# *Graphene - unusual electronic properties of a model 2D solid*


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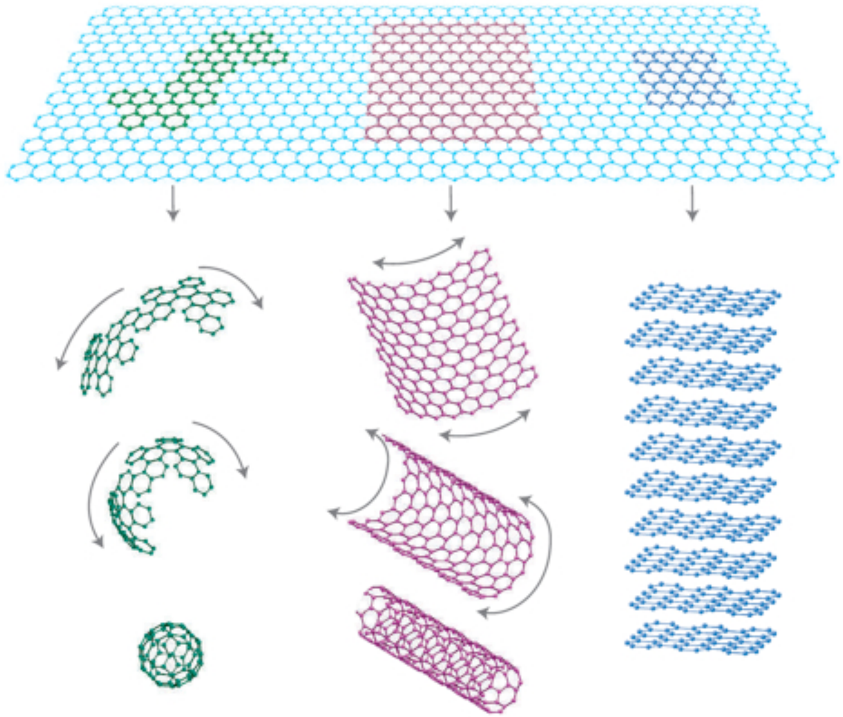
[2]Advanced Light Source, Lawrence Berkeley Laboratory, USA

[3]University of Erlangen


- Graphene - old and new
- Preparation - various ways
- band structure - from single layer onwards
- the bilayer
- friction in graphene
- defect-induced metal-insulator transition

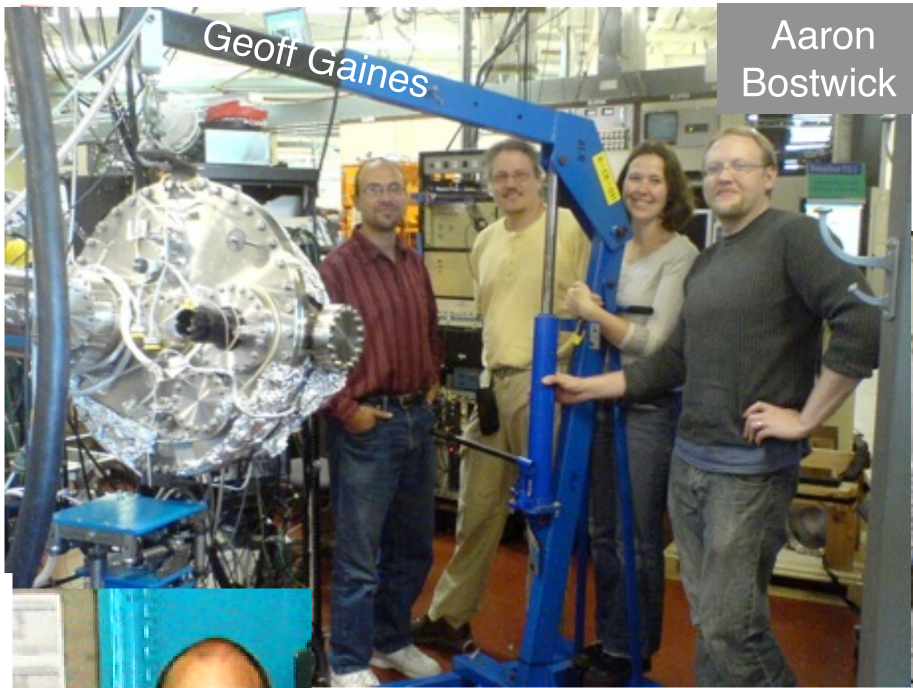
*full coverage of graphene many body physics and novel quasiparticles -> next talk by Aaron Bostwick*



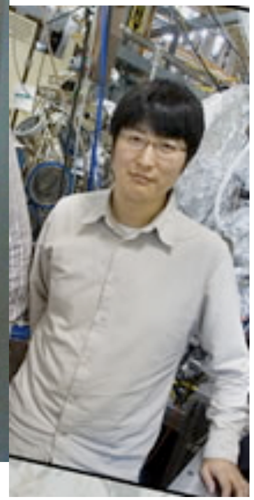
# the cooperation

Eli
Rotenberg

Jessica
McChesney

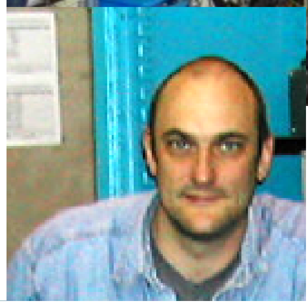



Taisuke
Ohta

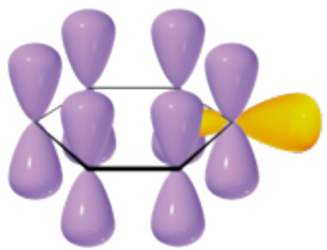


Max Planck
Society

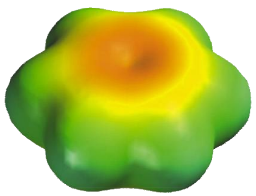
Thomas
Seyller



## benzene



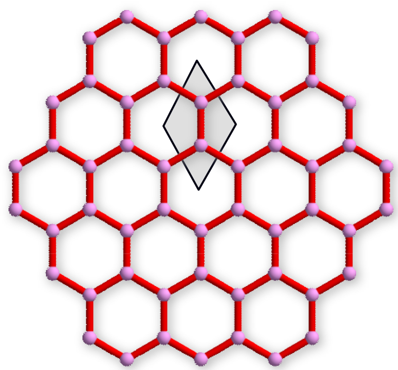
Delocalized π orbital



Delocalized σ orbital

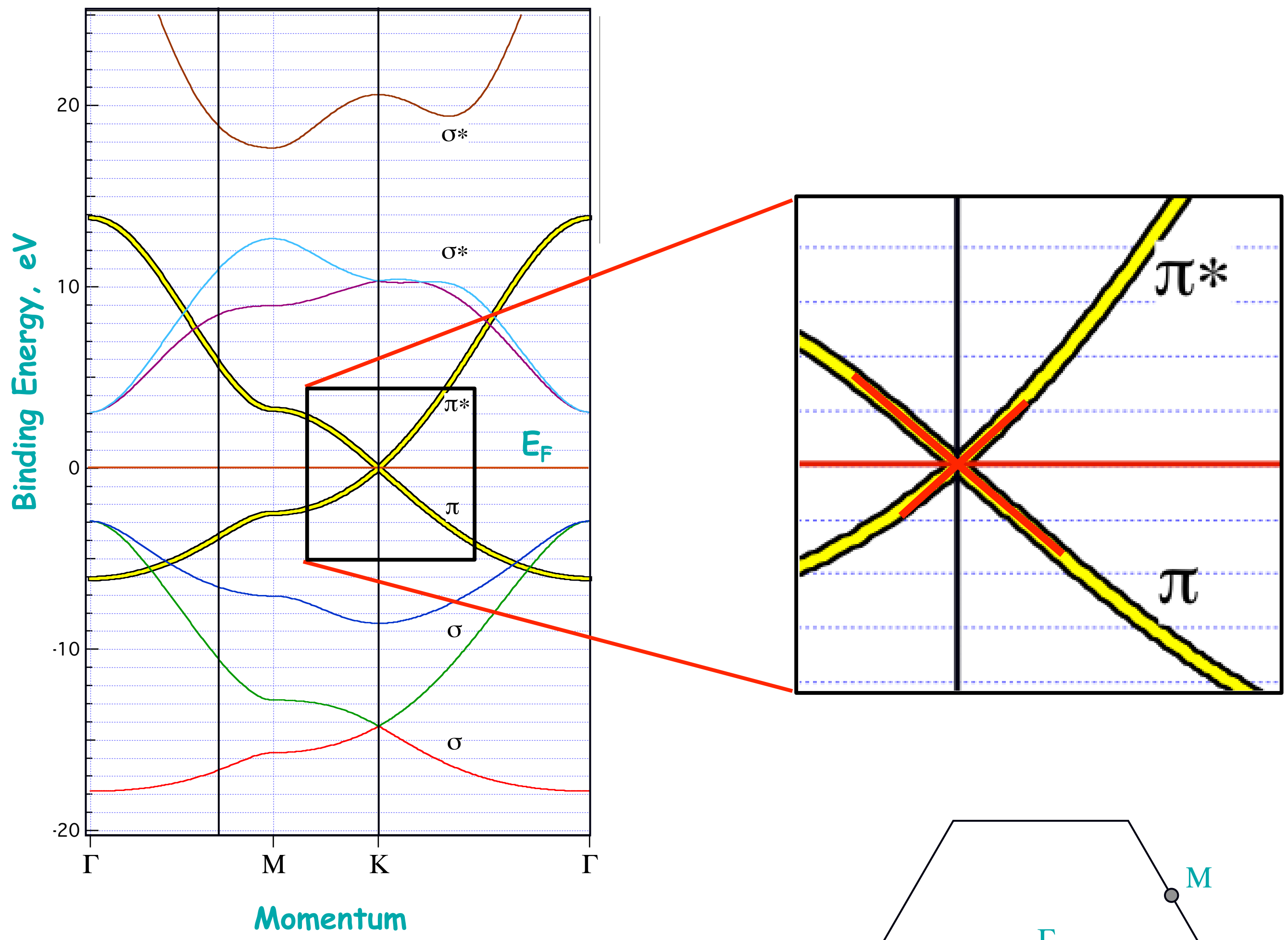
S. Gwaltney
Prentice-Hall

Real Space

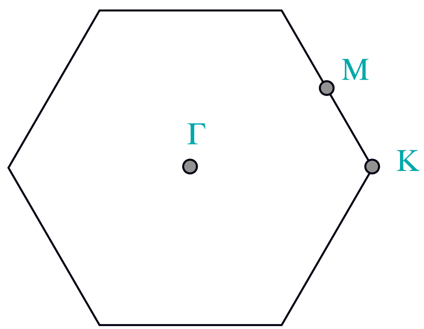


2 atoms in unit cell

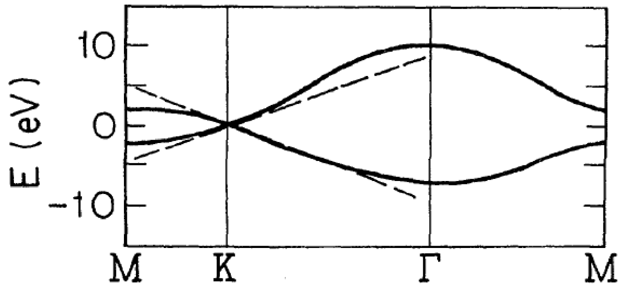
## graphene



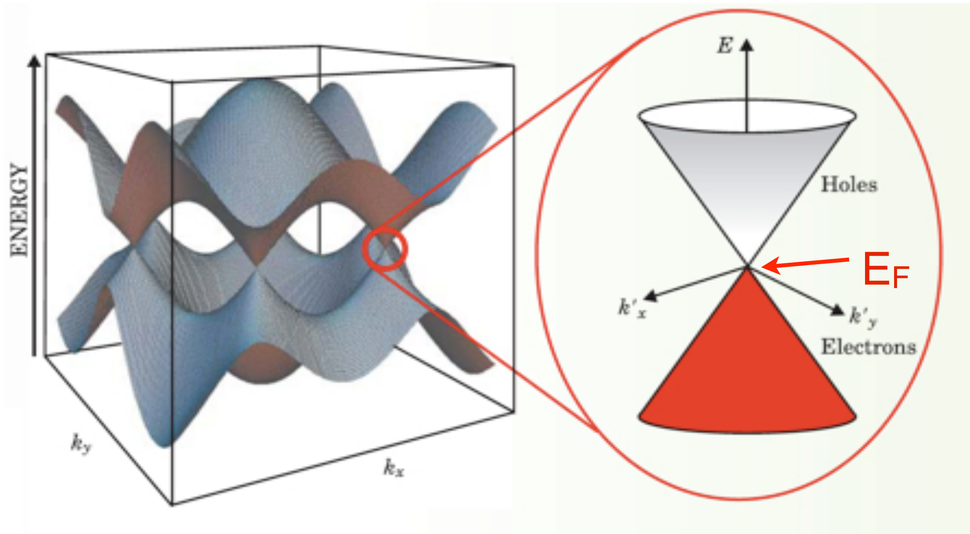

R.Saito,G.Dresselhaus, and M.S. Dresselhaus, Physical Properties of Carbon Nanotubes (Imperial College Press, 1998).




Reciprocal Space




P.R.Wallace, "The band theory of graphite". Phys.Rev. **71**(1947) J.Slonczewski and P.R.Weiss, Phys. Rev. **109**, 272(1958) D.P.DiVincenzo and E.J.Mele, Phys. Rev. B **29**, 1685(1984)

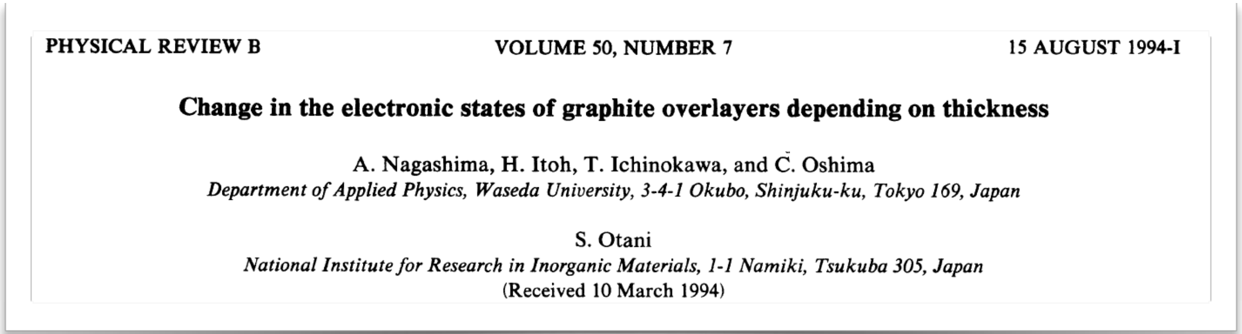



from Physics Today 2006

- charge carriers described by Dirac's equation for **massless particles** $\hbar v_F k \bullet \sigma |\Psi\rangle = E|\Psi\rangle$ (strictly because of lattice symmetry and 2-atom unit cell)
- linear conical bands centered on the K points $E_1(k_0+\kappa) = E^0 - (\frac{\hbar p_0}{m})\kappa$
- bands cross at the "Dirac point" (no gap)
- electrons have zero effective mass, travel at a fixed "speed of light" $v_F \approx c/300$.
- but as Fermions, they are coupled via the Coulomb interaction.
  - quasiparticle excitations: electron-hole pairs, plasmons, phonons

but without transport data -> no attention

# Graphene not new - had been studied well before 2005



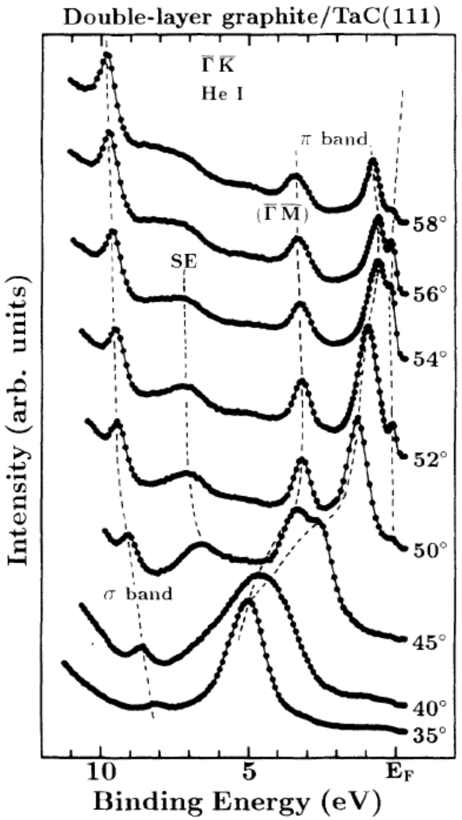
PHYSICAL REVIEW B VOLUME 50, NUMBER 7 15 AUGUST 1994-I

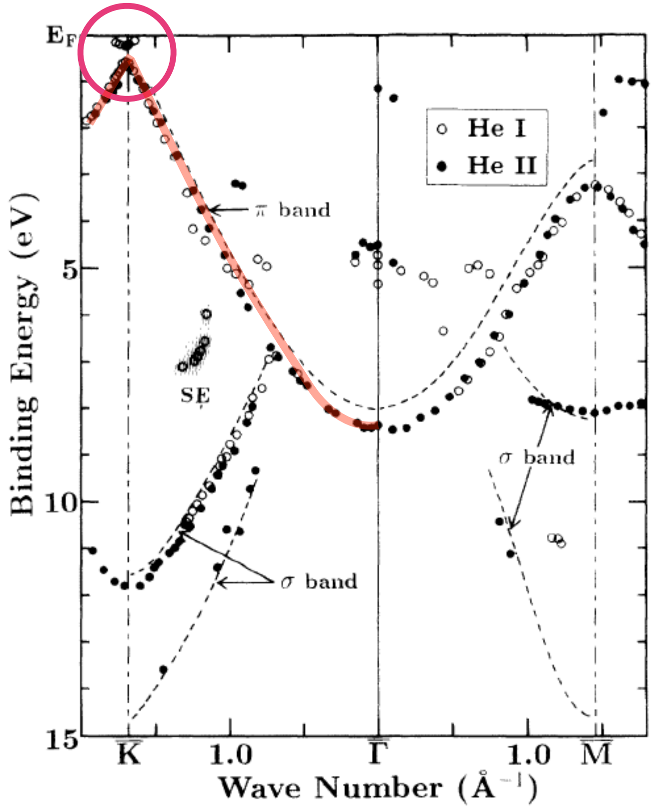
**Change in the electronic states of graphite overlayers depending on thickness**

A. Nagashima, H. Itoh, T. Ichinokawa, and C. Oshima
*Department of Applied Physics, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169, Japan*

S. Otani
*National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba 305, Japan*

(Received 10 March 1994)

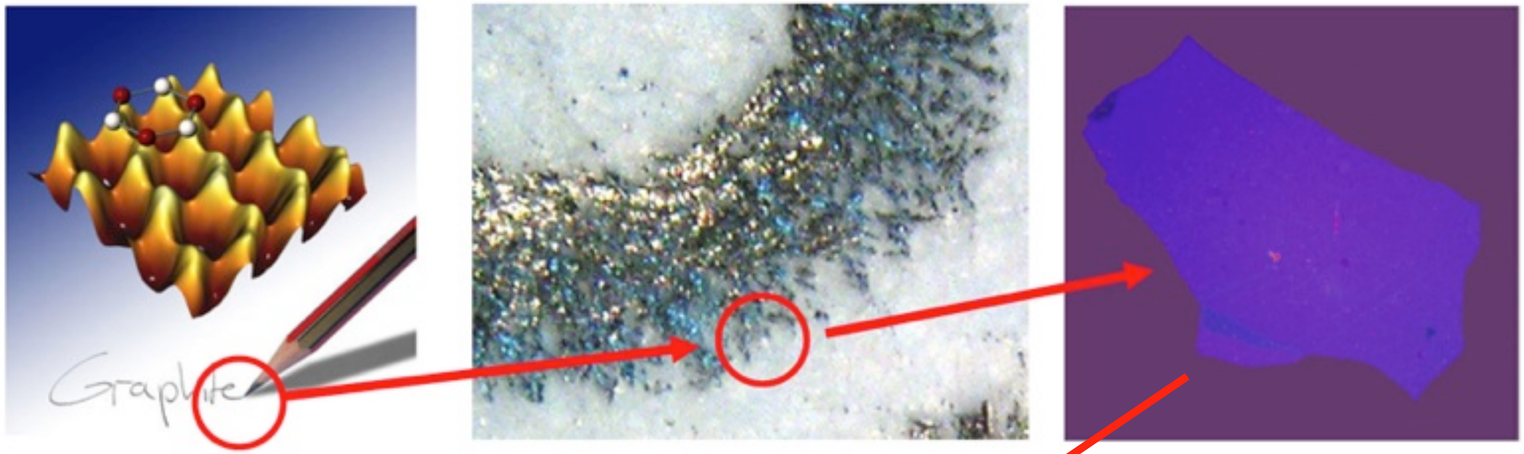



Electronic states of graphite overlayers formed on the TaC( 111) surface have been investigated with the use of STM and ARPES. ... The thickness of the overlayer has been adjusted precisely to be either one or two monolayers. The physical properties of the monolayer graphite film are modified by chemical bonding at the interface. ...

see also Himpsel et al, Surf.Sci. **115**, L159(1982)

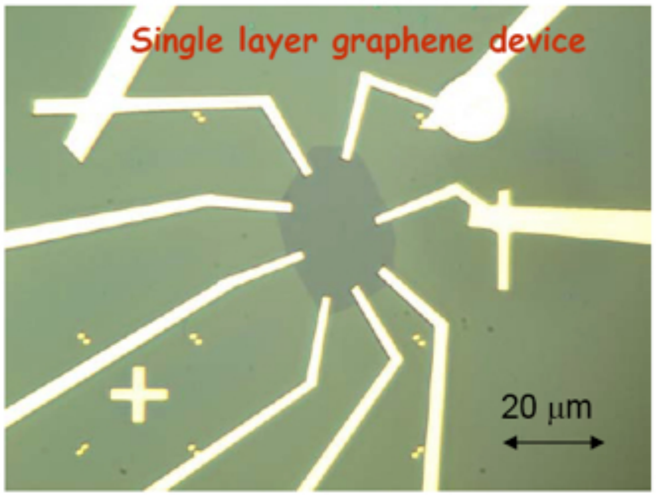
# experimental realisation of graphene by the “scotchtape” method, “invented” in 2004



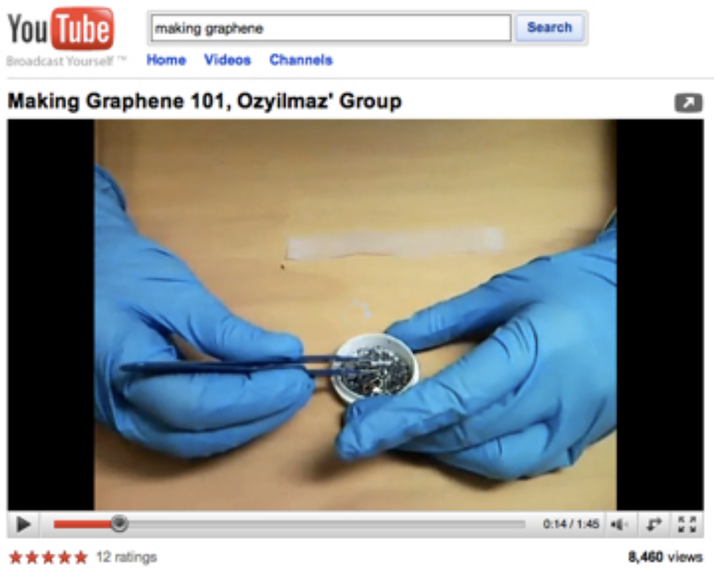

from A. Castro Neto

Novoselov et al, Science 306, 666 (2004)

K.S.Novoselov, D.Jiang,F. Schedin, Booth, TJ, V.V.Khotkevich, S.V.Morozov, and A.K.Geim, PNAS 102, 10451(2005)



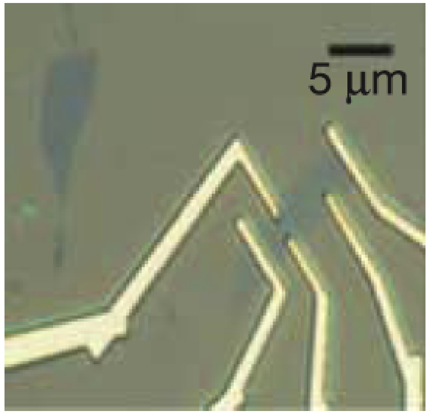

Zhang, Tan, Stormer and Kim (2005)
Novoselov et al (2005)

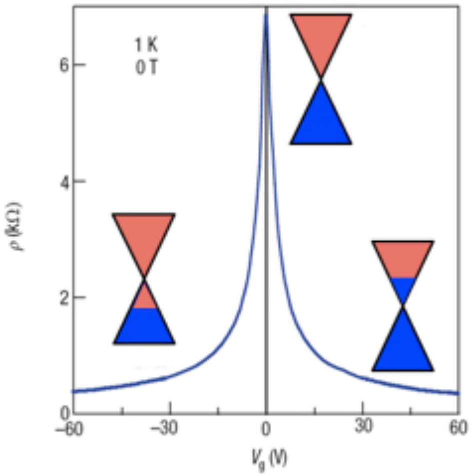



http://www.youtube.com/watch?v=rphiCdR68TE

# field effect and quantum Hall effect  Geim and Kim groups

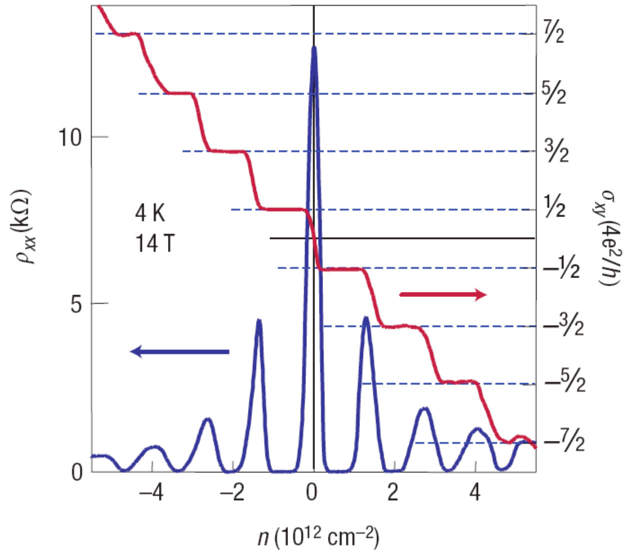
- strong field effect
- large carrier mobilities
- resistivity is quantized, minimum resistivity even at vanishing carrier concentration



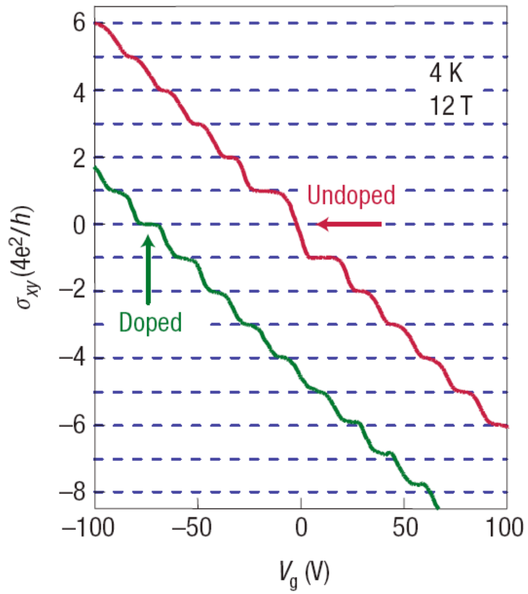




- $\sigma_{xy}$ quantized in plateaus with spacing $\nu 4e^2/h$
- longitudinal resistivity $\rho_{xx}$ vanishes on plateaus - ballistic transport

Single layer graphene




bilayer graphene



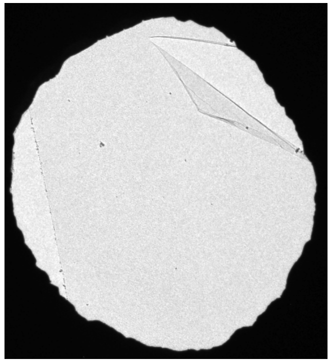

K.Novoselov et al., Nature **438**, 197(2005);
Y.Zhang et al., Nature **438**, 201(2005)

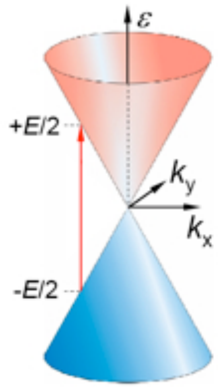
Normal QHE ladder shifted by 1/2 - carriers at K acquire a Berry phase of $\pi$ when executing a full orbit at n = 0

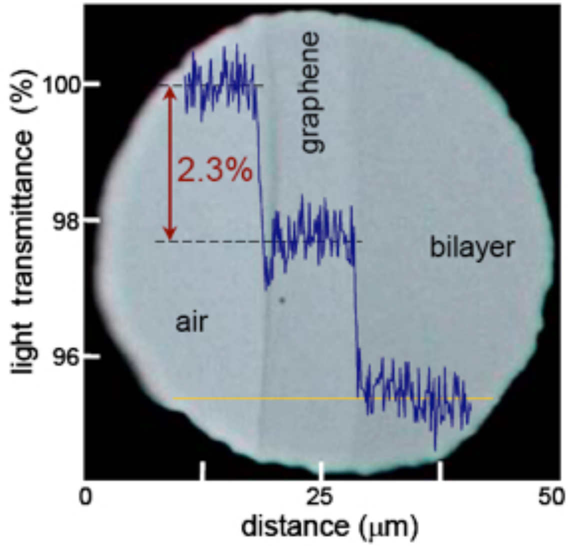
-> signature of relativistic behaviour of Dirac fermions

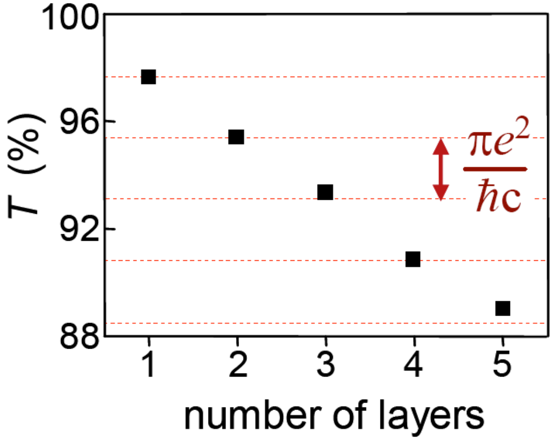
A. K. Geim and K. Novoselov *"The rise of graphene"*, Nature Materials **6**,183(2007);
A. K. Geim "*Graphene: Status and Prospects*", Science 324 (2009)

## Optical transmission






optical conductivity G for conical dispersion relation $\varepsilon = hv_F|k|$ predicted as

$G_0 \equiv e^2/4h$

Optical transmission per monolayer

$T = (1+2\pi G_0/c) - 2 = (1+0.5\pi\alpha)-2 \approx 1-\pi\alpha$

$\alpha$ fine structure constant

-> seeing the fine structure constant !

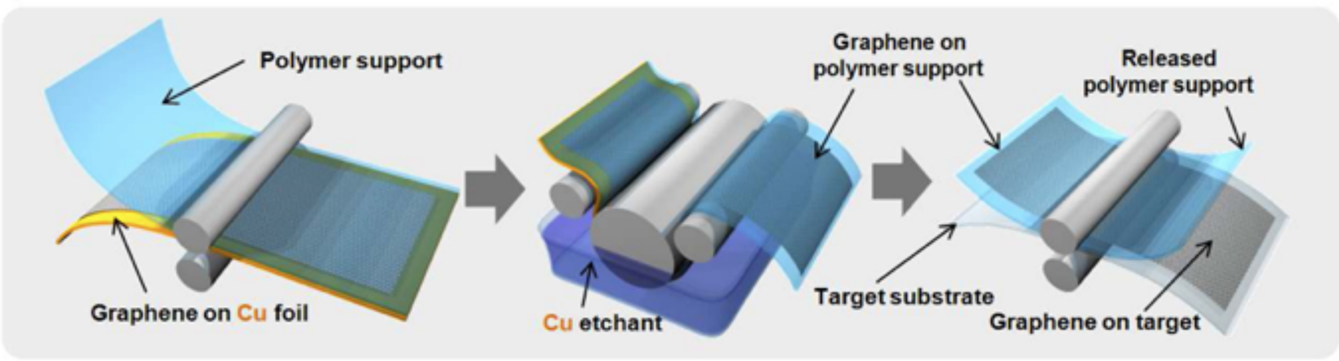
Nair et al., Science **320**, 1308(2008)

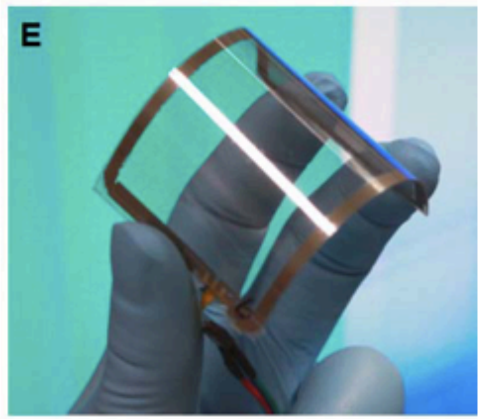
Application: transparent conductive coating, replaces ITO

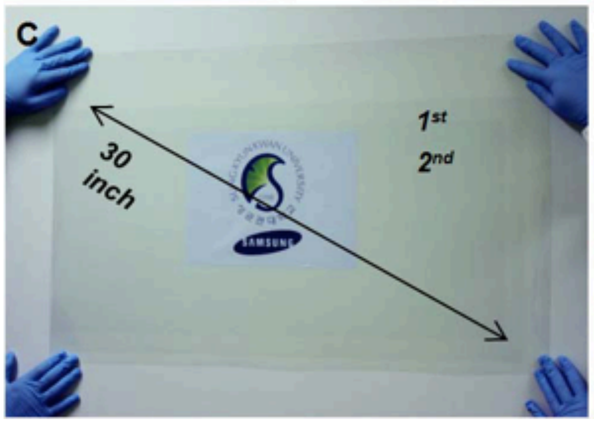
## other ways to prepare graphene

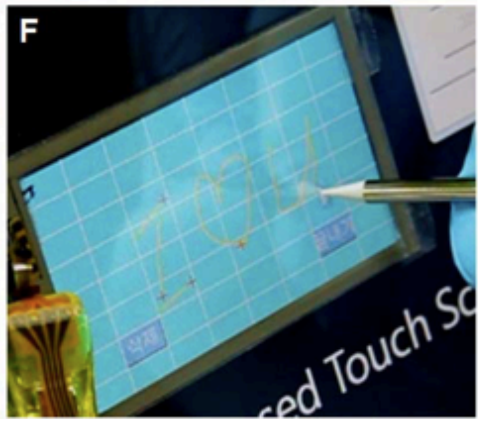
- decomposition of silicon carbide top layers (van Bommel et al., 1974, de Heer 2004, Seyller 2006)
- chemical reaction on metals (~ 1989 Oshima et al., 1998 Dedkov and coworkers)
- various chemical methods (graphene oxide etc., 2007 - 2009)
- transfer methods from growth on metals (2009)

## mass production of large scale graphene sheets

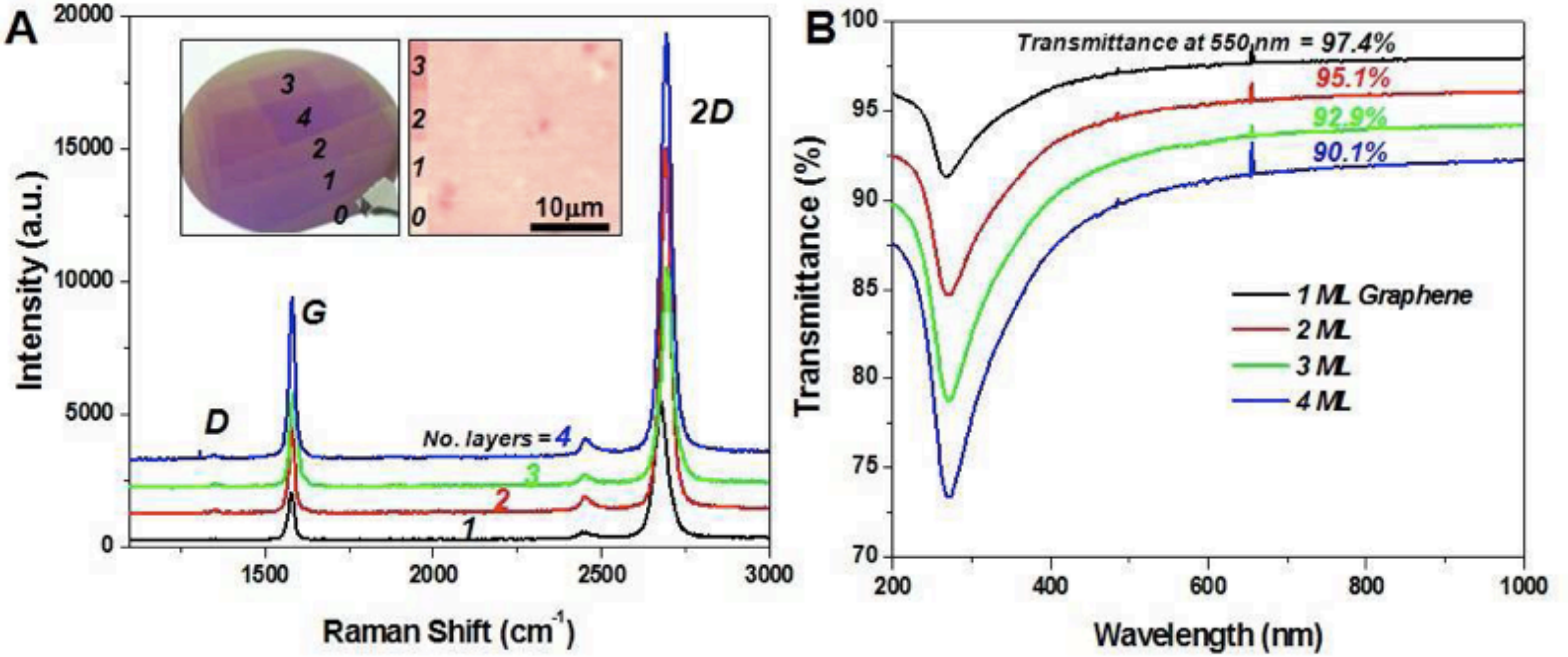


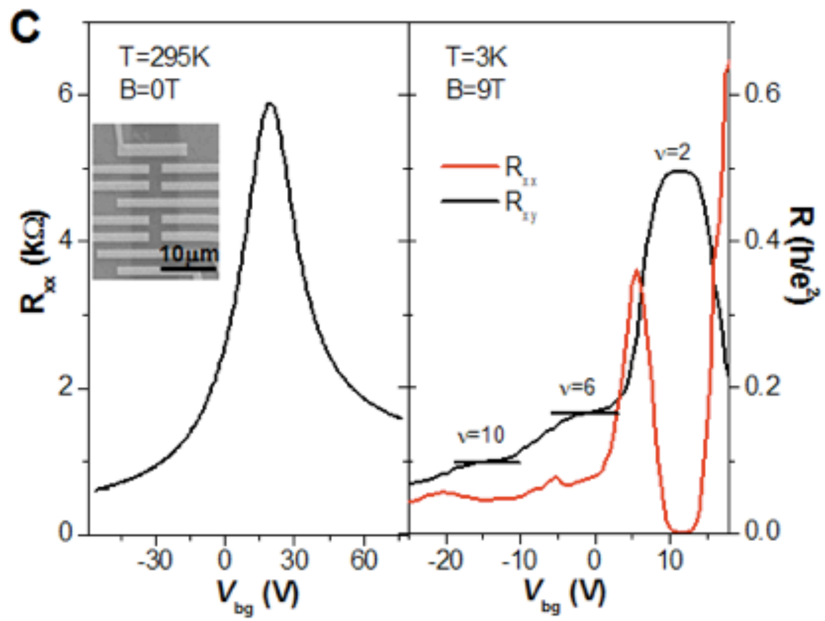

30-Inch Roll-Based Production of High-Quality Graphene Films for Flexible Transparent Electrodes
S. Bae et al., ArXiv 0912.5485 preprint




30-Inch Roll-Based Production of High-Quality Graphene Films for Flexible Transparent Electrodes

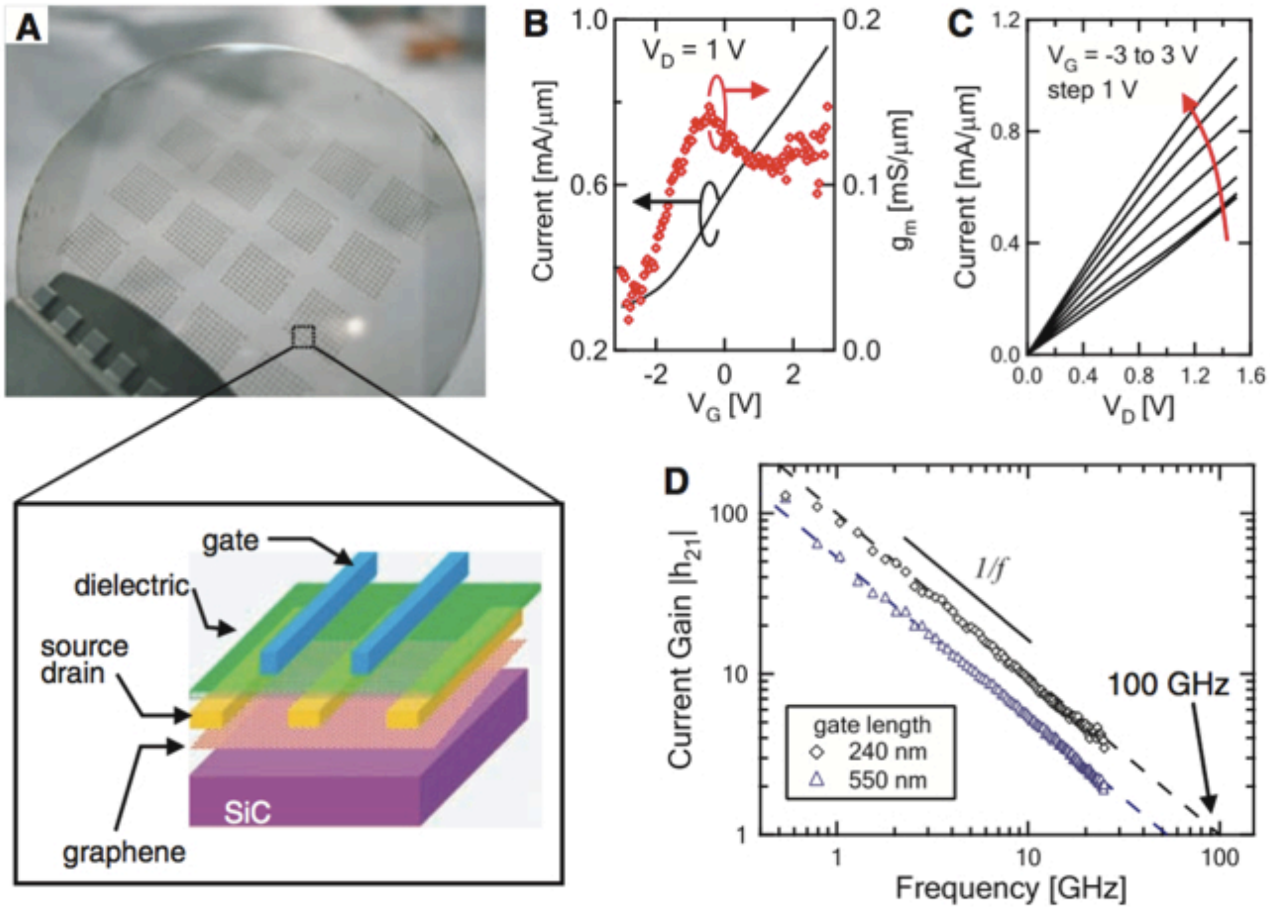
S. Bae, H. K. Kim, X. Xu, J.Balakrishnan, T. Lei, Y. I. Song, Y. J. Kim, B. Ozyilmaz, J.-H. Ahn1, B. H. Hong, S. Iijima

ArXiv 0912.5485 preprint



# Graphene based electronics

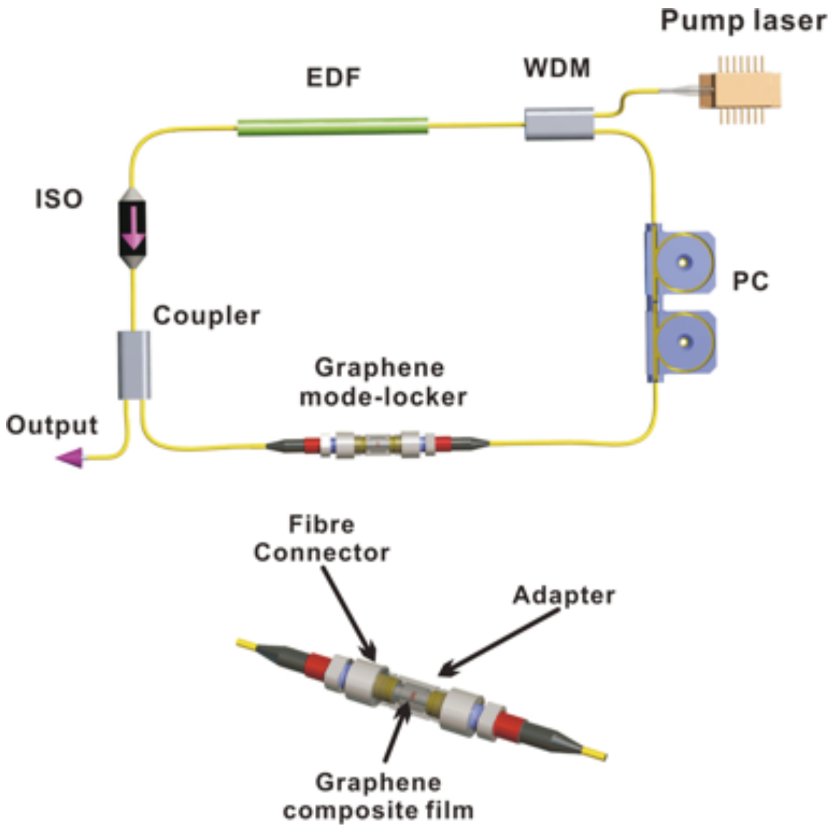
- high mobility (up to 250.000 Vs/cm$^2$), not strongly dependent on T
- long mean free path, ballistic transport over microns
- room temperature Quantum Hall effect



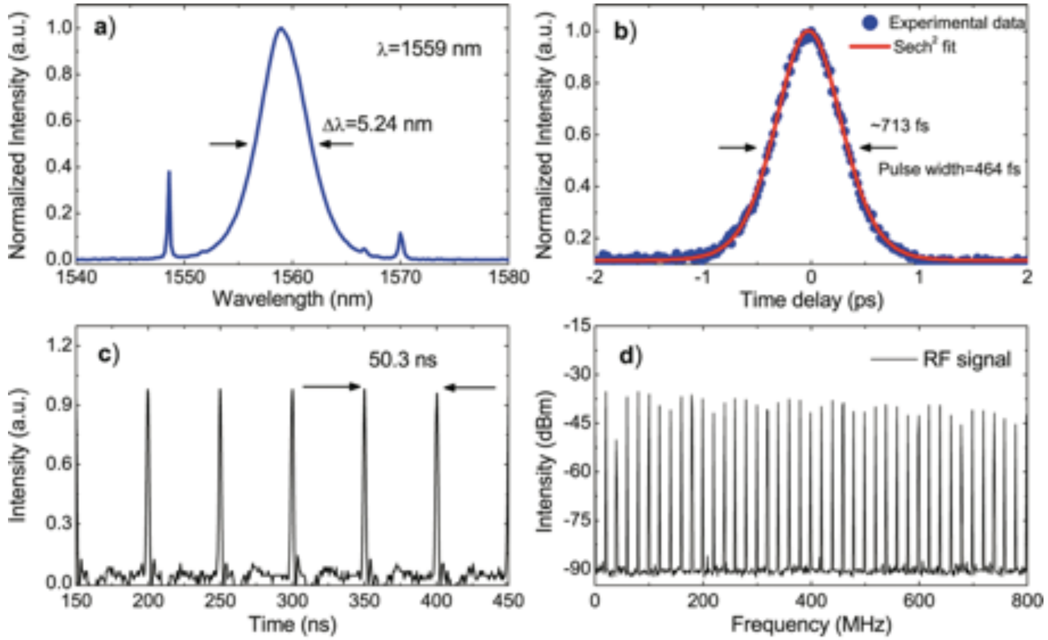

Lin et al., (Avouris group at IBM), Science **327**, 662 (2010)

(A) Image of devices fabricated on a 2-inch graphene wafer and schematic cross-sectional view of a top-gated graphene FET. (B) The drain current, $I_D$, of a GFET (gate length $L_G$ = 240 nm) as a function of gate voltage at drain bias of 1 V with the source electrode grounded. The device transconductance, $g_m$, is shown on the right axis. (C) The drain current as a function of $V_D$ of a graphene FET (LG = 240 nm) for various gate voltages. (D) Small-signal current gain $|h_{21}|$ as a function of frequency f for a 240-nm- (◇) and a 550-nm-gate (△) GFET at $V_D$ = 2.5 V. Cutoff frequencies, $f_T$, were 53 and 100 GHz for the 550-nm and 240-nm devices.

# graphene as absorber in a passively mode-locked laser




Graphene mode-locked fiber laser and mode-locker assembly. ISO, isolator; WDM, wavelength division multiplexer; PC, polarization controller; EDF, erbium-doped fiber.




Mode-locked pulses characteristics. (a) Output spectrum; spectral resolution 0.1 nm. (b) Autocorrelation trace of output pulses; delay resolution 20 fs. (c) Oscilloscope trace. (d) Wideband RF spectrum up to 0.8 GHz.

Sun et al. (Ferrari group), ACS Nano **4,** 803 (2010)

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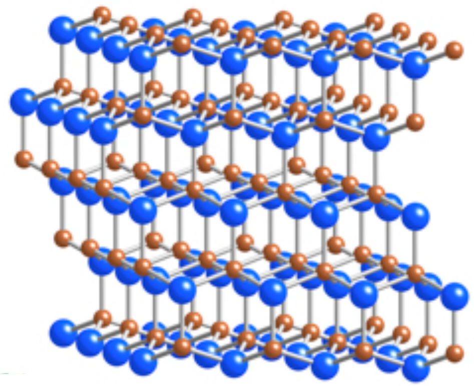
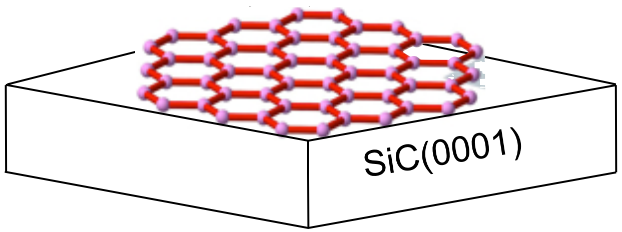
- Conductance fluctuations and field asymmetry of rectification in grap… Today
- Graphene Dirac fermions in one-dimensional inhomogeneous field pr… Today

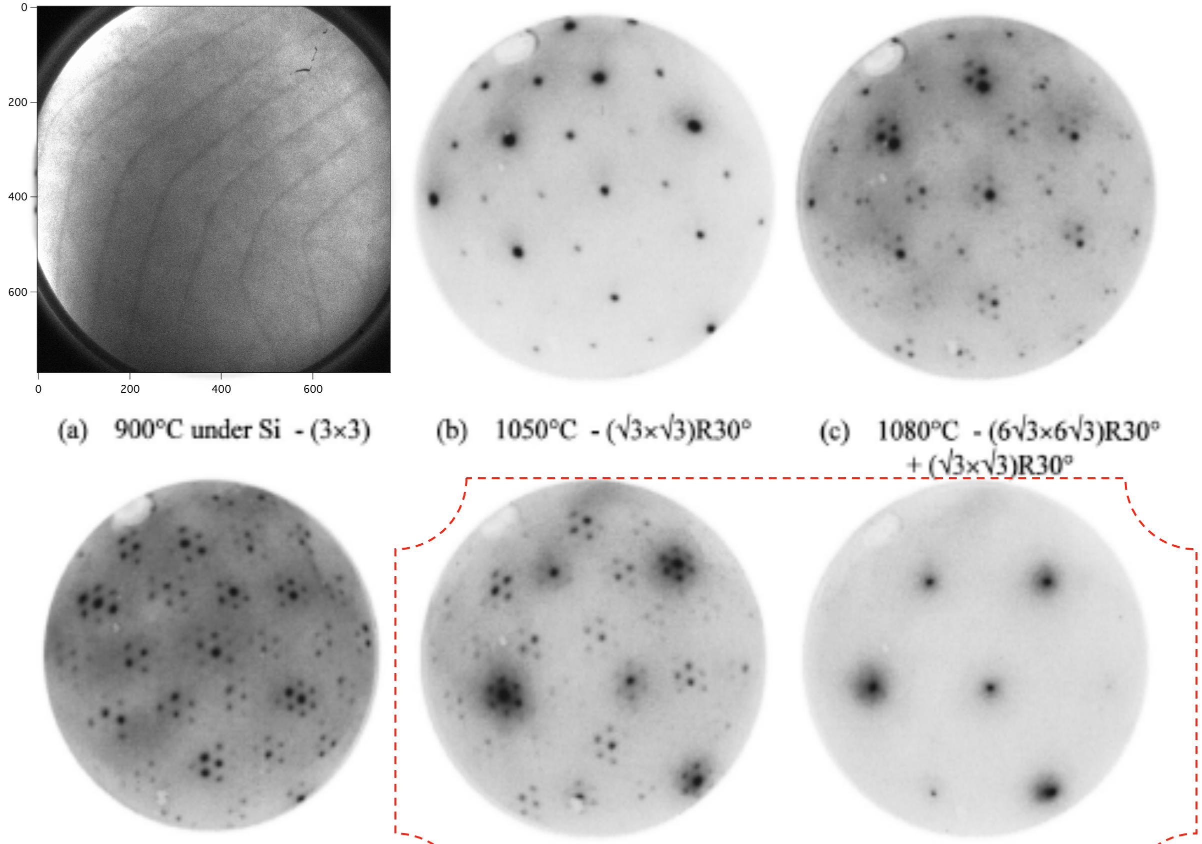
# GrapheneTimes
blog

## preparation of large scale *epitaxial* graphene layers by thermal decomposition from SiC(0001) (silicon face) for basic research (and applications ?)






Real space image, and electron diffraction; LEEM cooperation with Andy Schmid, LBL




(a) 900°C under Si - (3×3) (b) 1050°C - (√3×√3)R30° (c) 1080°C - (6√3×6√3)R30° + (√3×√3)R30°

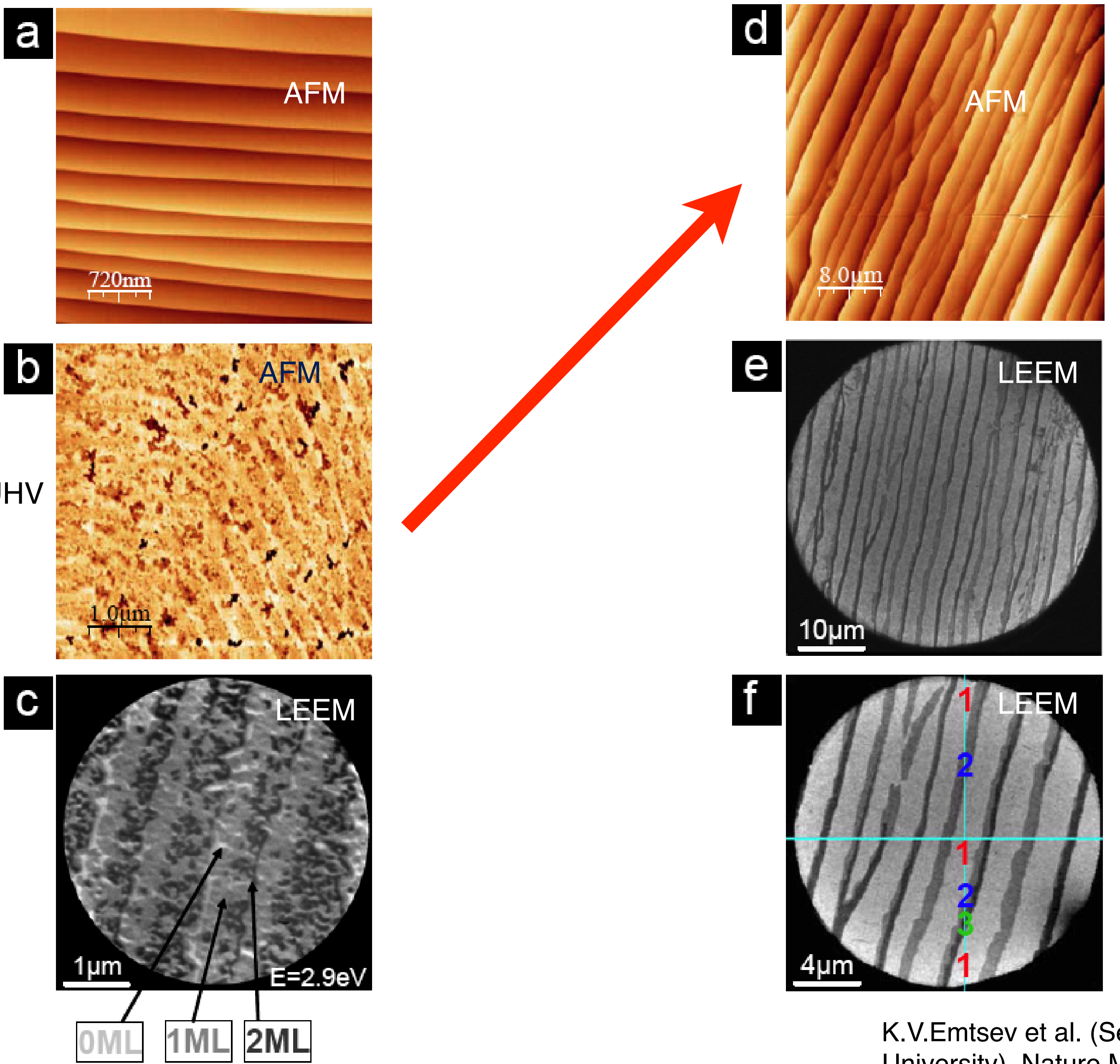
(d) 1150° C - (6√3×6√3)R30° (e) 1250° C - (6√3×6√3)R30° (f) 1400°C - graphite

I.Forbeaux et al., Phys.Rev. B 58, 16396(1998);Th. Seyller et al., Surf.Sci 600,3906 (2006); Th.Seyller et al., Appl. Phys A 85 ,71 (2006); C.Berger et al., Science 312, 1191 (2006) ultrahigh vacuum graphitization

annealed under 900 mbar of argon at 1600 C

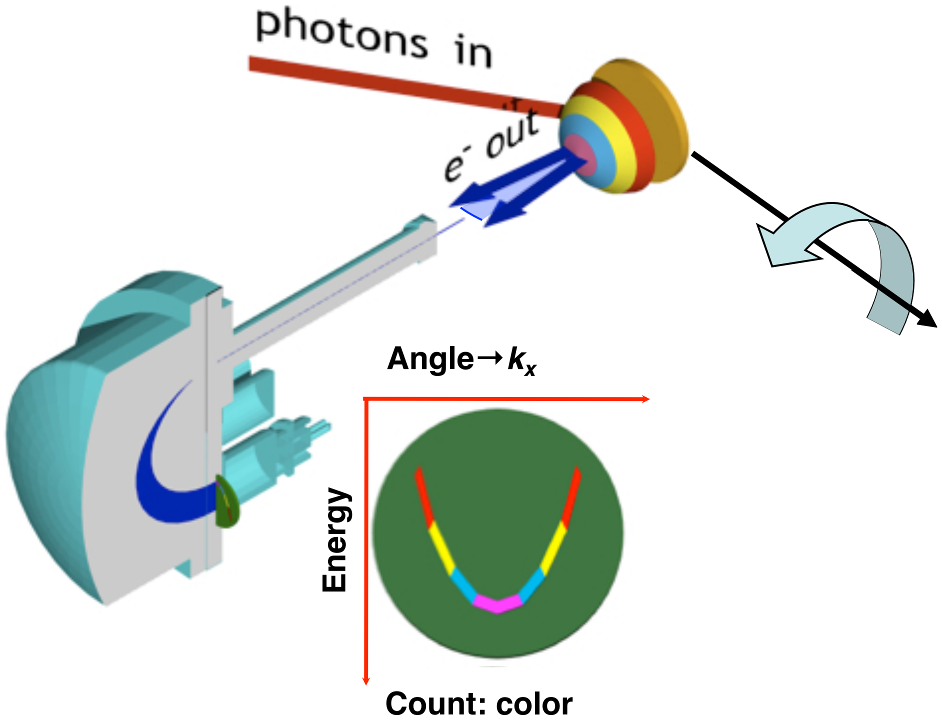
hydrogen
treated SiC

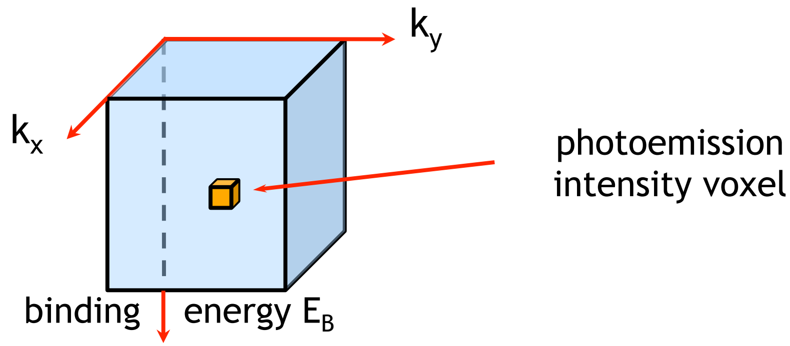
1280° C in UHV
-> graphene

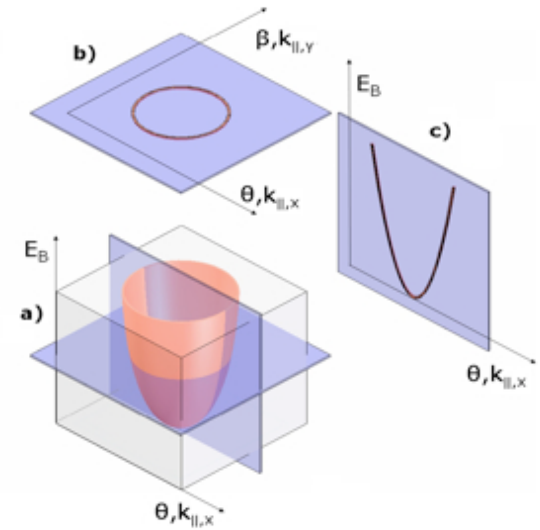


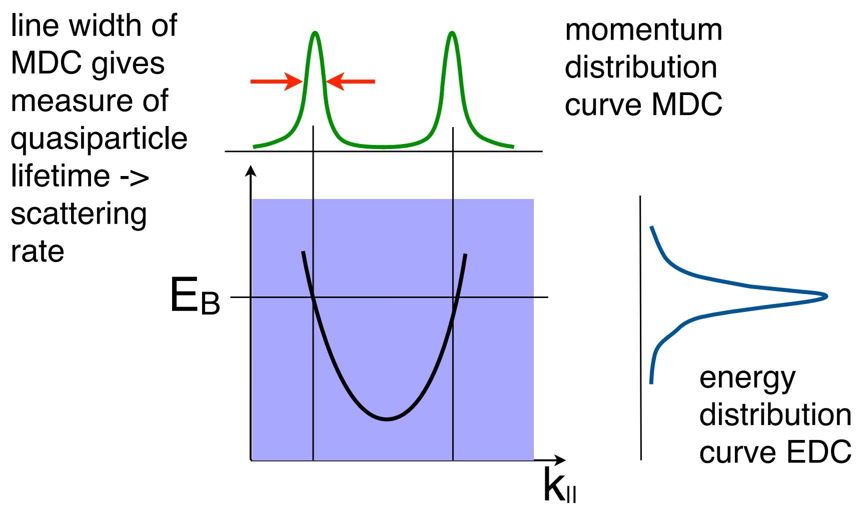

K.V.Emtsev et al. (Seyller group, Erlangen University), Nature Materials 8, 203(2009)

# angle-resolved photoemission to study the electronic structure of graphene



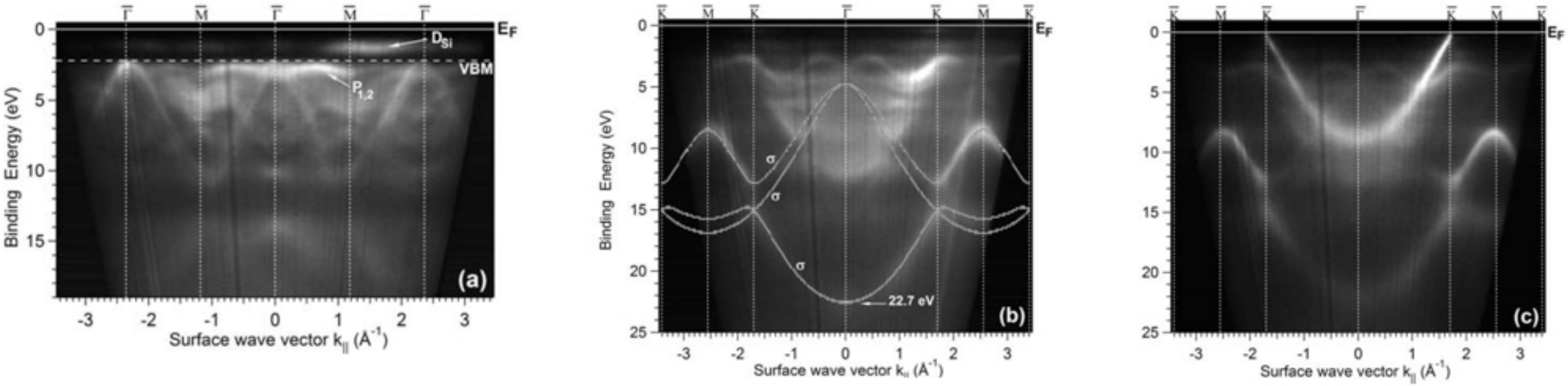



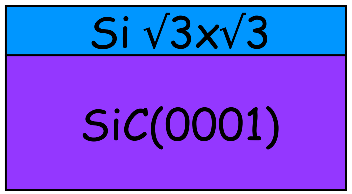



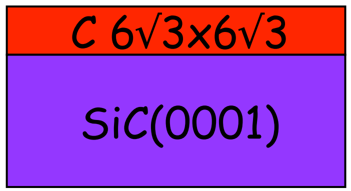



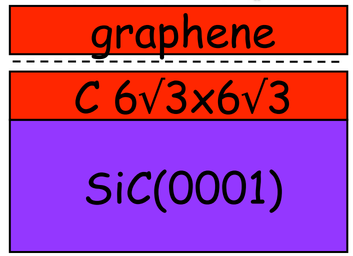

can be used to determine the band structure of a solid from the spectral function based on direct, k-conserving transitions

# From SiC to graphene



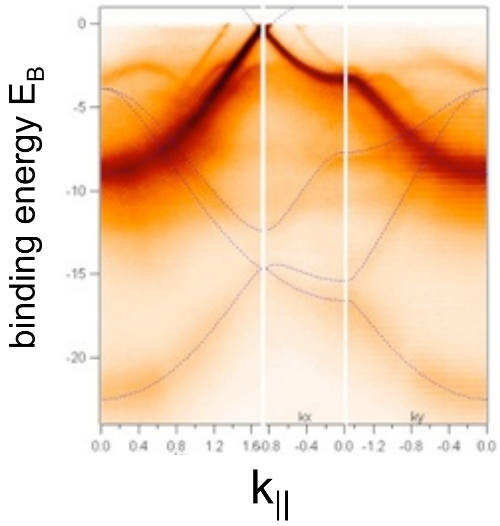

*sp*$^2$-bonded $p_z$ hybridized with SiC; π band not developed

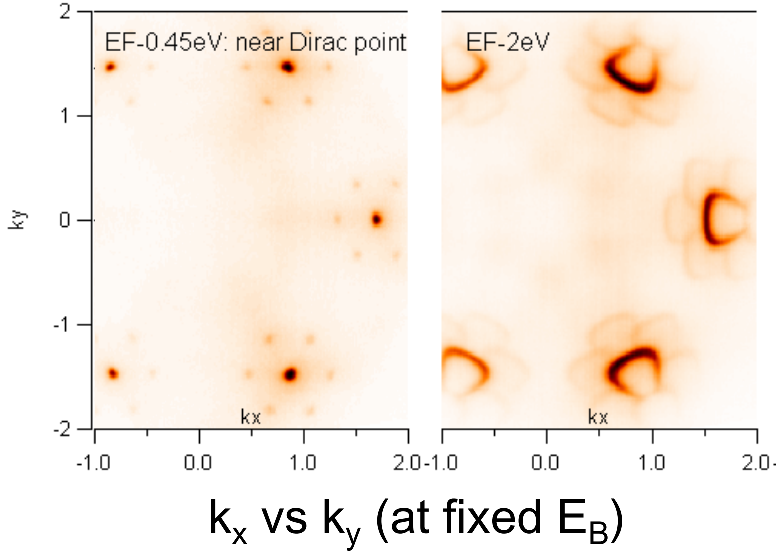
*sp*$^2$-bonded $p_z$ derived band, van der Waals-bonded to 6√3 layer

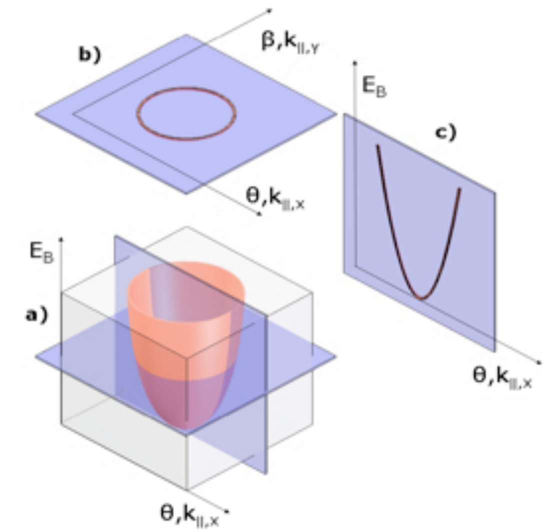
passivating C 6√3x6√3 layer decisive !

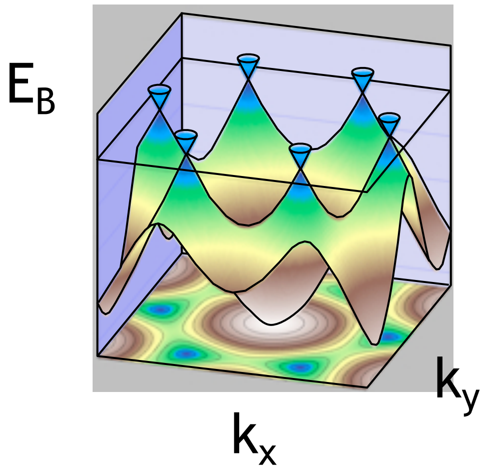
K.V.Emtsev et al., MRS Mat.Sci. Forum 556-557,526 (2007)

# single layer band structure

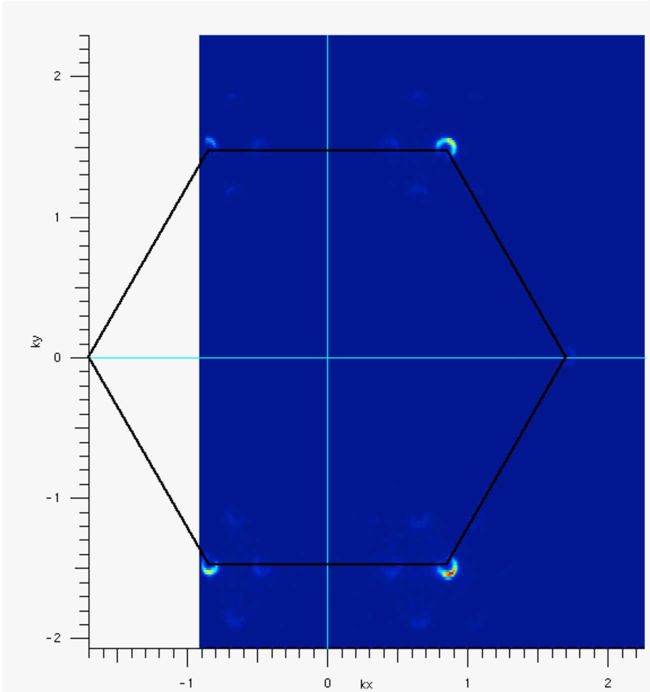


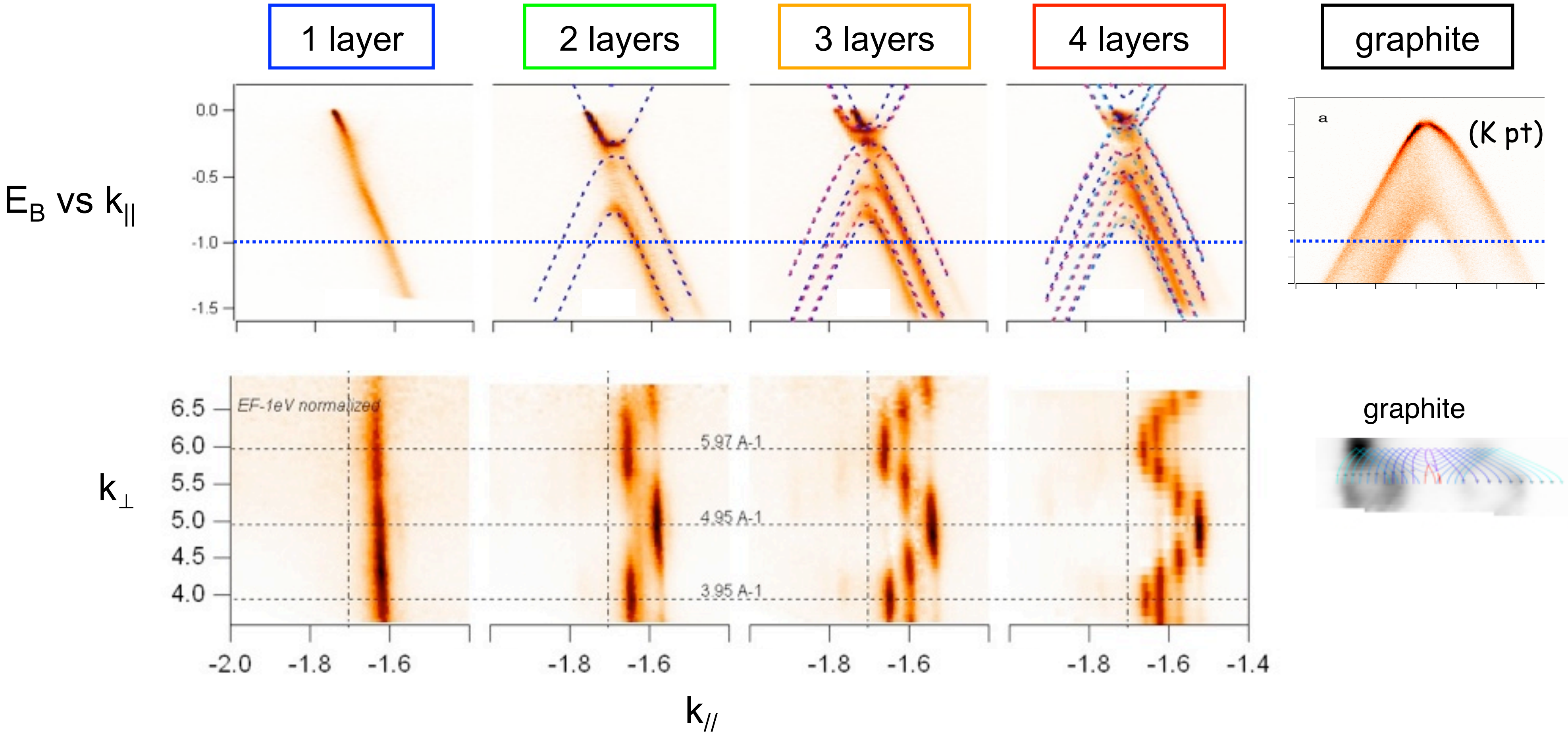




Saito, R., G. Dresselhaus, et al. (1998). *Physical Properties of Carbon Nanotubes*, Imperial College Press.



pure 2D to quasi-2D conversion of films with # of layers by further annealing (Si face)

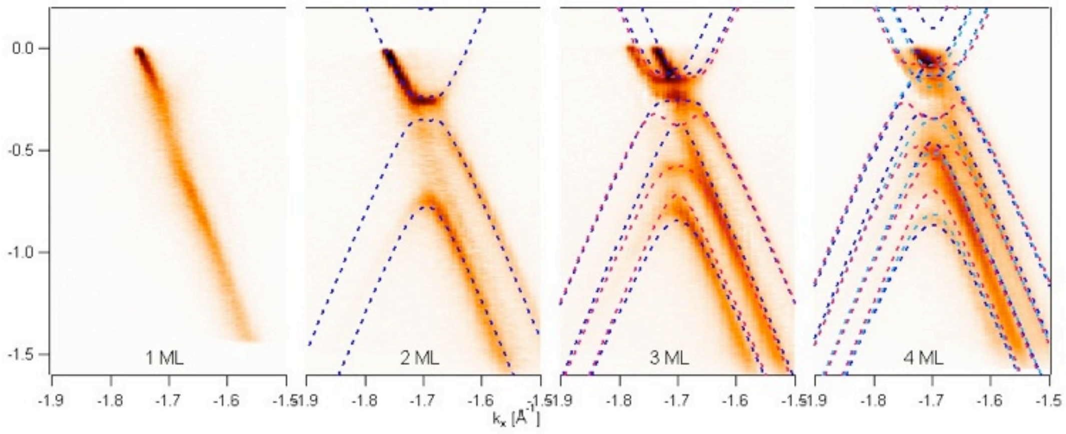



Interlayer interaction changes the nature of wave function from pure-2D (single layer) to quasi-2D (multilayers)

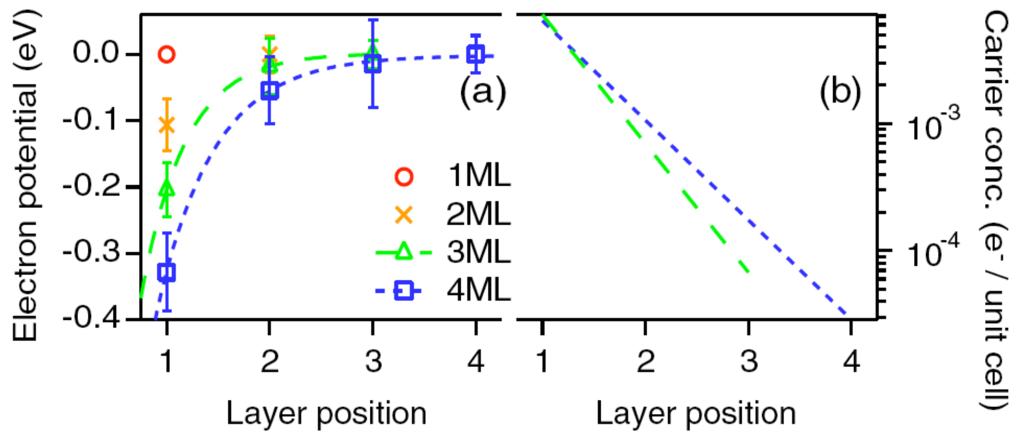
Intensity oscillations with $k_\perp$ correspond to out-of-plane periodicity of graphene layers - analogy to quantum well states

T. Ohta et al., PRL 98, 206802 (2007)

# Quantitative evaluation of band structure




| N | v ($10^6$m/sec) | n | $E_D$ | $E_1$ | $E_2$ | $E_3$ | $E_4$ | $\gamma_1$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 1.1 | 7.4 | -0.44 | -0.44 | | | | |
| 2 | 1.05 | 8.2 | -0.30 | -0.36 | -0.24 | | | 0.48 |
| 3 | 1.02 | 8.6 | -0.21 | -0.31 | -0.17 | -0.15 | | 0.48 |
| 4 | 1.02 | 7.4 | -0.15 | -0.27 | -0.13 | -0.13 | -0.10 | 0.45 |
| inf | 0.91 | | | | | | | 0.35 |

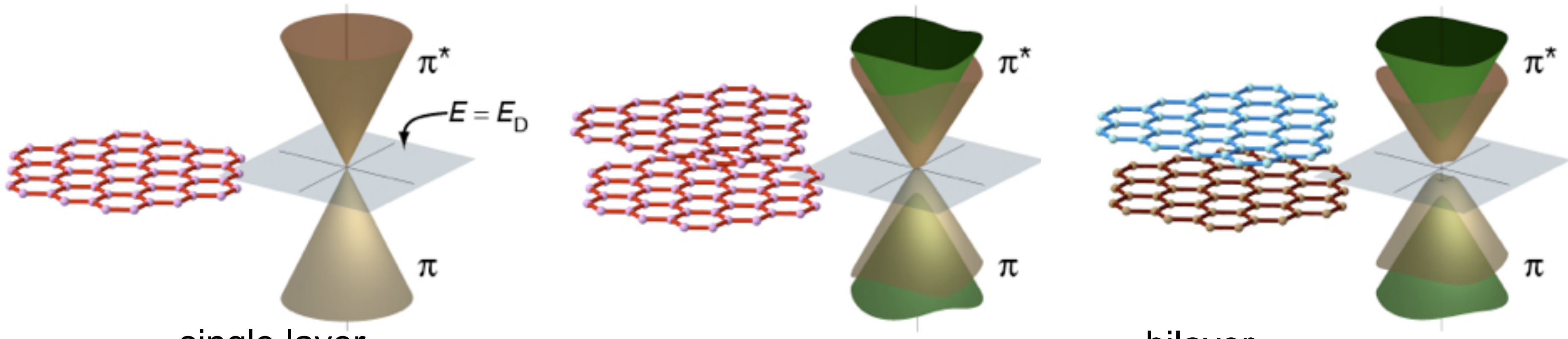



- $E_i$ on-site Coulomb energy
- v Fermi velocity
- $\gamma$ interlayer hopping integral
- n charge density in $10^3$ electron per 2D unit cell

Tight binding band parameters to reproduce measured band structure for N= 1 - 4 layers of graphene and graphite (N inf).

T. Ohta et al., PRL 98, 206802 (2007)

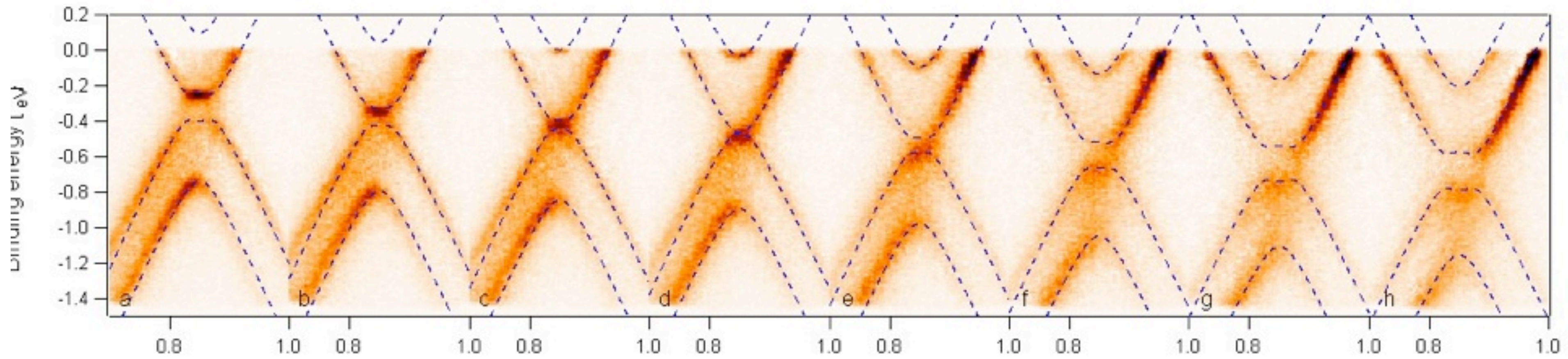
# Bilayer graphene - control of the $\pi$ - $\pi^*$ gap by doping




single layer

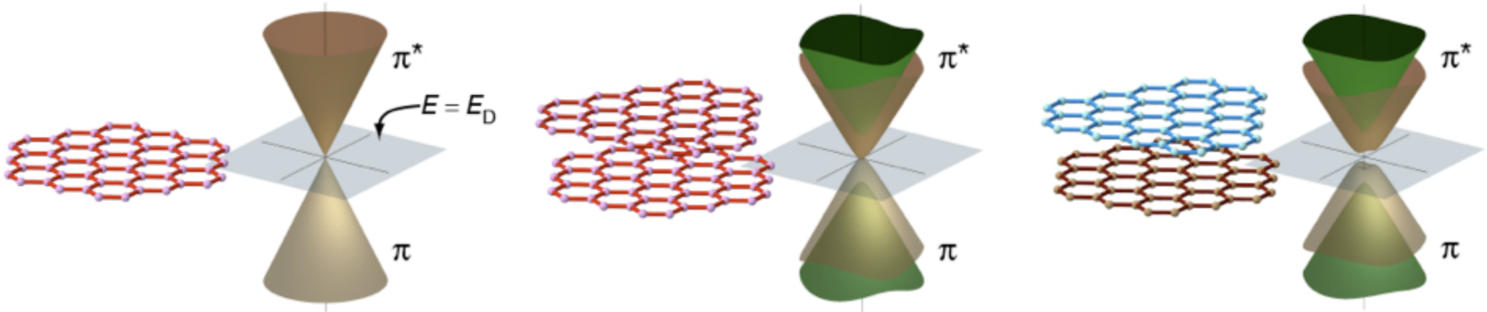
bilayer

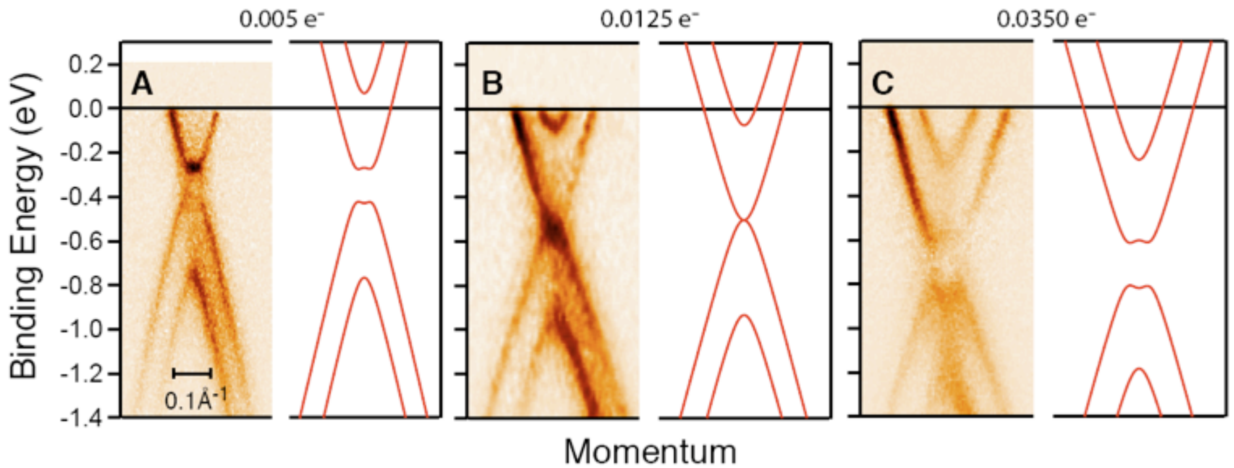
• variation of carrier concentration - electron doping by deposition of potassium

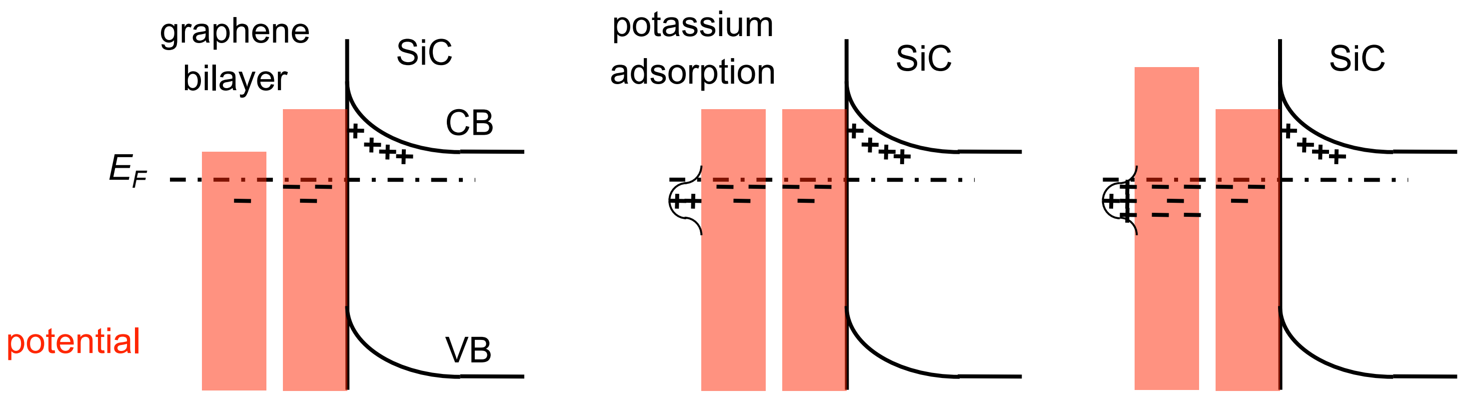



T.Ohta et al., Science **313** 951 (2006)

# The bilayer: closing and re-opening of the π - π* gap by doping




Non-equal charge distribution due to short interlayer screening length

adapted from T. Ohta et al., Science 313, 951 (2006).

## Other roads towards Dirac-Fermion charge carriers: multilayers of graphene on Sic(000-1) carbon face - behave like stacked single layers

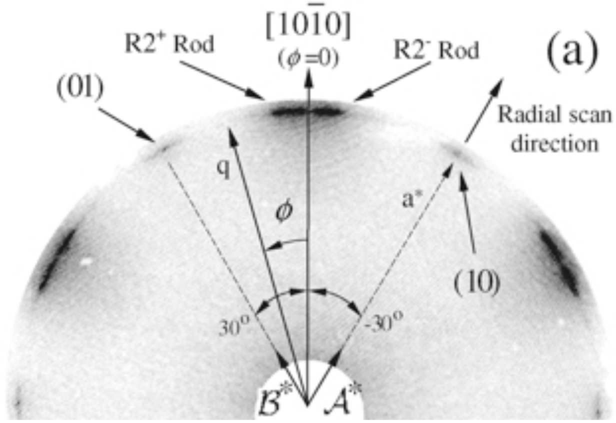
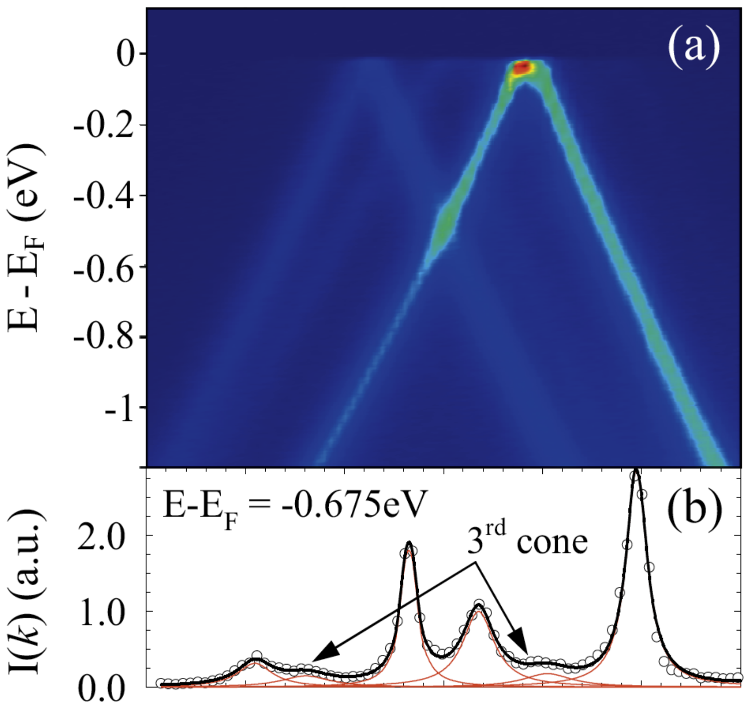



FIG. 1. (a) LEED image acquired at 67.9 eV from 4*H*-SiC0001  with 10 graphene layers

graphene on C-face: multilayers decoupled by rotational in specific angles exhibit electronic structure and transport as single layer graphene

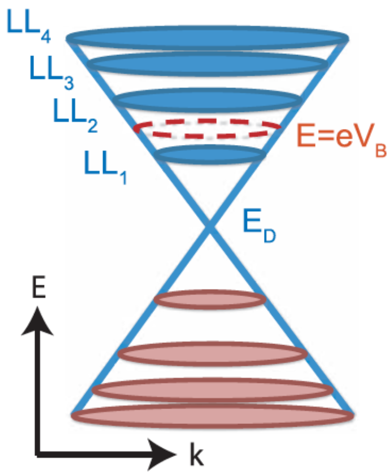
Hass et al., PRL **100,** 125504 (2008)



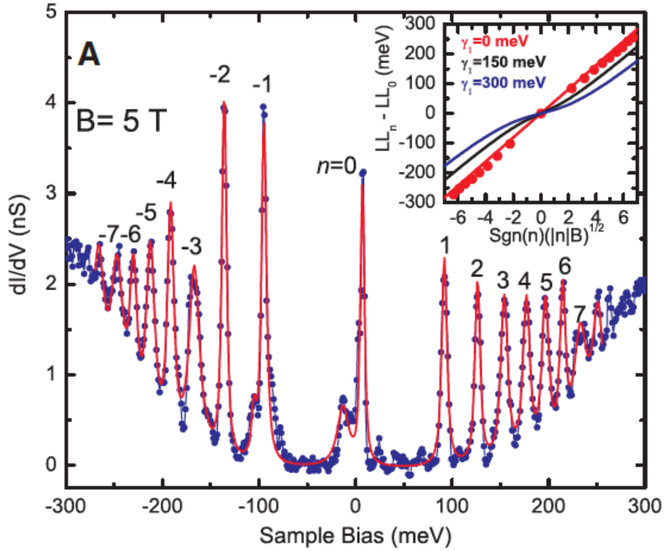

ARPES band structure of an ~11-layer C-face graphene film grown on 6H-SiC.

M. Sprinkle, P. Soukiassian, W. A. de Heer, C. Berger, and E. H. Conrad *Epitaxial graphene: the material for graphene electronics*   phys. stat sol. RRL, 1–3 (2009)

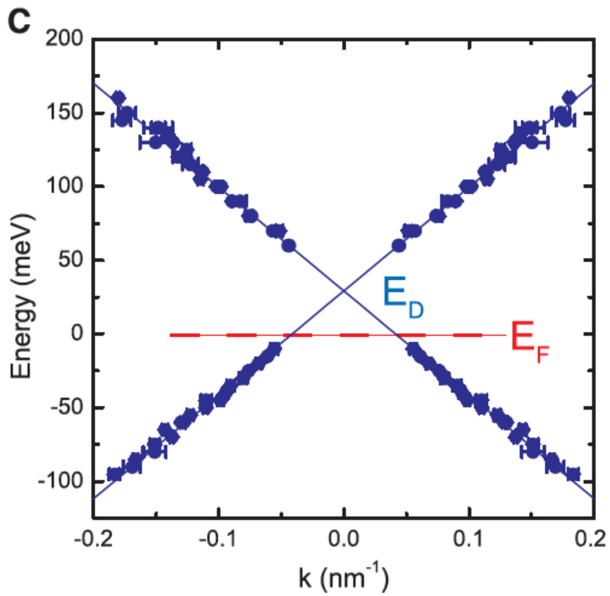
# tunneling magneto-conductance oscillations (TMCOs) in epitaxial graphene




schematic diagram of graphene band dispersion and Landau levels in magnetic field



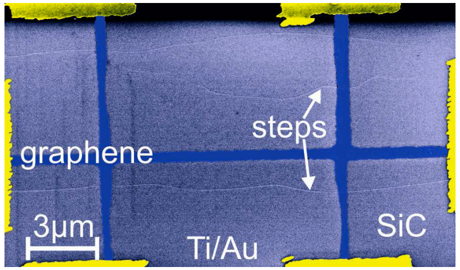

on SiC(000-1), carbon face



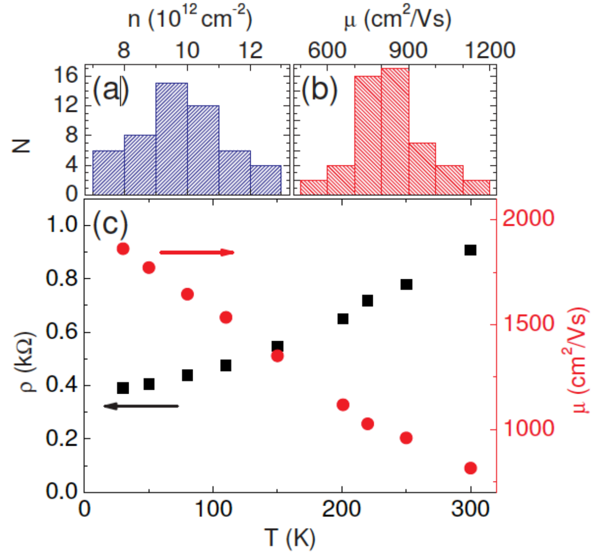

*Observing the Quantization of Zero Mass Carriers in Graphene*
Miller et al., Science 324, 924(2009)

mapping of graphene bands from TMCOs

# QHE effect observed in epitaxial graphene on SiC(0001)

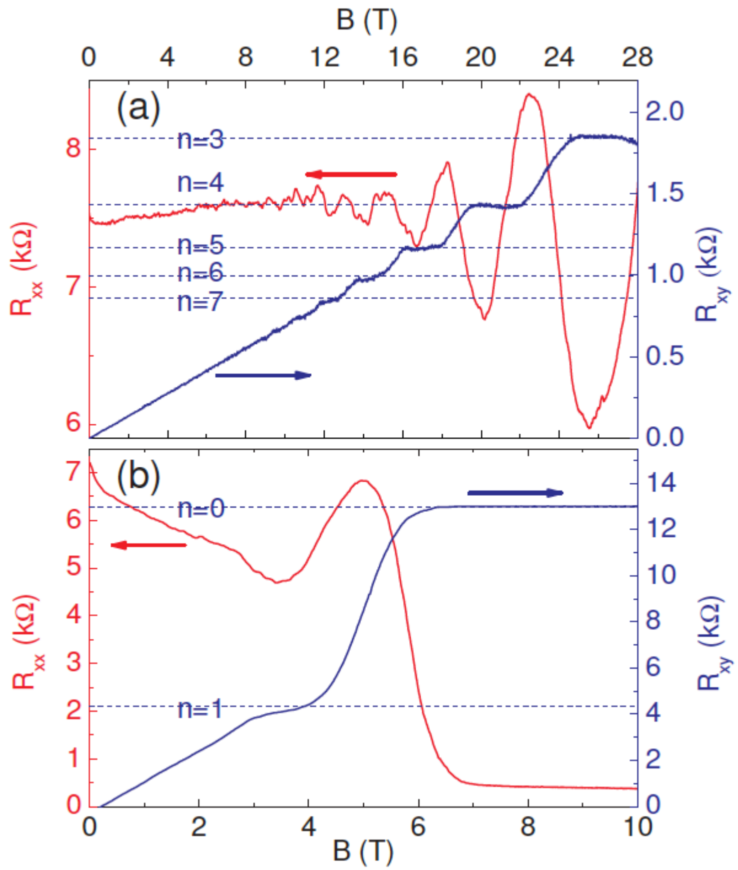



AFM of single layer Hall bar




mobility at RT and charge density for range of samples

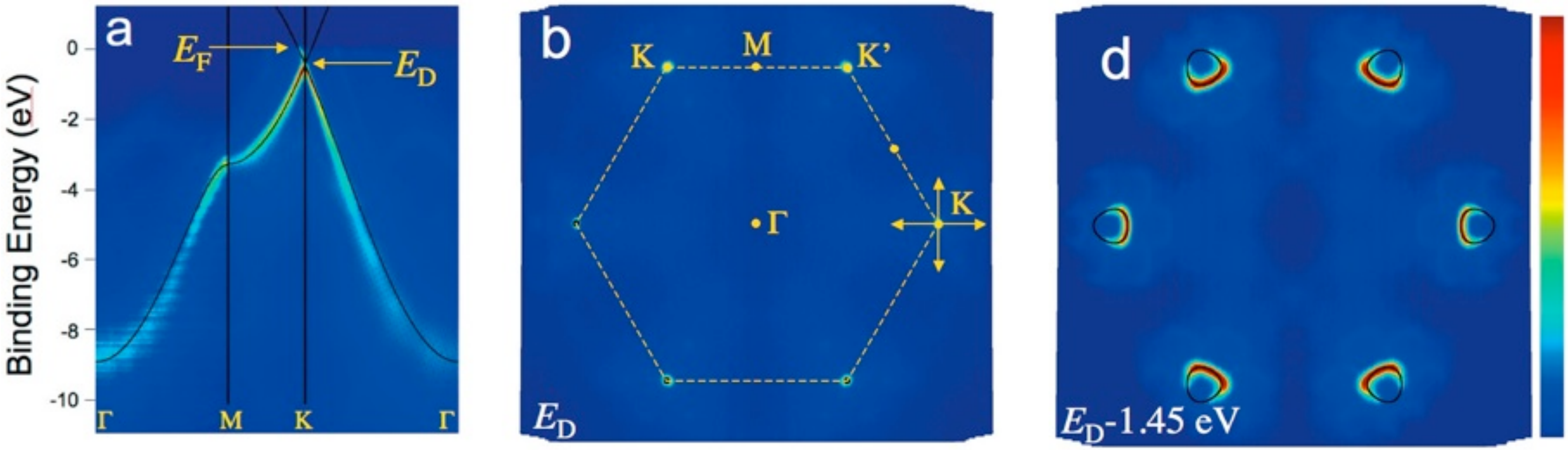
μ ~29.000 at 25 K

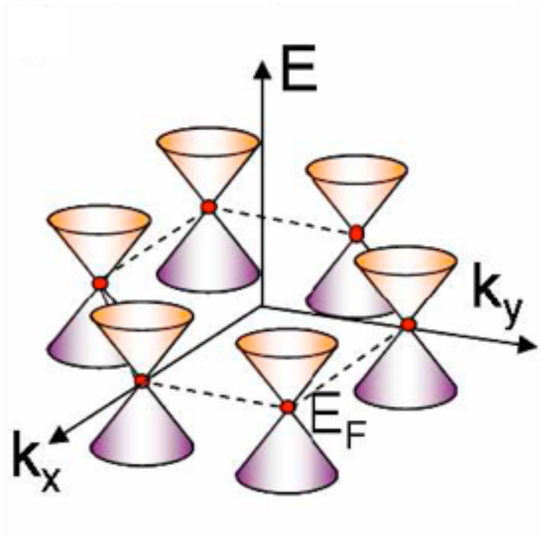


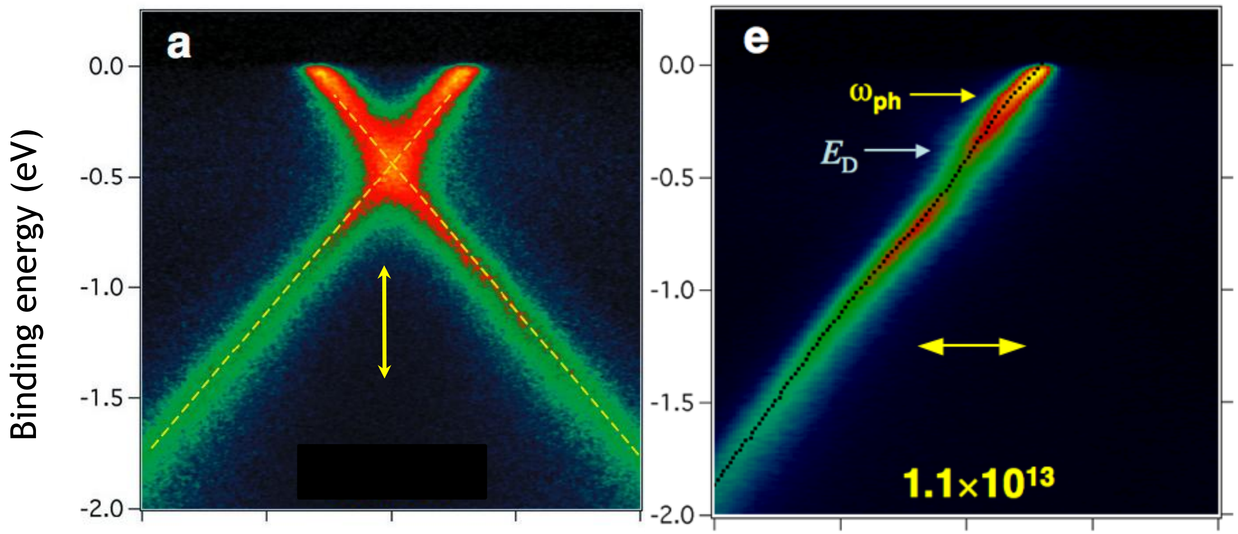

QHE oscillations in epitaxial graphene

*Quantum oscillations and quantum Hall effect in epitaxial graphene* Jobst et al., (Seyller group), Phys.Rev. B 81, 195434 (2010)

# band structure of single layer graphene on 6H-SiC(0001)



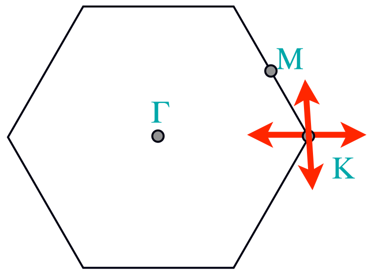



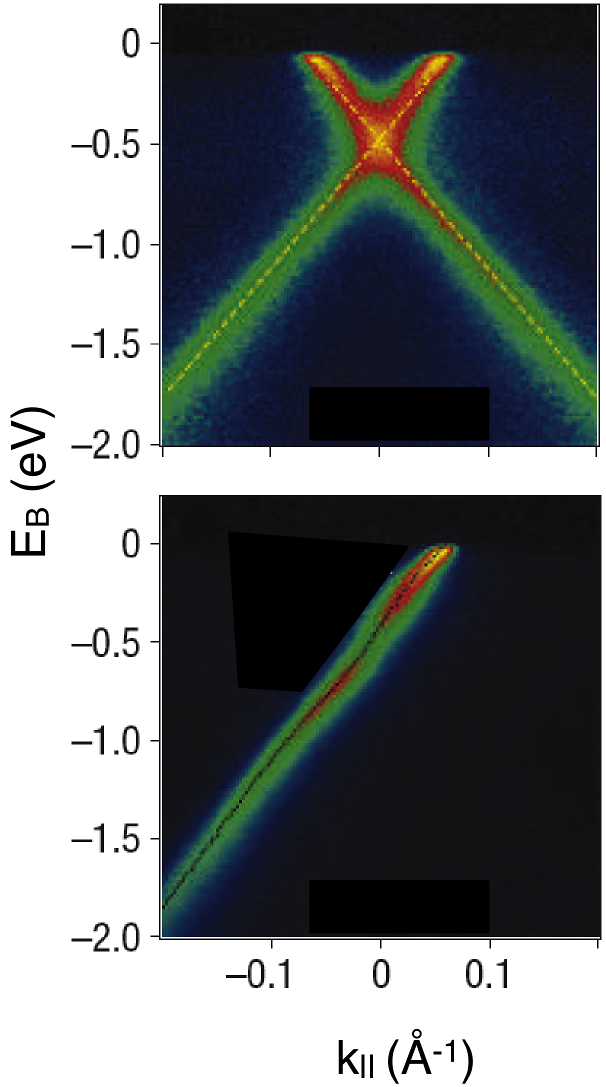



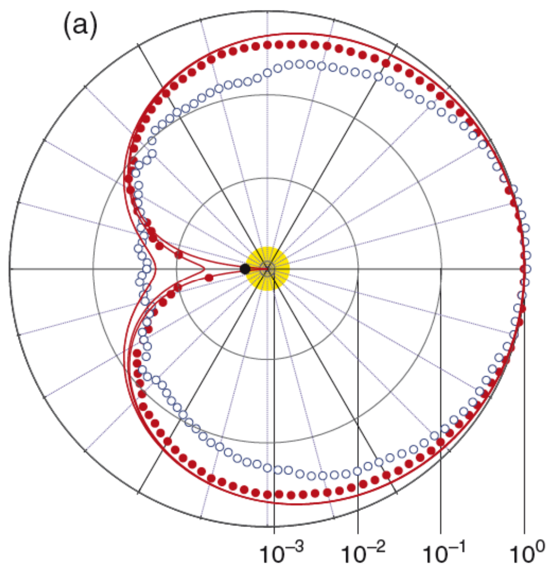

A.Bostwick et al., Nature Physics **3**, 36 (2007)

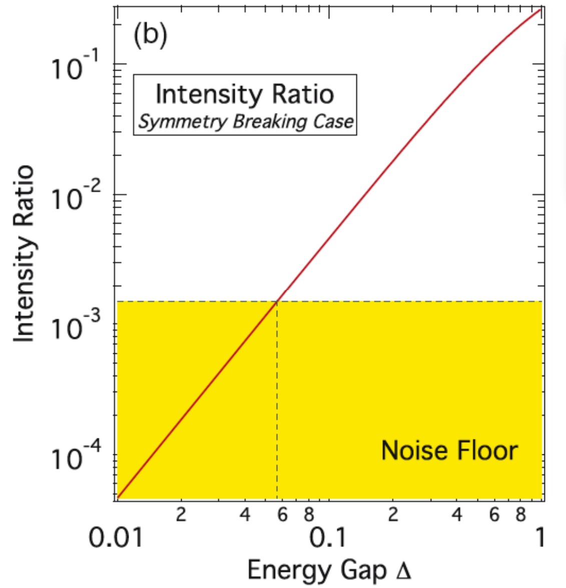
$k_{||}$

# quantitative analysis of symmetry breaking



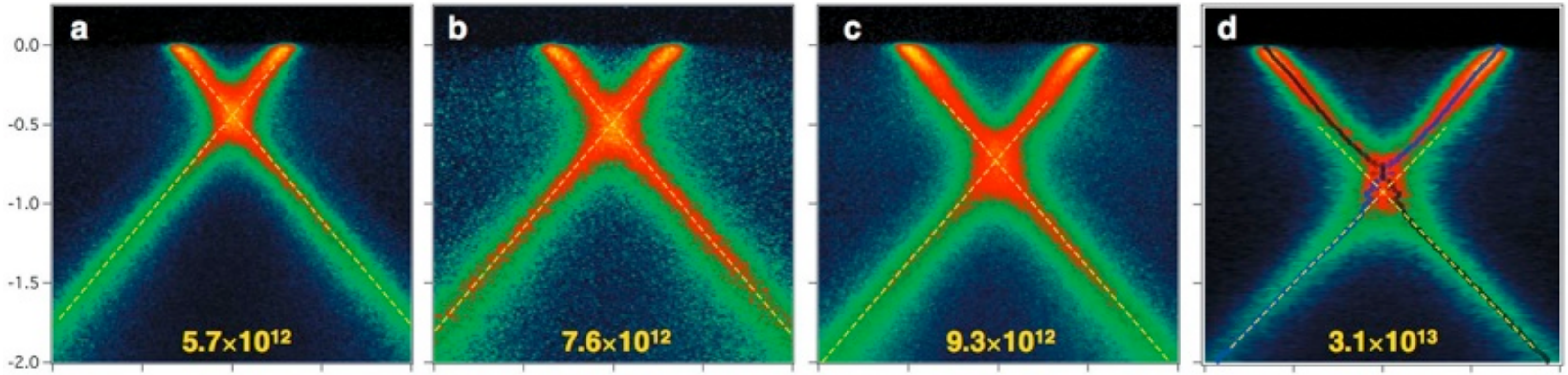



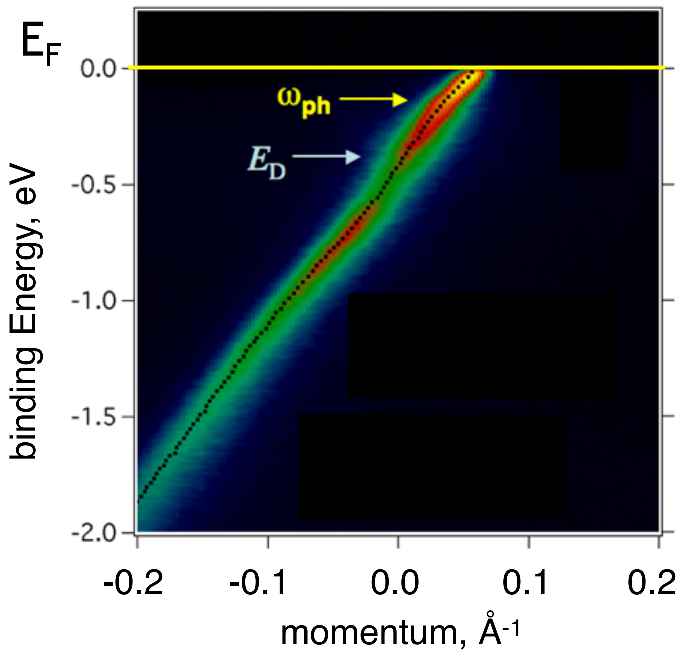




A.Bostwick et al., “Symmetry breaking in few layer graphene films”, New J Phys **9**, 385(2007)

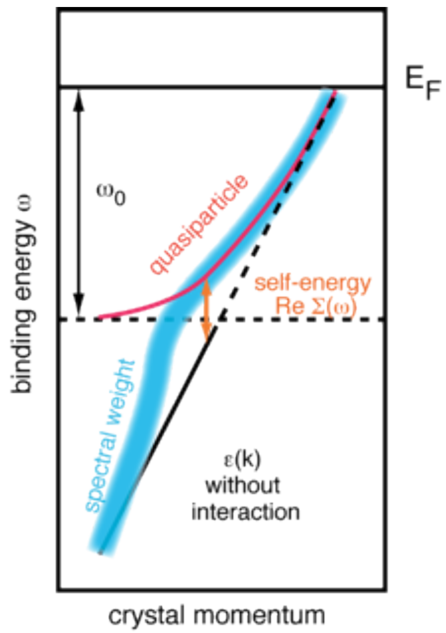
# A closer look at the Dirac point and $E_F$ : many-body effects

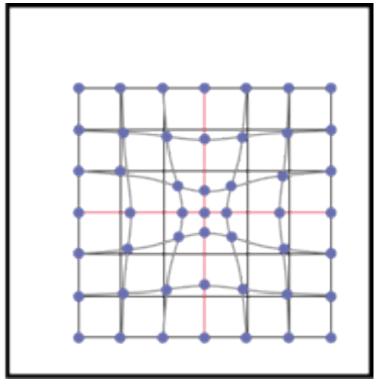



Clear deviations from the linear dispersion; enhanced by doping




Bostwick et al, Nature Physics 3, 30 (2007)

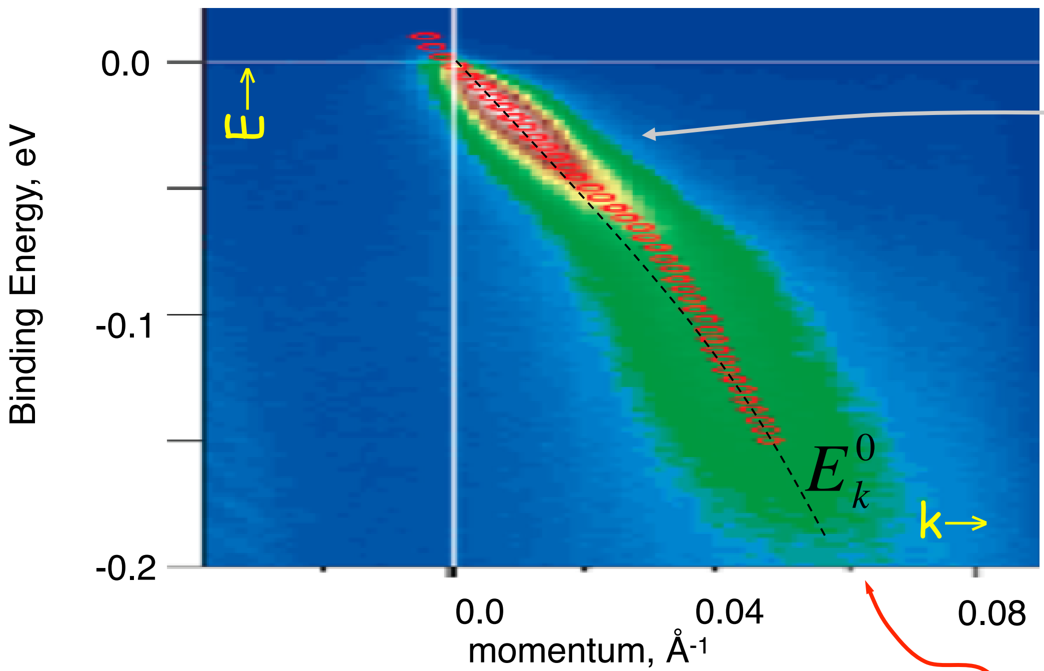


from J.Schaefer, Appl. Phys. 80 (2005)

"Dressing" of the (hypothetical) bare band by many body excitations

## Many body effects and photoemission - “kinkology”




BSCCO Superconductor Results [1]

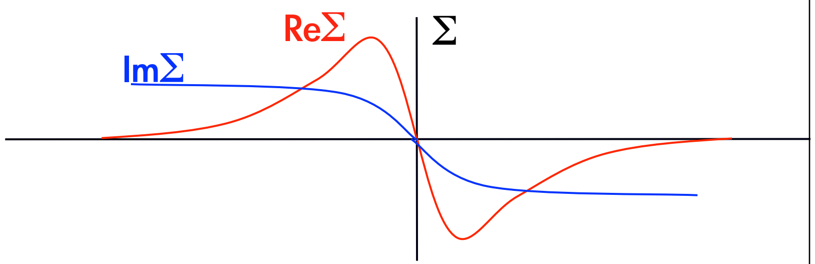
Kinks are due to many-body interactions, not details of the single-particle bandstructure $E^0_k$

use line width in momentum distribution curve to derive lifetime, i.e. Im $\Sigma$

what is measured - spectral function A(k,E)

$$A(k,E) = \frac{1}{\pi} \frac{\mathrm{Im}\Sigma(k,E)}{\left[E - E^0_k - \mathrm{Re}\Sigma(k,E)\right]^2 + \left[\mathrm{Im}\Sigma(k,E)\right]^2}$$

Single particle band




$$\Sigma(k,E) = \mathrm{Re}\,\Sigma(k,E) + i\,\mathrm{Im}\,\Sigma(k,E)$$

energy shift

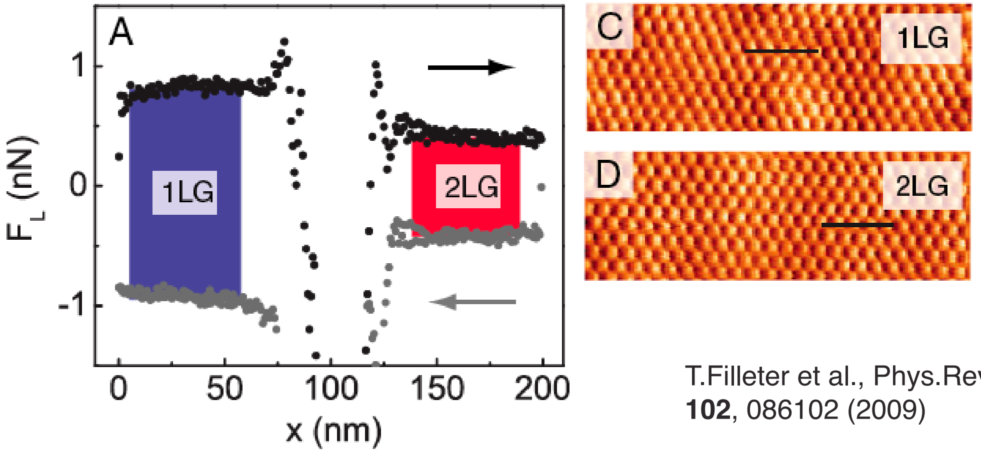
lifetime broadening

$\Sigma$ self energy


[1] Koralek et al, Phys. Rev. Lett. 96, 017005 (2006)

see also A.Kaminski et al., PRL **86**, 1070 (2001), and New.J.Phys. **6**, 98 (2004)

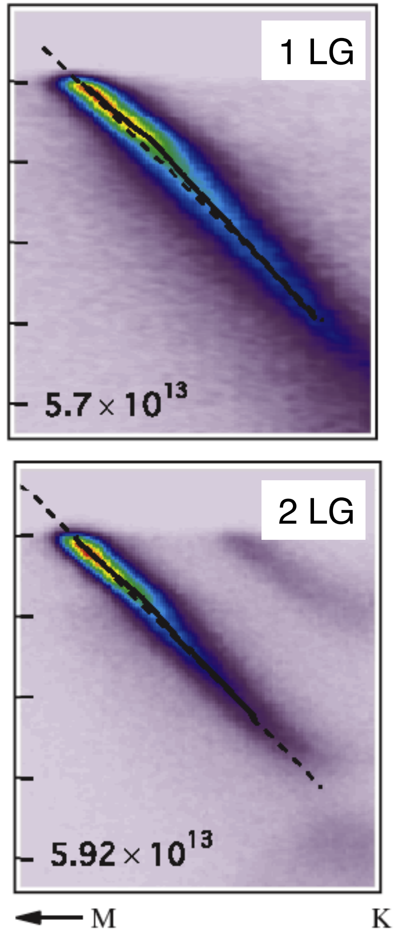
# Apply analysis of many-body effects in photoemission: friction in single and bilayer graphene through AFM

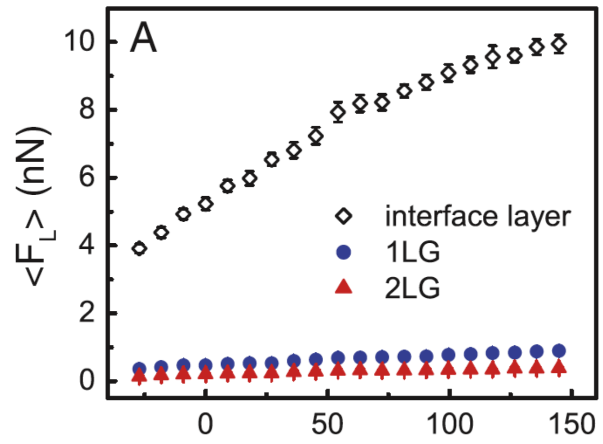



T.Filleter et al., Phys.Rev.Lett **102**, 086102 (2009)

Friction loop recorded on a boundary region of the sample with adjacent areas of single (1LG) and bilayer (2LG) films

spectral function for single and bilayer graphene (doped)

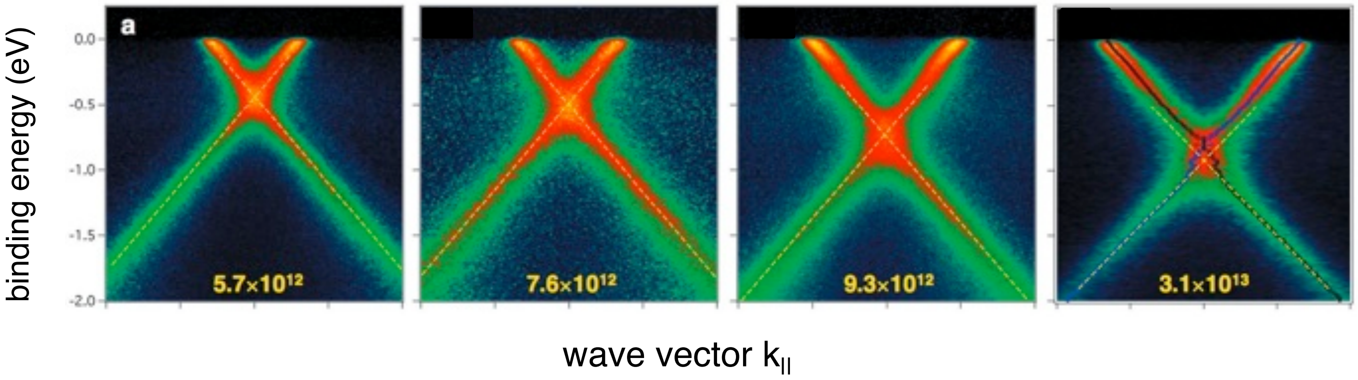


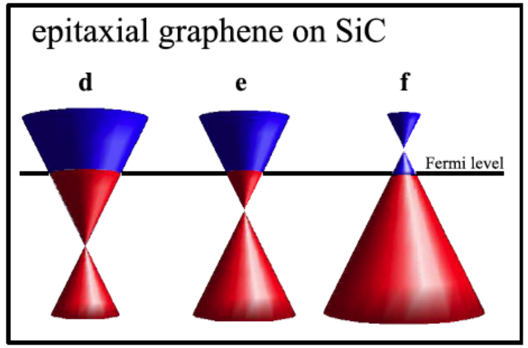

Average lateral force as a function of normal force simultaneously recorded on the carbon rich interface layer, single (1LG), and bilayer (2LG) graphene.

Friction on SiC is greatly reduced by a single layer of graphene and reduced by another factor of 2 on bilayer graphene. Friction contrast between single and bilayer graphene arises from a large difference in electron-phonon coupling

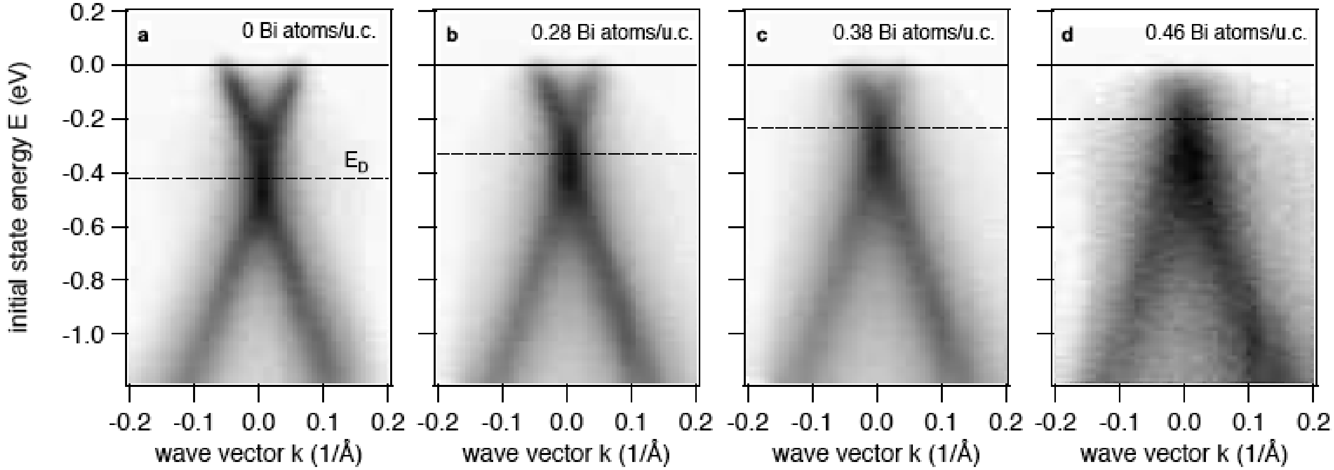
# Change electronic properties by n- and p doping in epitaxial graphene on SiC(0001)




Alkali metal doping



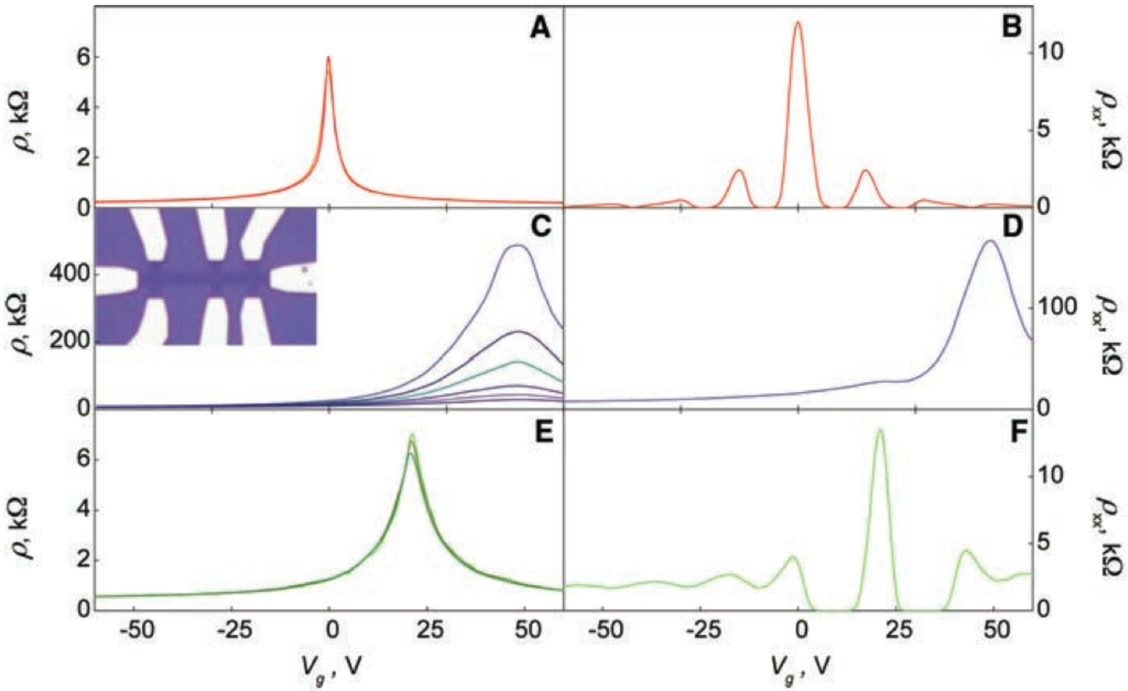

Bostwick et al., Nature Physics **3**, 36(2007)




Gierz et al., Nano Letters **8**, 4603 (2008)

hole doping also possible with $NO_2$, Sb, Au…

# “functionalizing” graphene... ⇨ graphane




pristine

hydrogen plasma treated

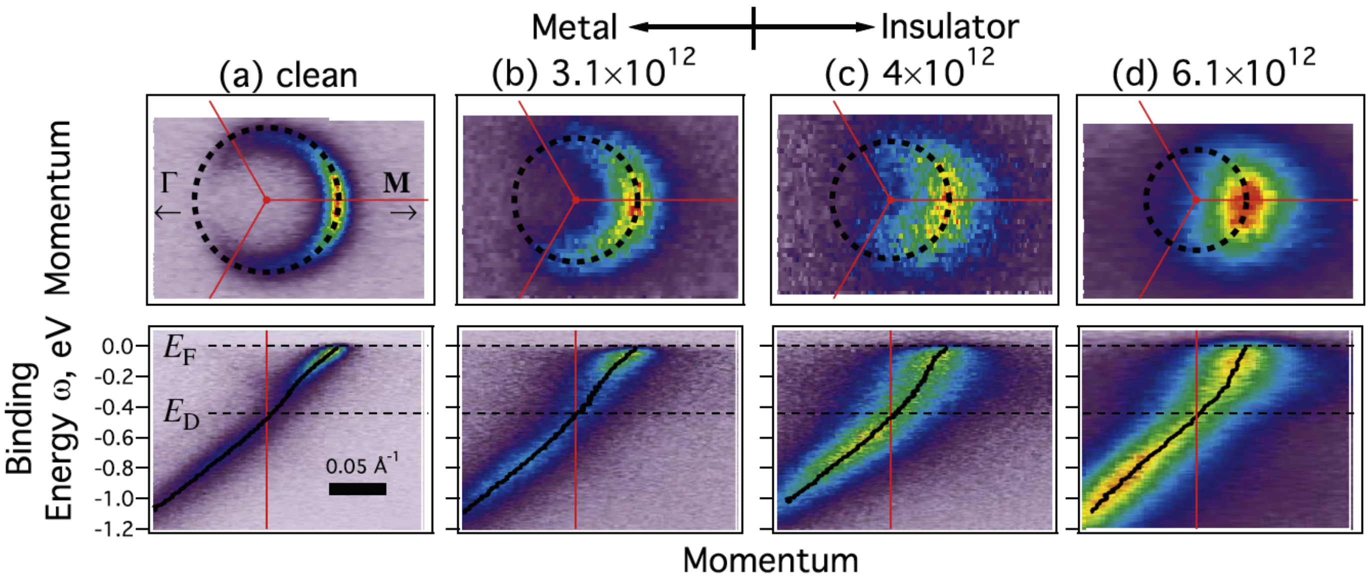
annealed, clean

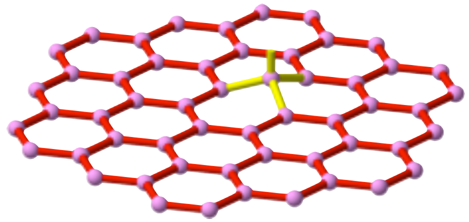
resistance quantum Hall effect

*Control of Graphene’s Properties by Reversible Hydrogenation: Evidence for Graphane*
D. C. Elias et al., Science 323, 610(2009)

Coverage? Structure? Defects?

# exposing graphene to low atomic hydrogen



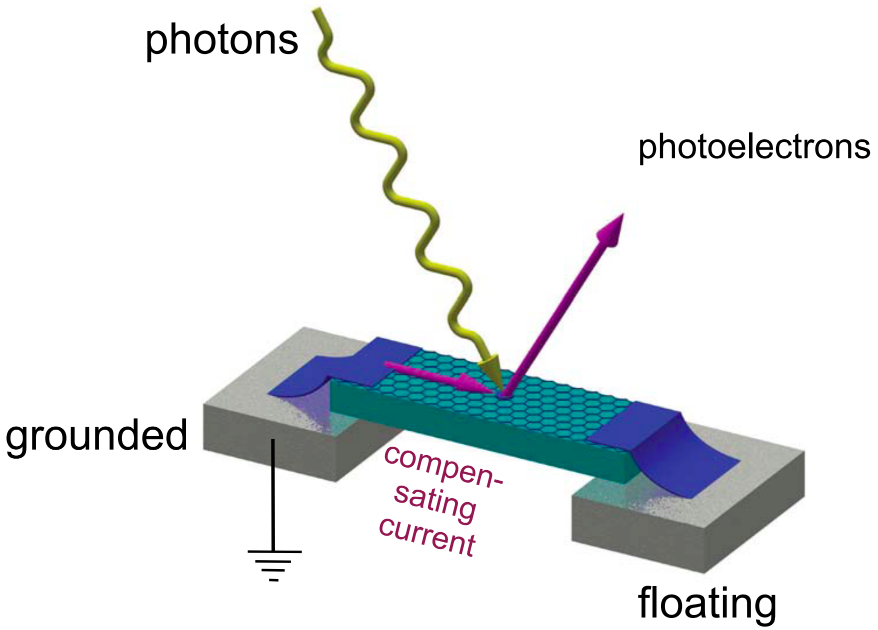
atomic hydrogen saturates the carbon atom π bond - probe the effect on the remaining π electrons

Fermi surfaces and associated band structure cuts through the graphene K point for (a) clean, and (b)–(d) as a function of $n_H$ indicated in H atoms per $cm^2$.

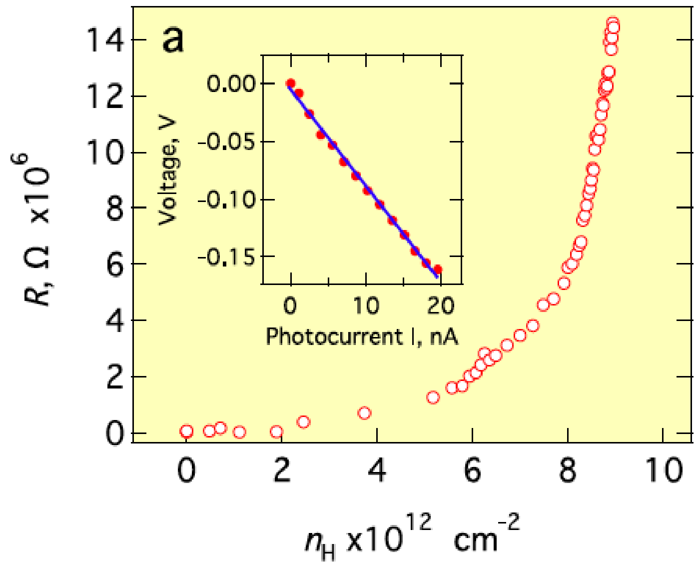
adsorption of **0.5 % of a monolayer** (!) H atoms induces strong changes in spectral function and sample resistance

Aaron Bostwick et al., PRL **103**, 056404 (2009)

# Combine photoemission and conductivity by contactless "four point probe" experiment




Voltage drop across sample causes distance-dependent shift of reference level



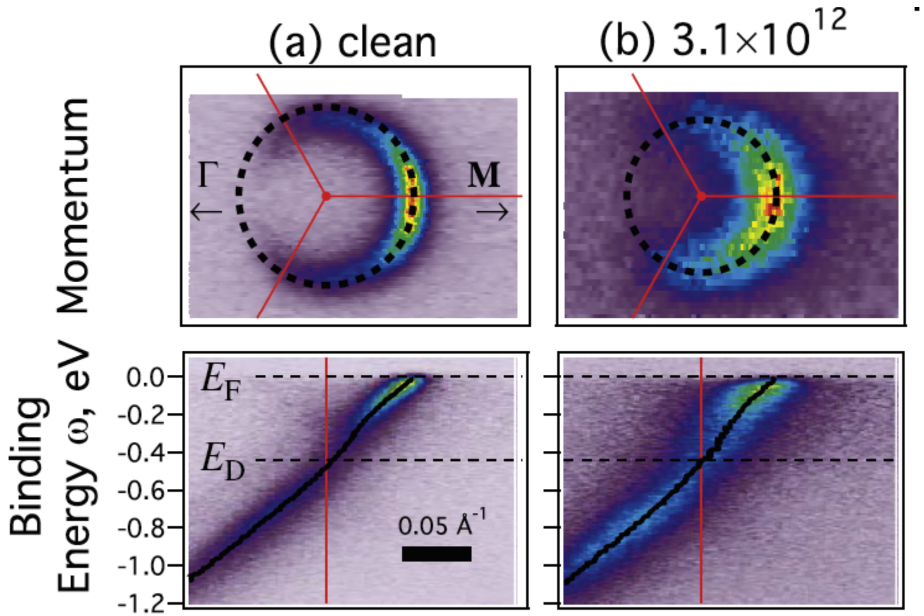

compensating current (red arrow) for emitted photoelectrons induces *spectrum shift* for resistances larger than 0.2 MΩ

(atomic) hydrogen adsorption induces metal-insulator transition in graphene

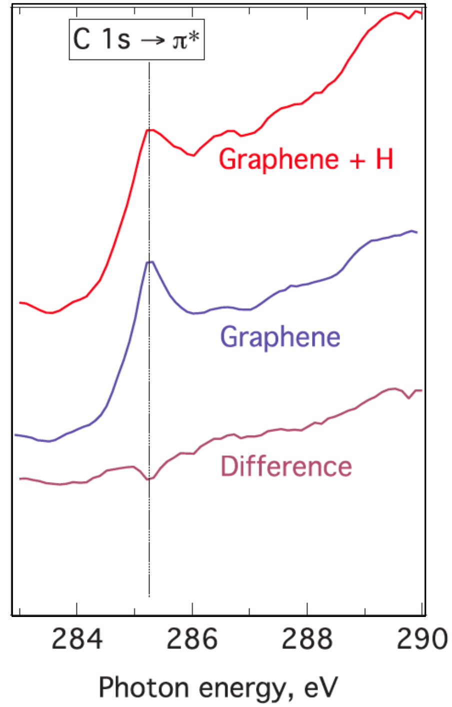
(this is **not** graph**a**ne)

# determination of hydrogen coverage

hydrogen coverage from doping level n.



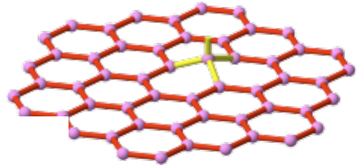

From carbon 1s NEXAFS

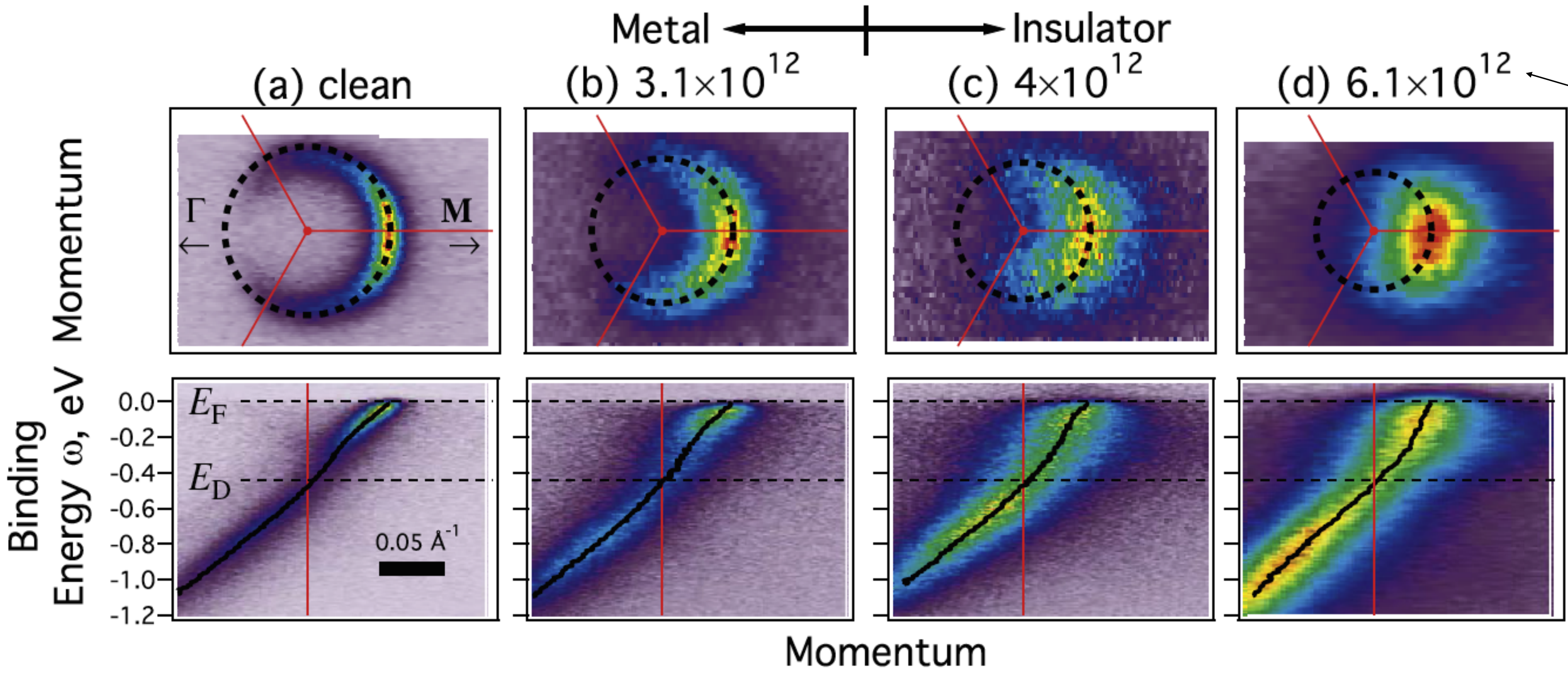



- circular Fermi surface -> surface area in k-space is $F = 2\pi k_F^2$
- Brillouin zone area B = 7.5 $Å^{-2}$ -> total charge per Brillouin zone Q=2F/B.
- real space: unit cell area A = 5.24 $Å^2$ -> charge density is n = Q/A
- clean samples: $k_F$ = 0.06 $Å^{-1}$ -> initial charge density $n_0$ = 1.15 x$10^{13}$ e/$cm^2$
- assume that each adsorbed H atom removes p = 1 electron from the graphene Fermi surface

Peak at the C1s → π* transition reflects the conversion of $sp^2$ to $sp^3$-coordinated carbon bonding.

## atomic hydrogen strongly modifies graphene spectral function





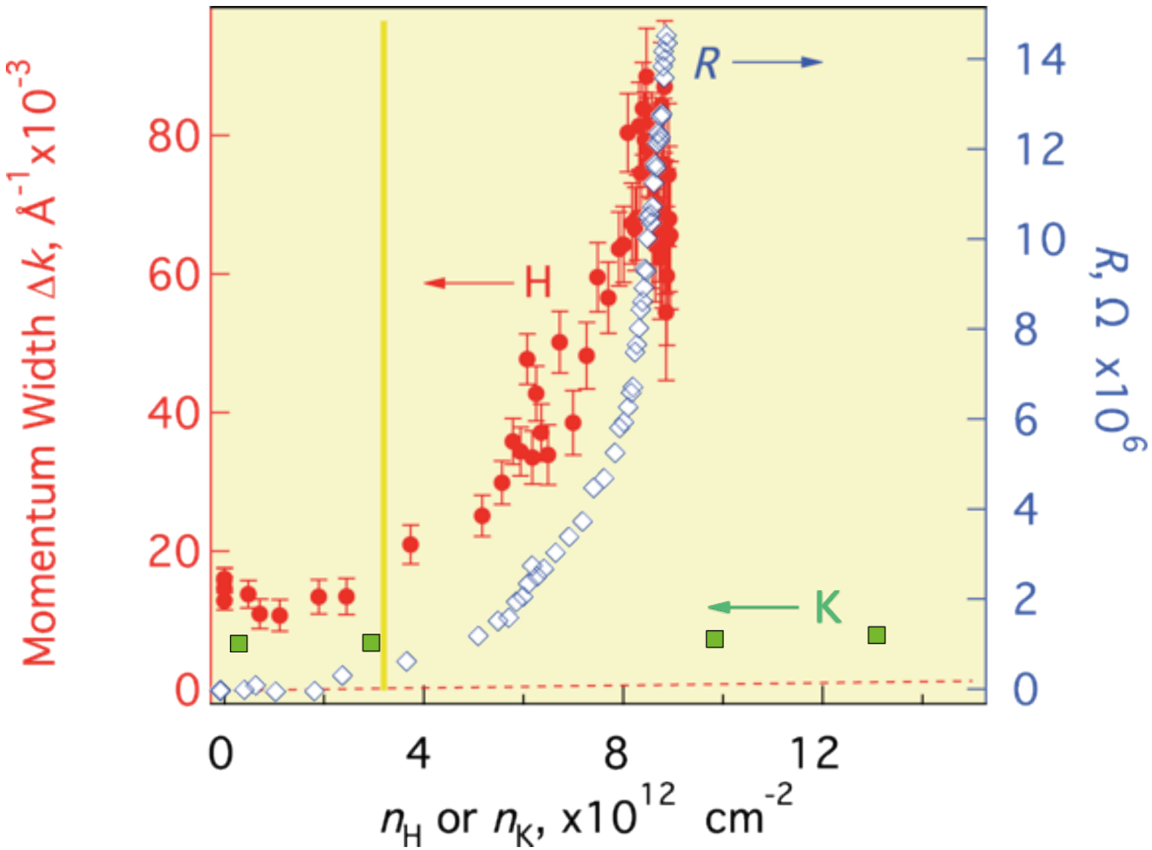

~0.5 % (!) of a monolayer

Fermi surfaces and associated band structure cuts through the graphene K point for (a) clean, and (b)–(d) as a function of $n_H$ indicated in H atoms per cm².

- Fermi surface exists at all coverages, gets smeared out -> no ordinary band insulator
- band shape changes
- scattering increases at $E_F$, **quasiparticle picture breaks down**

Bostwick et al., PRL **103**, 056404 (2009)

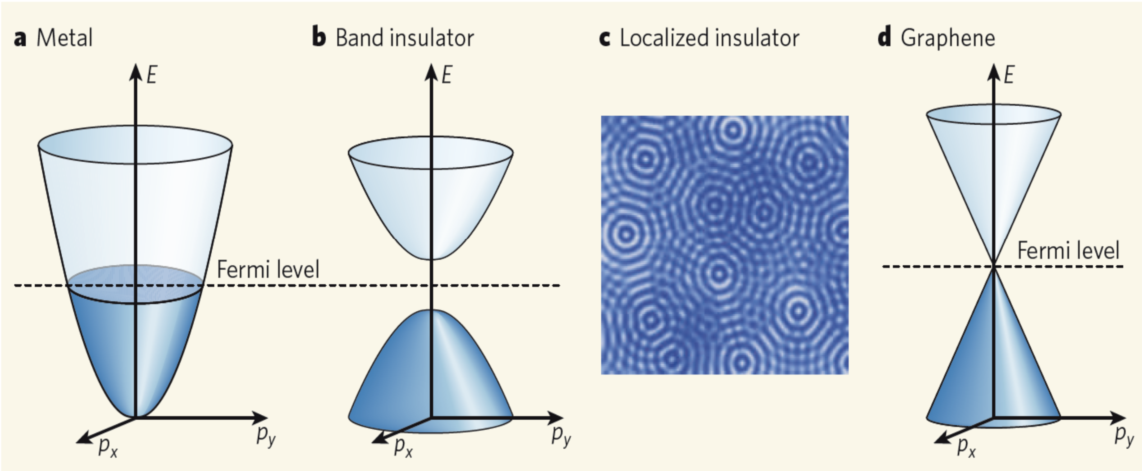
# Metal-insulator transition




-> hydrogen-induced defects cause reversible metal-insulator transition at extremely low coverages

Bostwick et al., PRL **103**, 056404 (2009)

# Metal-insulator transition through localization




M. S. Fuhrer and S. Adam, Nature (News&Views) 458 (2009)

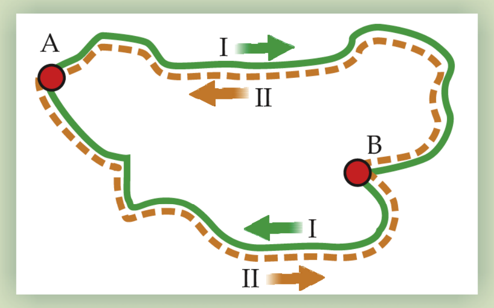



**Figure 2.** Interference effects influence the propagation of waves in a disordered medium. If two waves follow the same path from A to B, one going clockwise and the other counterclockwise, they interfere constructively on returning to A.

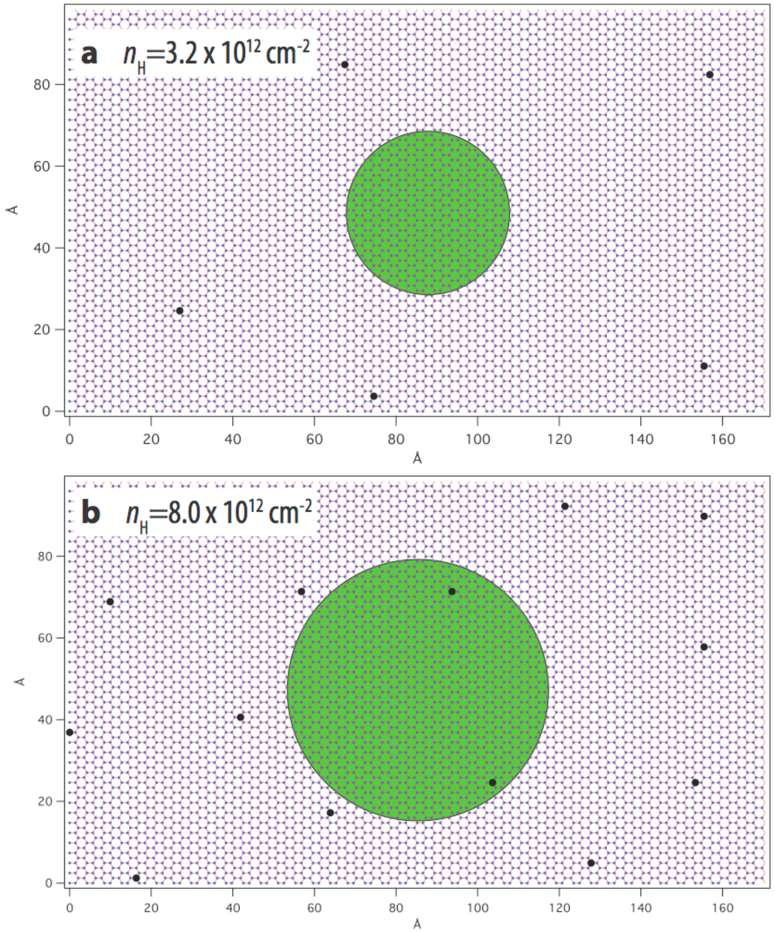
"Fifty years of Anderson localization" A. Lagendijk, B. van Tiggelen, and D.S. Wiersma, Physics Today August 2009 p.24

graphene with hydrogen defects not a band insulator, but insulating behaviour because of (Anderson?) carrier localization

# defect density and Fermi wave vector radius

simulated hydrogen coverages and electron wavelength ~$1/k_F$

Green circle has radius $1/k_F$ from measured Fermi surface area.




below

metal-insulator transition

above

# Summary

Band structure of single layer graphene - Dirac Fermions

Transition from single layer to FLG: layer-dependent carrier density, overlap integrals, Coulomb potentials

Two-layer: Controlling the electronic structure of graphene layers through out-of-plane symmetry breaking

- Relative potential in bilayer
- Control of the gap between π and π* states

correlate many body effects as observed in photoemission with macroscopic material properties: friction

metal-insulator transition induced by extremely small amounts of hydrogen - carrier localization