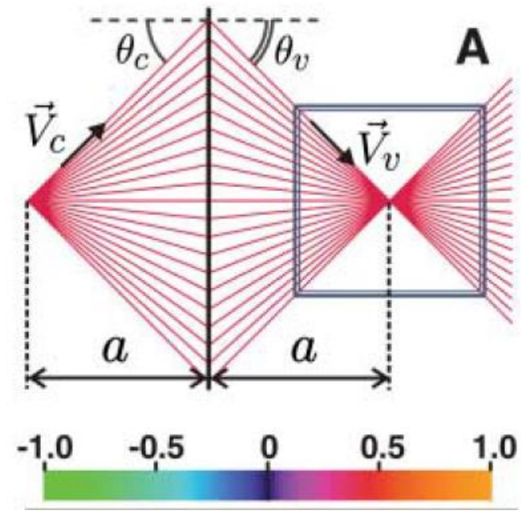


Fig. 2. Focusing of electrons by symmetric PNJ, $\rho_h = \rho_e$. (**A**) Classical trajectories of electrons diverging from a source at distance *a* from the junction become convergent after refraction. (**B**)

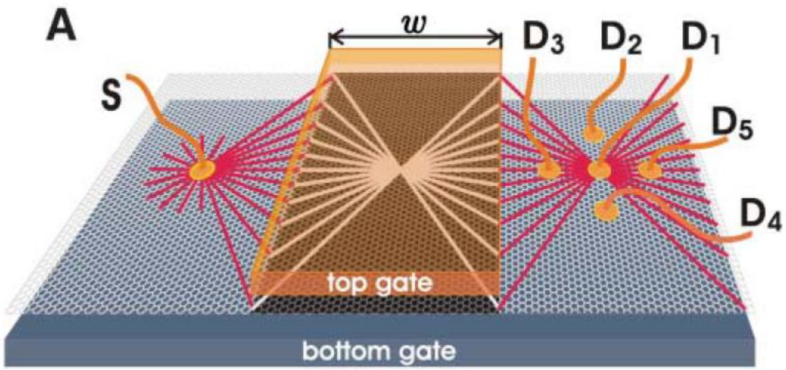
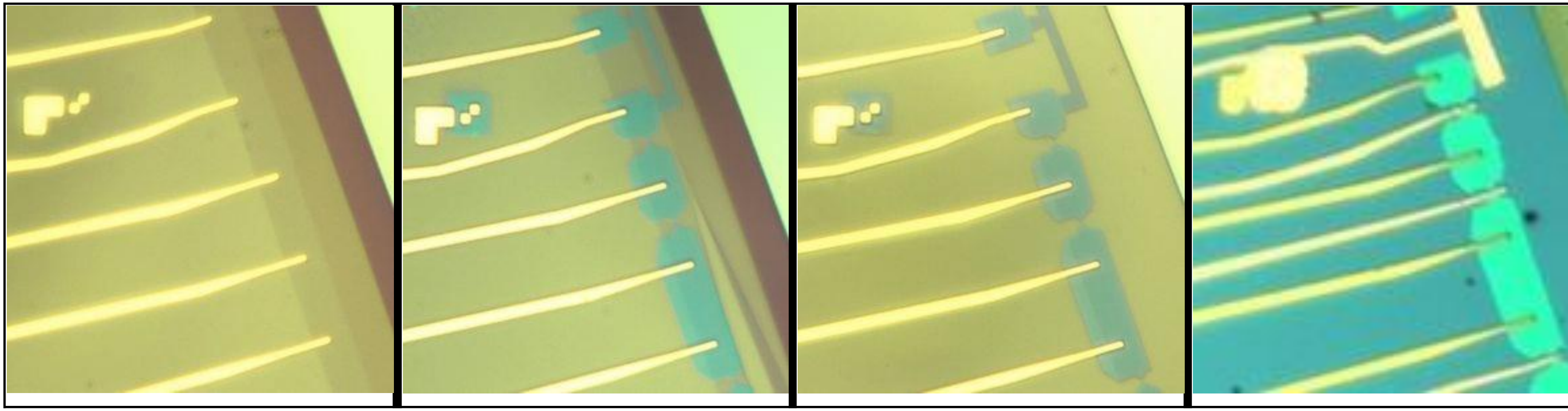


Fig. 4. (**A**) Electron Veselago lens and (**B** and **C**) prism-shaped focusing beam splitter in the ballistic *n-p-n* junction in graphene-based transistor.

From Graphene “Samples” To Graphene “Devices”



Contacts:

PMMA
EBL
Evaporation

Graphene patterning:

HSQ
EBL
Development

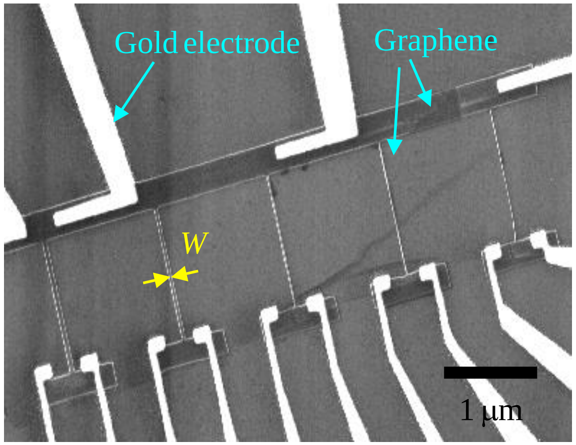
Graphene etching:

Oxygen plasma

Local gates:

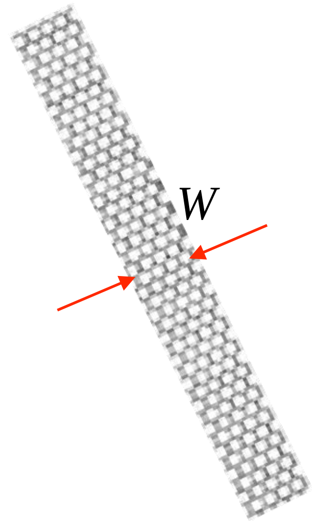
ALD HfO_2
EBL
Evaporation

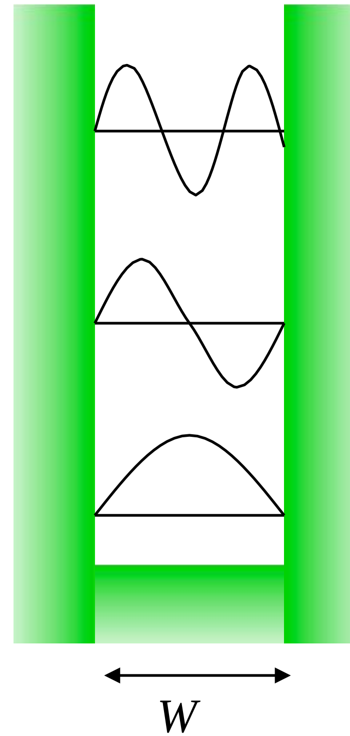
Graphene Nanoribbons: Confined Dirac Particles



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

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).
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M. Ezawa, Phys. Rev. B **73**, 045432 (2006).
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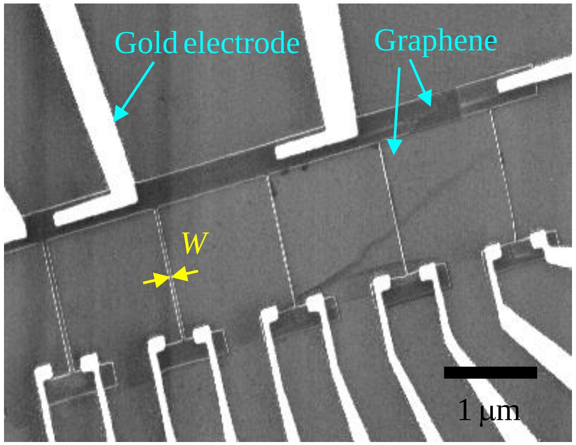
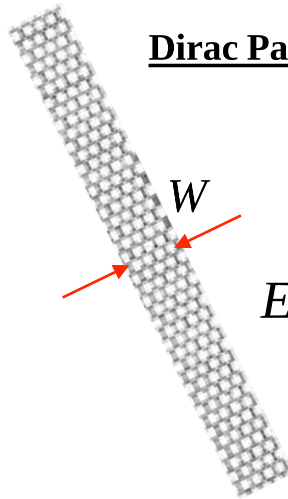
Graphene Ribbon Devices

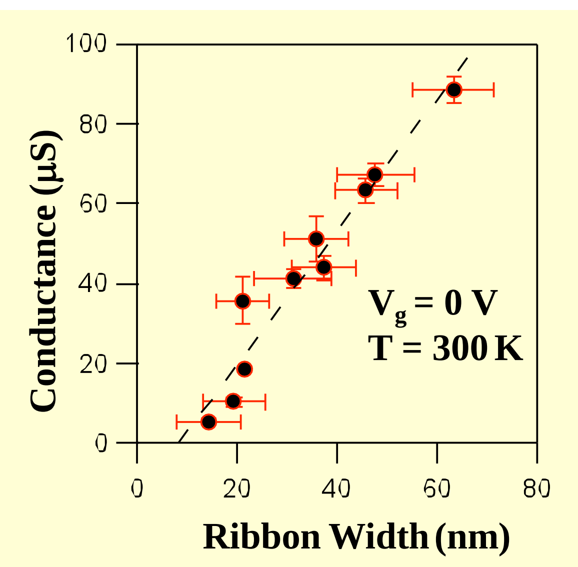


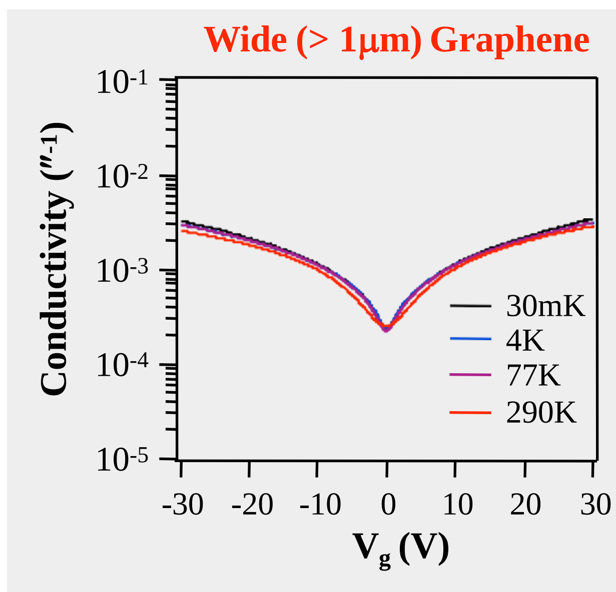
$10\ \text{nm} < W < 100\ \text{nm}$

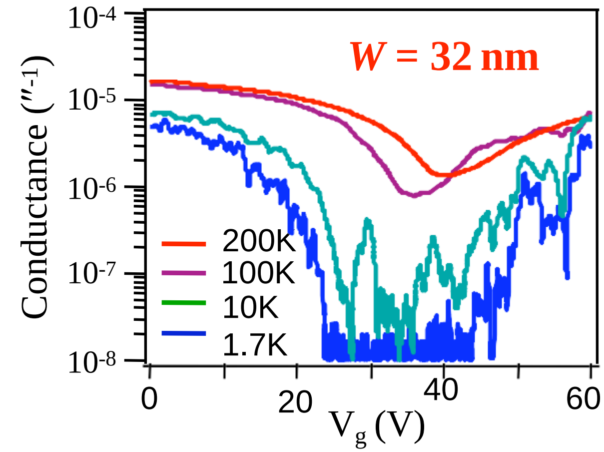


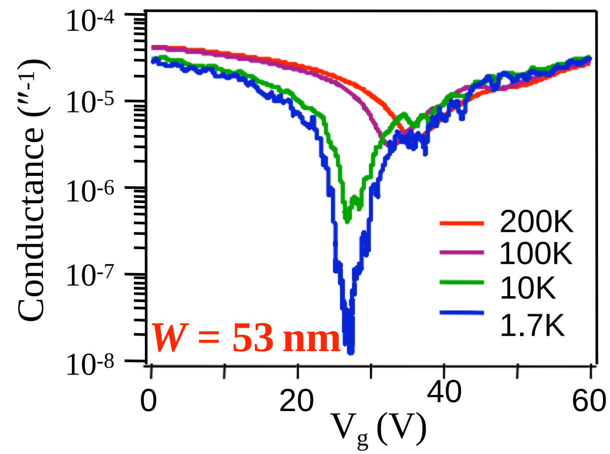
Dirac Particle Confinement

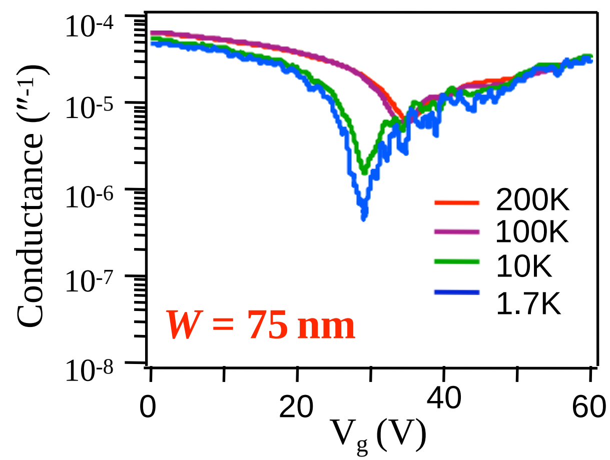
$$E_{gap} \sim \hbar v_F / W$$



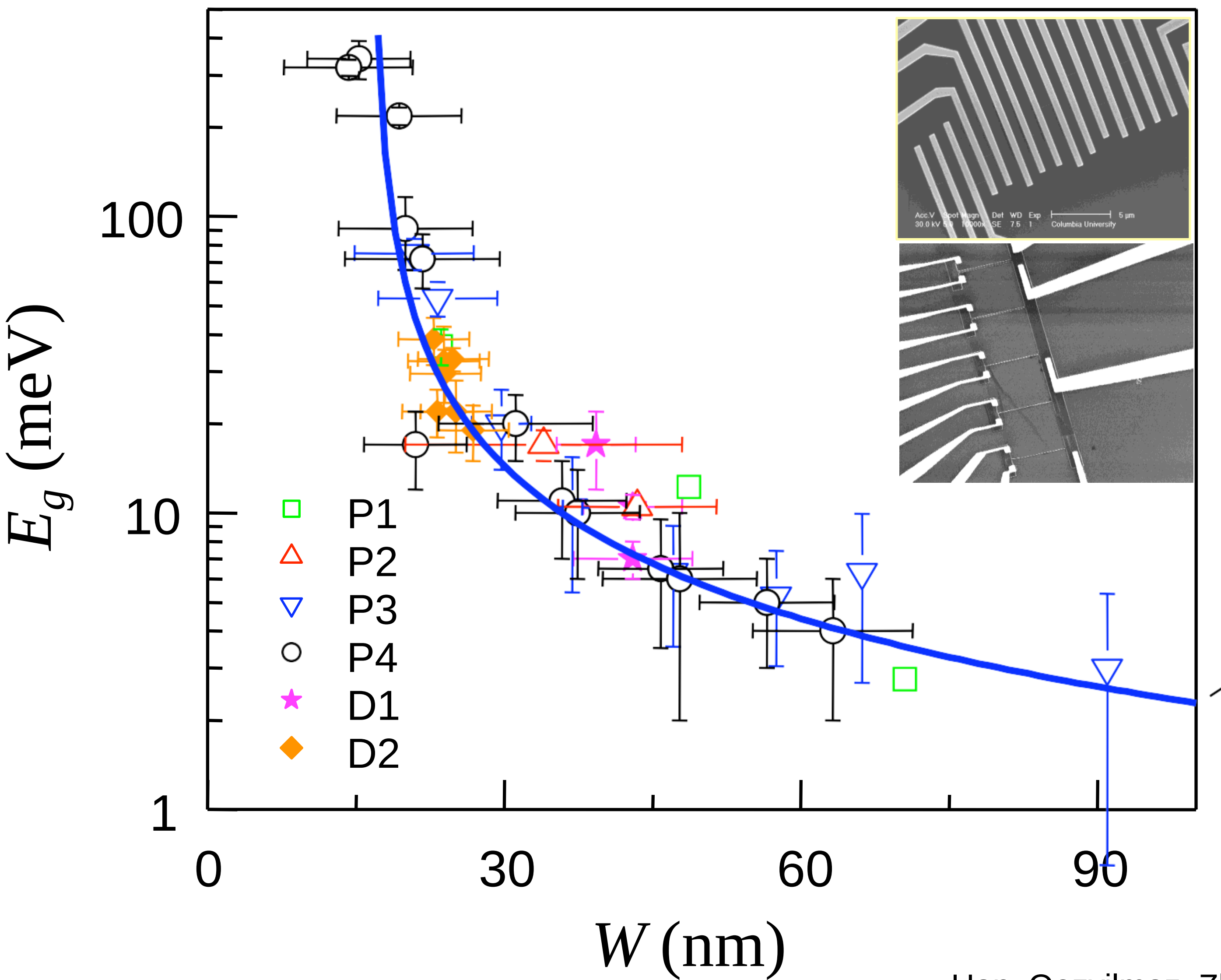








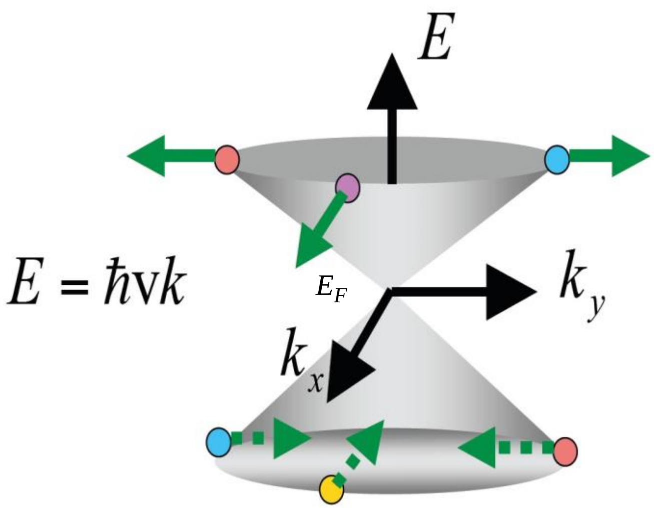
Scaling of Energy Gaps in Graphene Nanoribbons

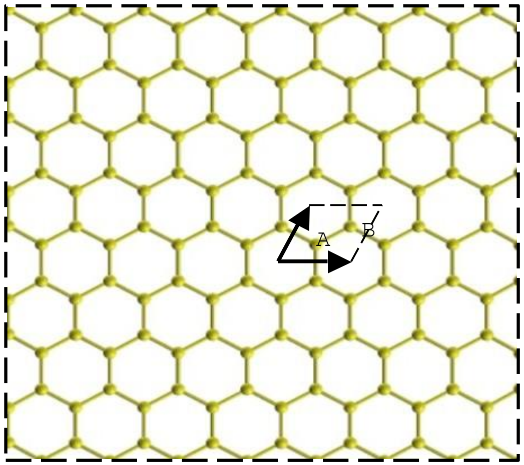


$E_g = E_0 / (W - W_0)$

Han, Oezyilmaz, Zhang and Kim PRL (2007)

Electronic Structure and Pseudospin Physics in Graphene



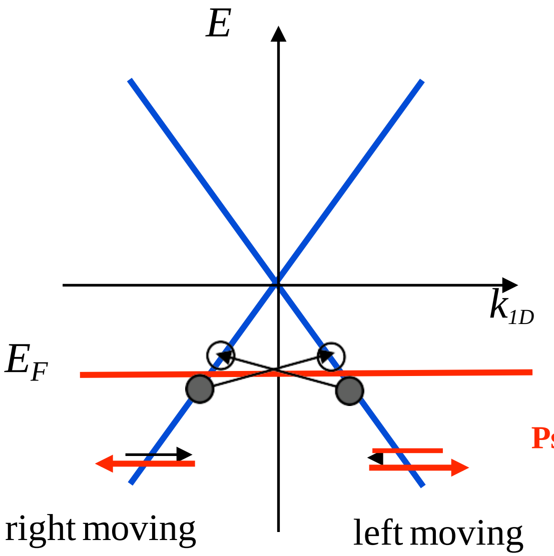


- Energy dispersion of the electron in graphene near the Fermi surface looks like that of ***light***, i.e., a cone.
- A pseudospin pointing along **k** associated with each state, describing the bonding character between the neighboring carbon atoms in the two sublattices.
- The ***chirality*** of graphene wavefunctions near the Dirac point suppresses backscattering events.

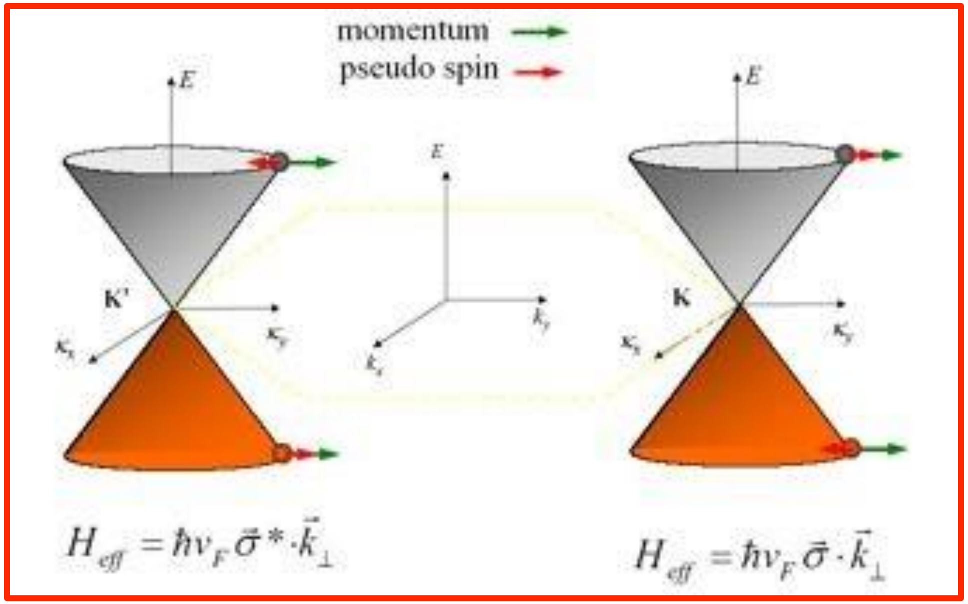
T. Ando, et al (1998); McEuen, Louie, et al (1999)

Extremely Long Mean Free Path: Hidden Symmetry ?

1D band structure of nanotubes



Low energy band structure of graphene

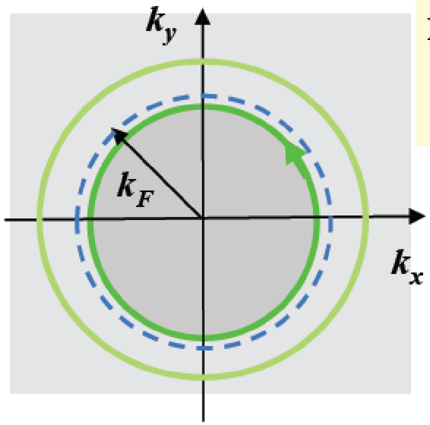


- Small momentum transfer backward scattering becomes inefficient, since it requires pseudo spin flipping.

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

Berry's Phase and Magnetoresistance Oscillations

Landau orbit near the Fermi level



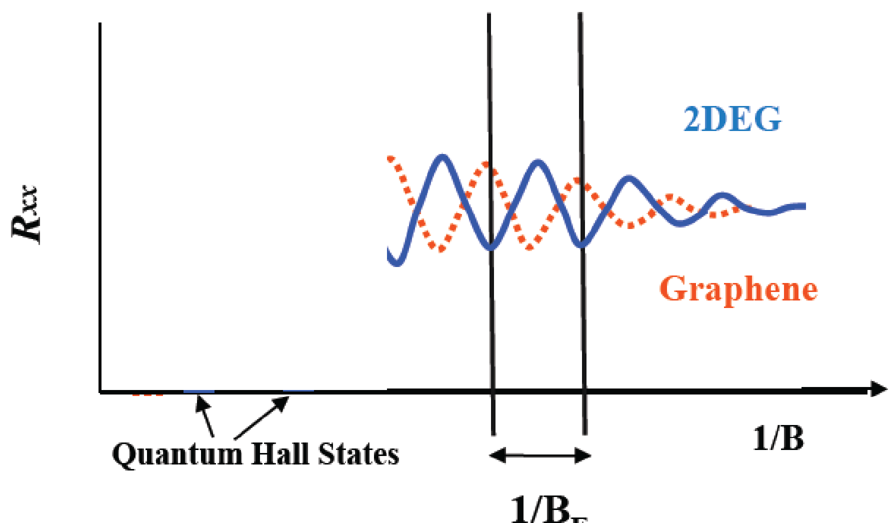
Magnetic flux in cyclotron orbit

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

$$\Phi_o = h/e$$

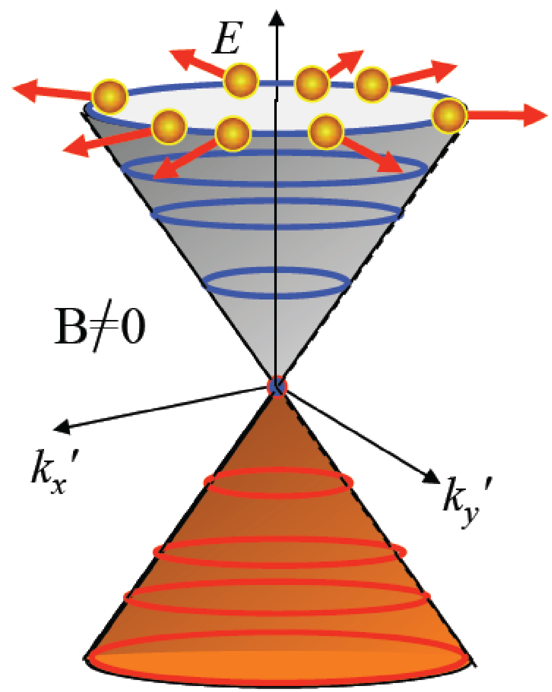
$$B_F = \Phi_o\, k_F^2/4\pi$$

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



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

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