Epitaxial Graphene
A new electronic material

Walt de Heer

School of Physics

Georgia Institute of Technology

Georgia Tech
W. A. de Heer, C. Berger,P. N. First,E. Conrad

X. Wu, M. Sprinkle, M. Ruan, Y. Hu, G. Rutter, L. Miller,
K. Kubista, J. Hass, N.Sharma,

NIST
J. Stroscio, and others (NIST)

CEA
P. Soukiassian

Soleil
A. Taleb-Ibrahimi A. Tejeda

CNRS
M. Potemski, G. Martinez, C. Faugeras

(other collaborators will be acknowleged later)

The History of Graphene

Graphitic layers on transition metals, carbides known since the early ‘70s

First identification of:

“monolayer of graphite”
“single-crystal plane”
“two-dimensional graphite”

SiC	Van Bommel, Surf. Sci. (1975)
LaB6	Oshima Appl Phys (1977)
Pt	Zi-Du Surface Science (1987)…
Ni	Rosei PRB(1983)
Ir	Kholin Surf Sci (1984)
Re	Gall Sov Phys Sol State (1985)
TaC	Aizawa PRL 1990
TiC	Nagashima, Surf Sci (1993)
Ru	Marchini (2007)
WC	TaC, HfC,…
SiC	Forbeaux (1998)

The breakthrough:
Gateable graphenes
Emphasis on transport

SiO_2	Novoselov Nature (2004) (Thin graphite)
SiC	Berger J. Chem Phys (2004) (Epitaxial graphiene)
SiO_2	Novoselov Nature (2005) (Exfoliated graphene)
SiO_2	Zhang Nature (2005) (Exfoliated graphene)

Graphene was experimentally well-known as a 2D crystal!
See, for example

Thin Solid Films 266 (1995) 229-233

N.R. Gall, E.V. Rut'kov, A.Ya. Tontegode

3.2. ***Monolayer graphite***

Graphite films of monolayer thickness form on the surface of many metals (Ir, Re, MO, Pt, Ni, Rh) ….

…Monolayer graphite films preserve their individuality as two-dimensional crystals on the surface of the metals [61]

…Valence saturation of monolayer graphite films leads to their catalytic passivity and to a weak bonding only by Van der Waals forces [9]. …

…many atoms (Cs, K, Ba, C, Pt, Si, Au, etc.) [6,19] and even molecules (C,) [20] can intercalate into MGF, penetrating between the graphite layer and the metal surface [6,19,21].

So why did it take so long for graphene to catch on?

Almost

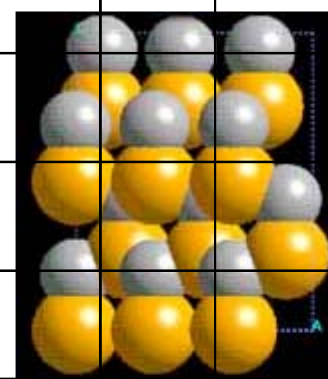
NOBODY CARED!

Epitaxial graphene is not an isolated single graphene sheet. However, it is easily made and it exhibits several graphene properties more clearly than exfoliated graphene!

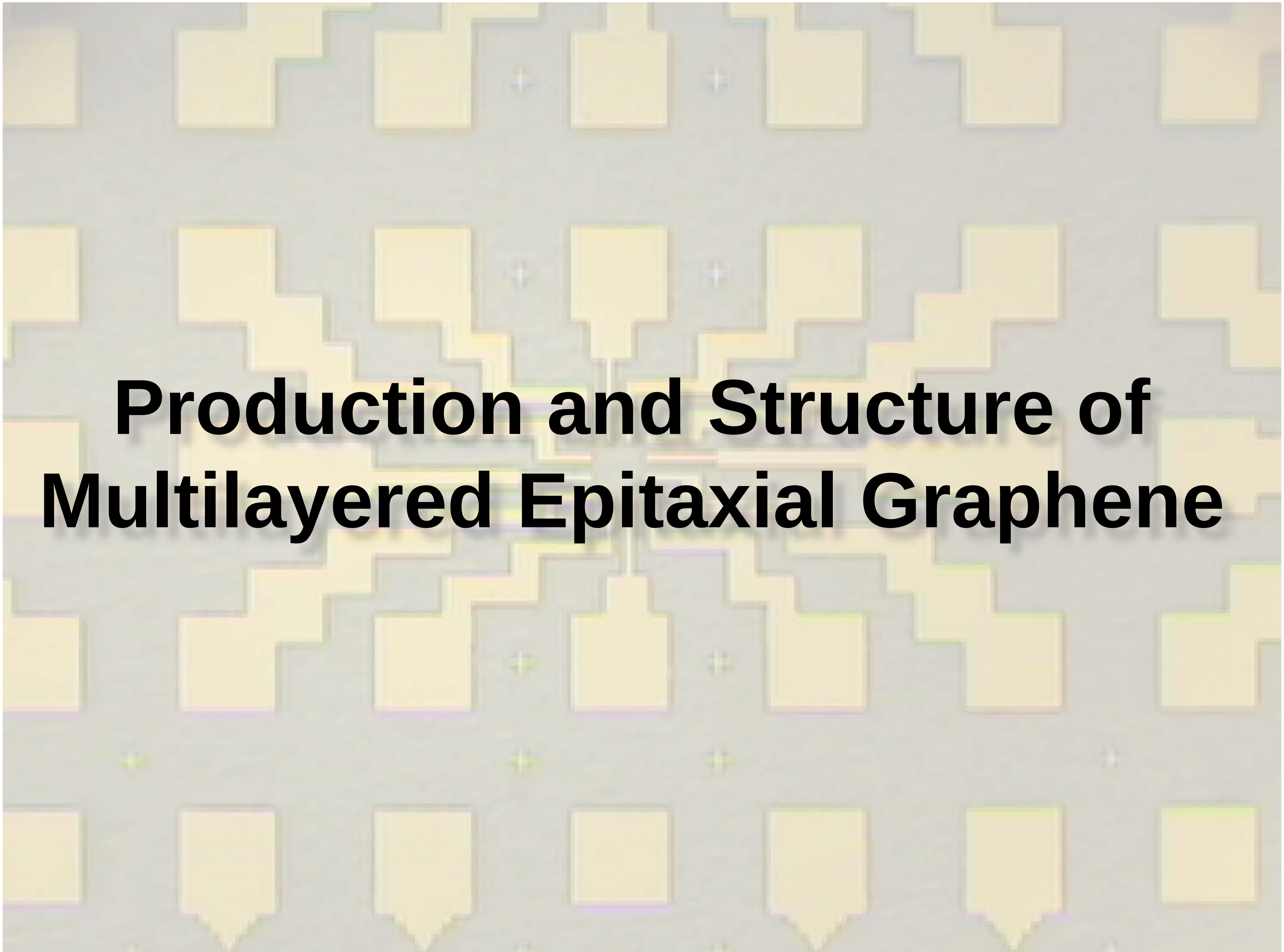
Graphene Properties

ITRS 2007 emerging material and research devices

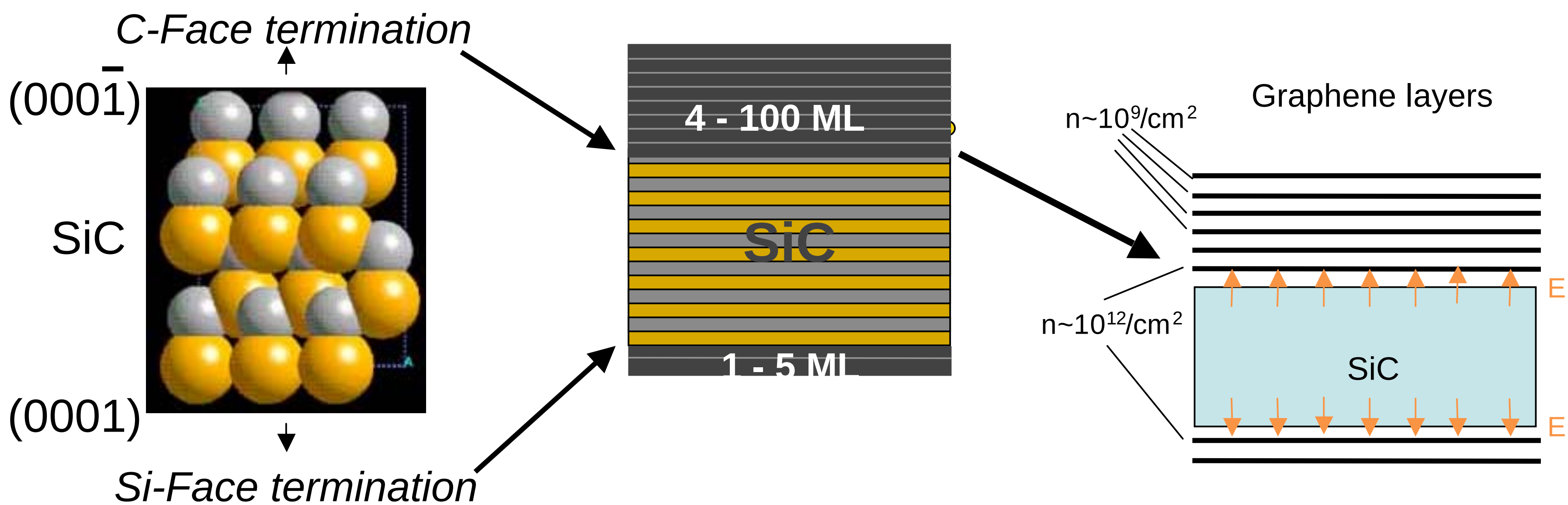
	Tape graphene	UHV Si-face	UHV C-face	Furnace Si-face	Furnace C-face
Scalability		✓	✓	✓	✓
Mobilities >10^5cm^2/Vsec					✓
Doping < 10^{10}/cm^2					✓
Berry's phase of π	✓				✓
Landau Level $E \propto \sqrt{B}$	✓				✓
Weak anti-localization					✓
Gapless Linear Dispersion		?✓		?✓	✓



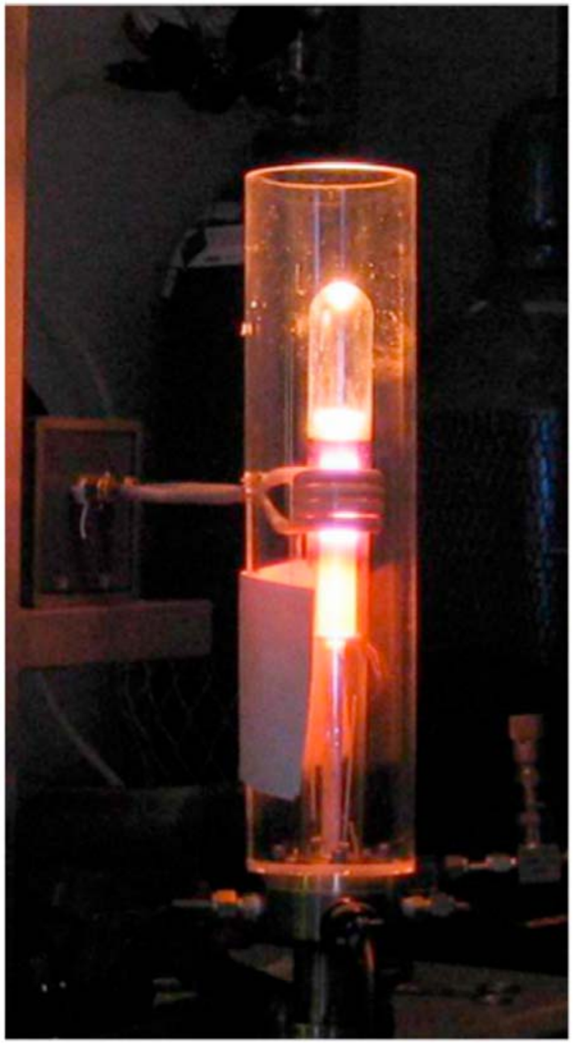
Production and Structure of Multilayered Epitaxial Graphene

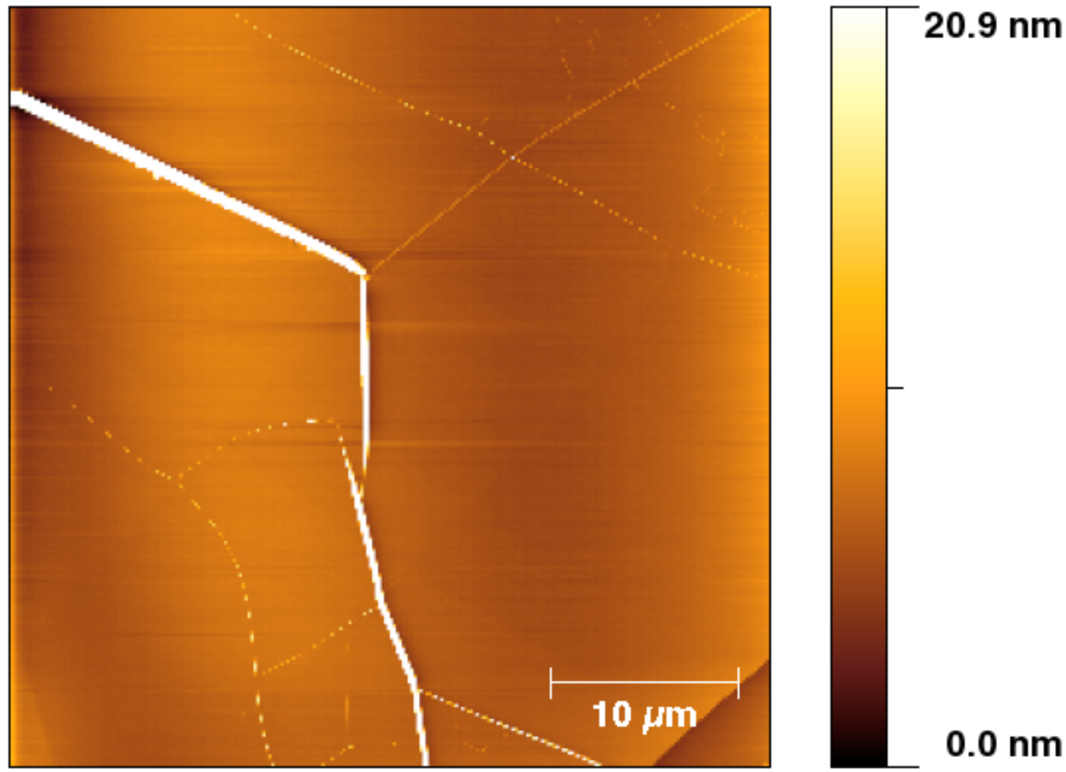


Epitaxial Graphene on SiC



AFM: C-face MEG



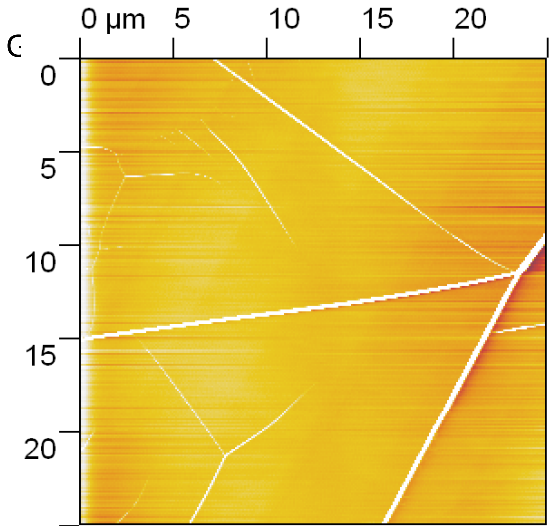


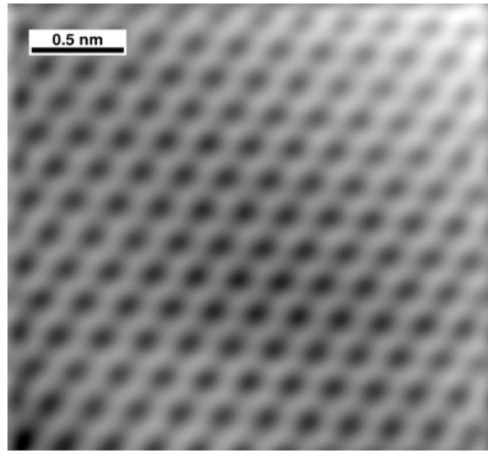
C-face, HV (~10^{-5} Torr)
RF induction furnace
~1450 °C, 7 min.

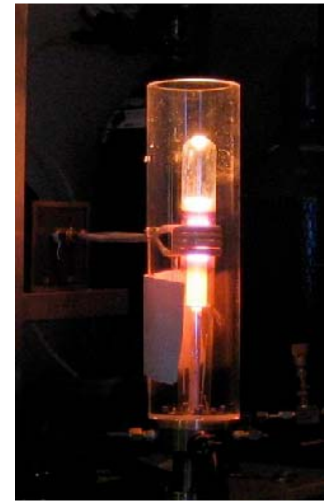
See M. Ruan W26.011

EPITAXIAL GRAPHENE on SiC

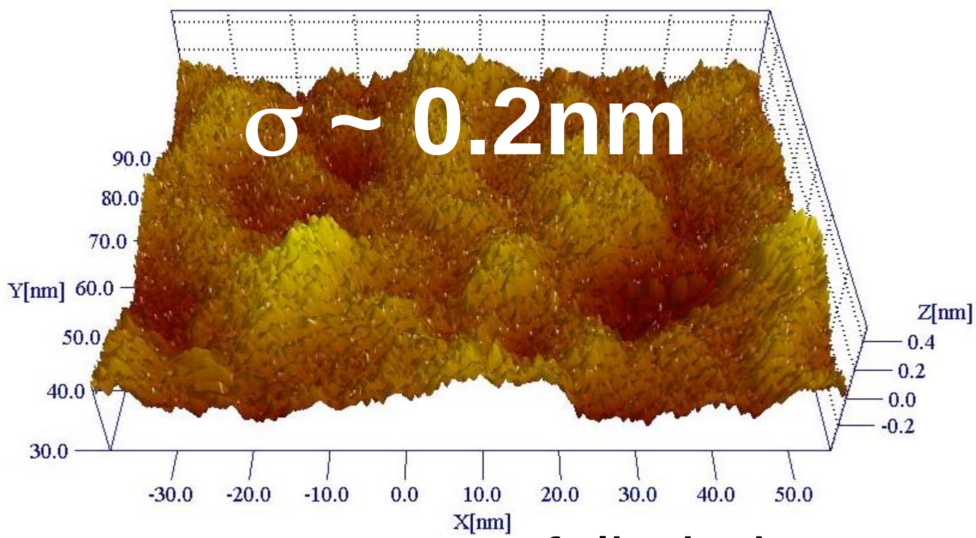
Graphene Growth





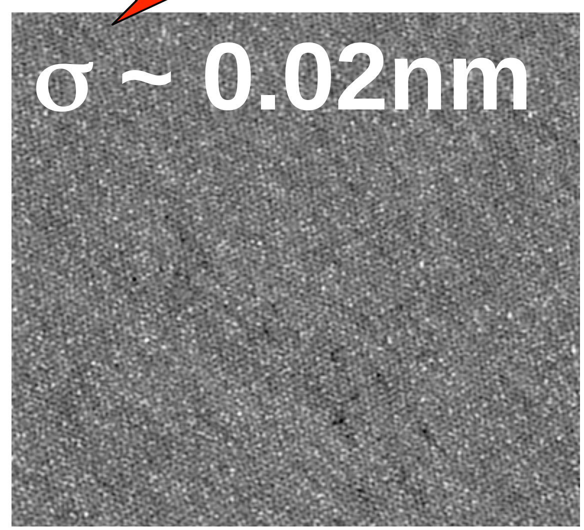


Furnace Growth
C-face



9 x 9µm

Exfoliaded



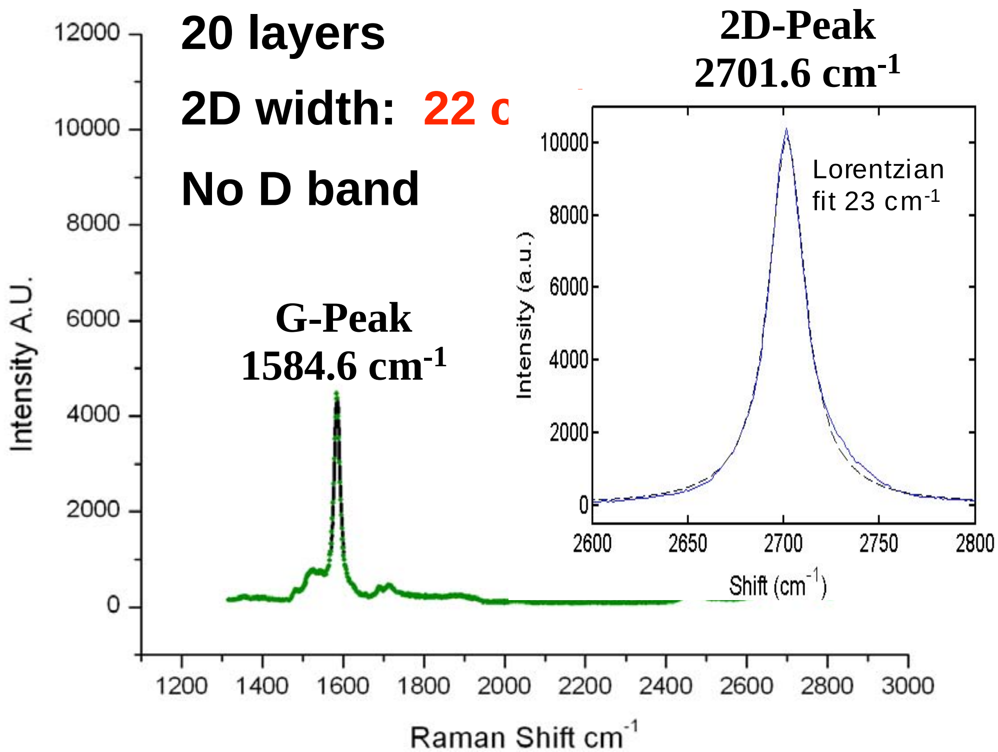
400 x 400nm

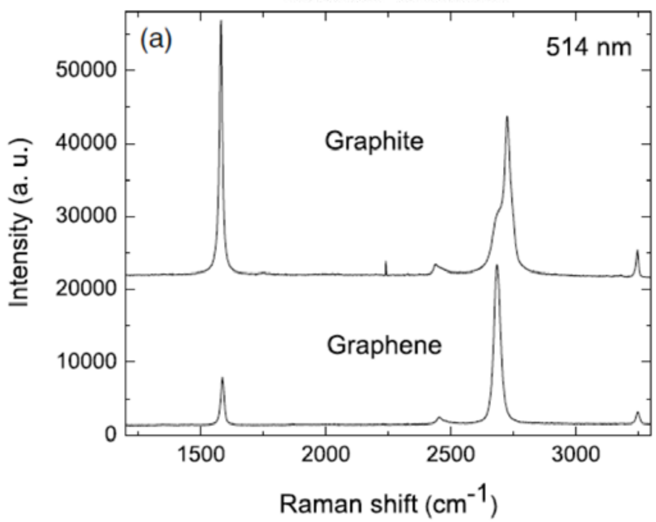
At least one sheet continuously covers the entire surface

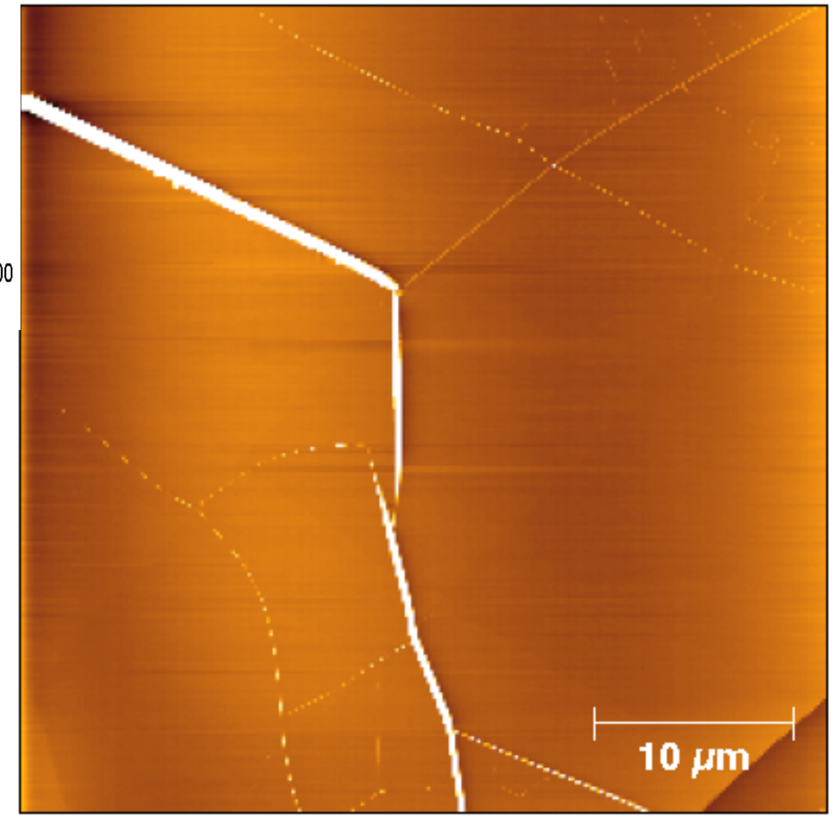
Important notes on furnace grown epitaxial graphene.

1. The GIT furnace grown graphene crystals are exceptionally well-formed compared to UHV grown material with is of poor quality
2. At least the top layer is continuous over the entire surface making MEG graphene crystals by far the largest quasi 2D crystals known.
3. The number of layers varies (at most) by about 1 layer in well-made samples.
4. The interface layer is n doped and probably more disordered than the other layers.

Raman Spectroscopy







A. C. Ferrari et.al. PRL **97,** 187401 (2006)

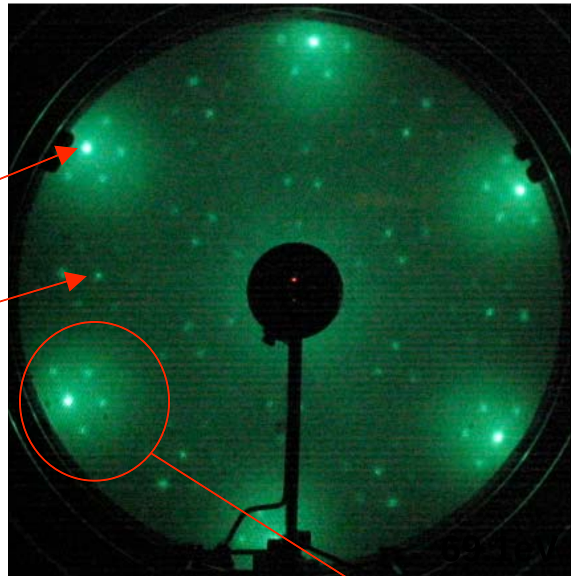
Stacking

Si face: Bernal (AB)

C-face Rotational stacking

(Multilayered epitaxial graphene)

Graphene/SiC Commensurability (LEED)

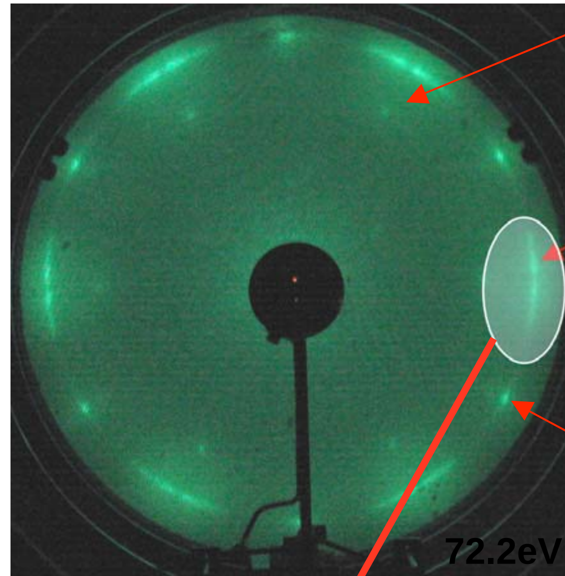


Graphene

SiC bulk

$(6\sqrt{3} \times 6\sqrt{3})_{SiC}R30^o$

Si-Face
UHV grown



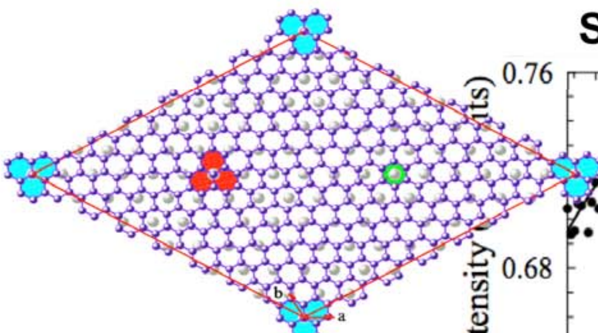
SiC bulk

Diffuse Graphene ring

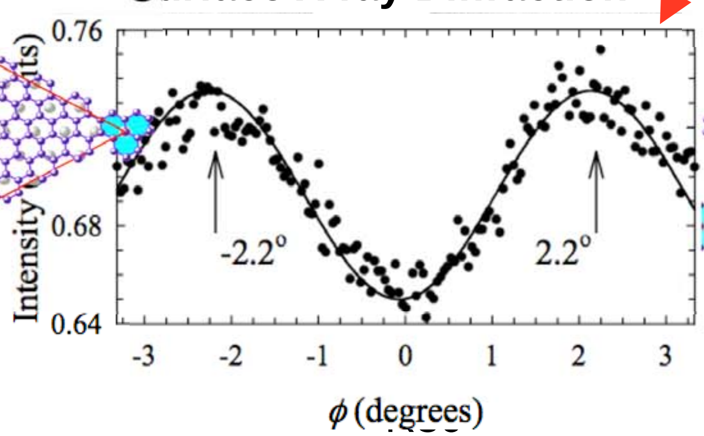
Graphene

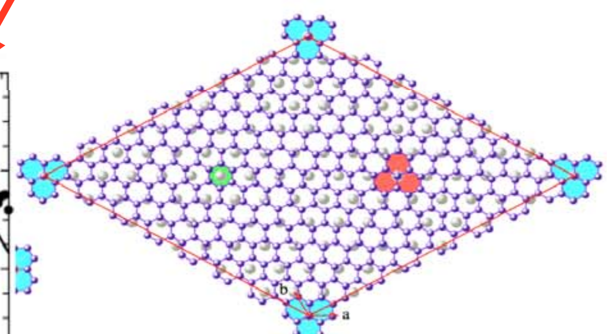
C-Face
furnace grown

Surface X-ray Diffraction



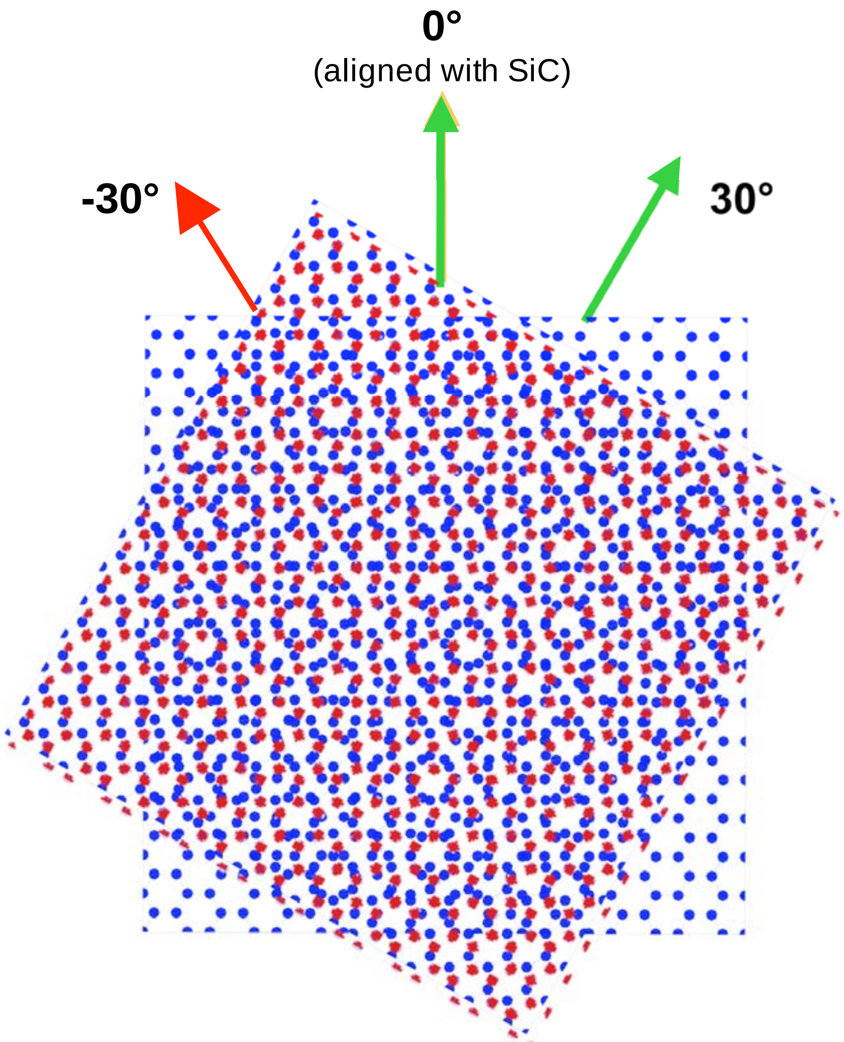
R-2.204º

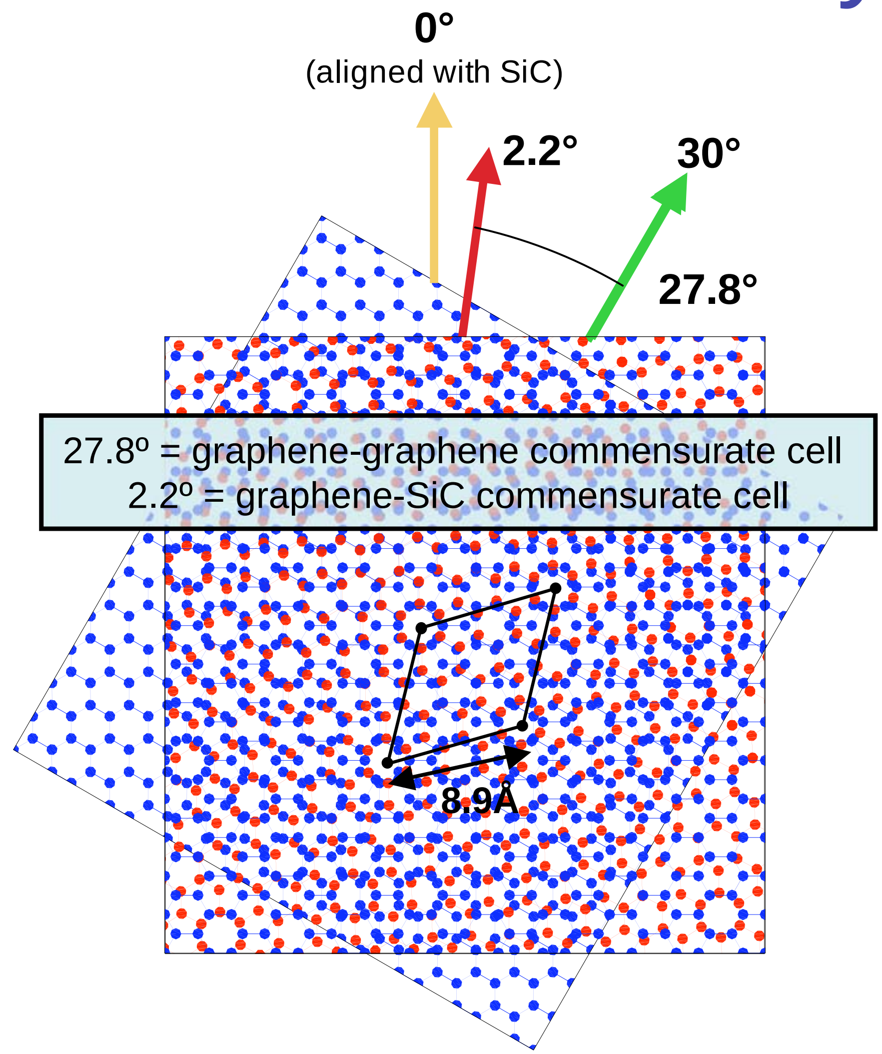




R2.204º

Graphene/Graphene Commensurability

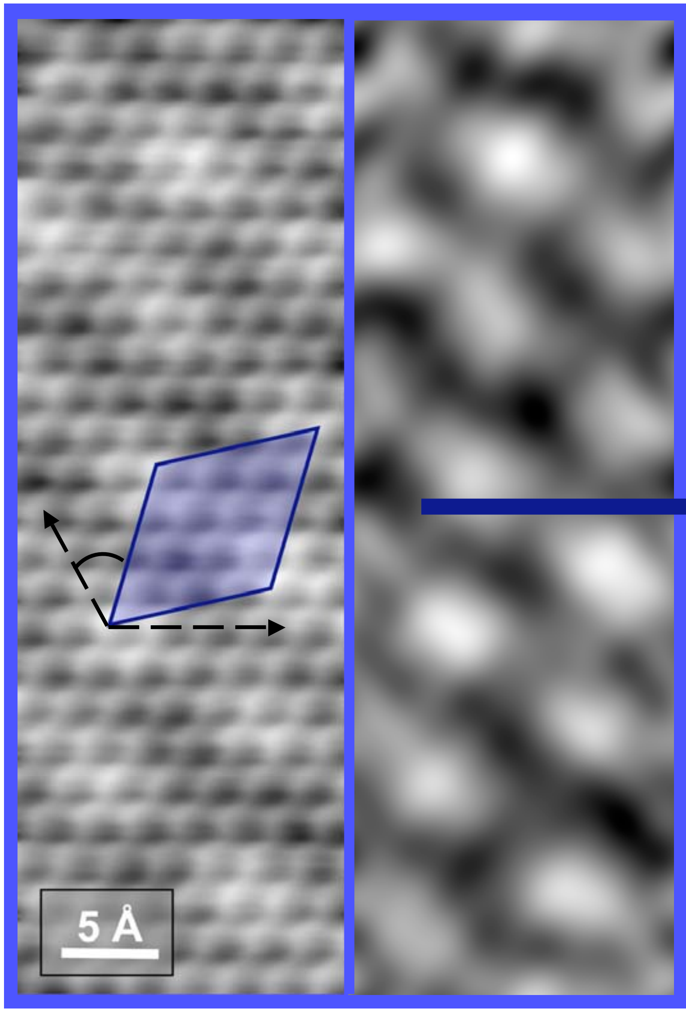




Si-face **Graphite (AB stacked)**

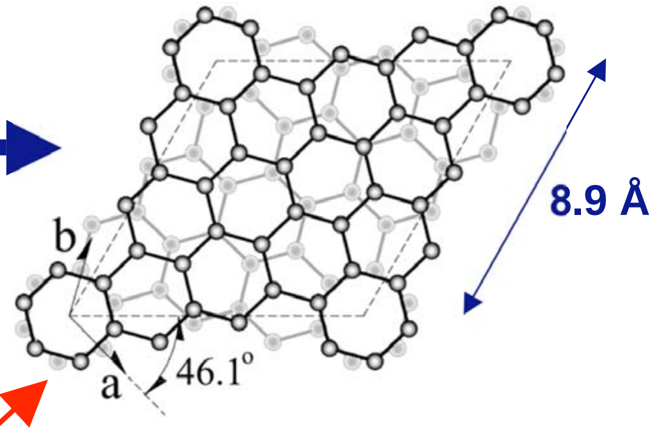
C-face (rotated phases)

STM evidence for rotated phases



Sample bias: -800 mV
Tunneling current: 100 pA

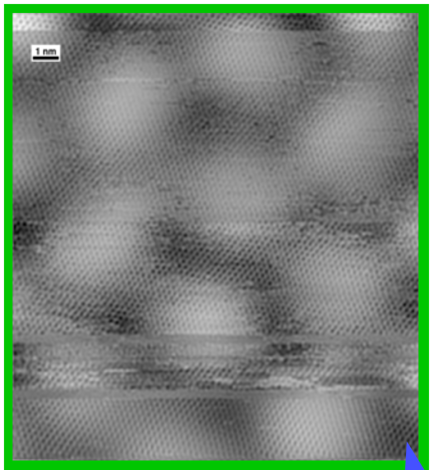
$(\sqrt{13} \times \sqrt{13})_G R46.1^o$



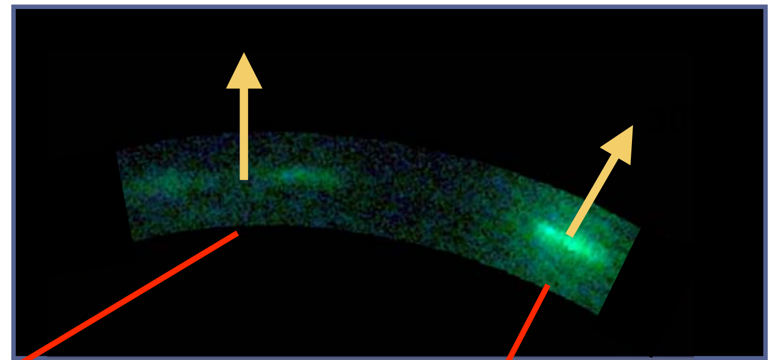
2 sheets with a relative rotation of 27.8^0

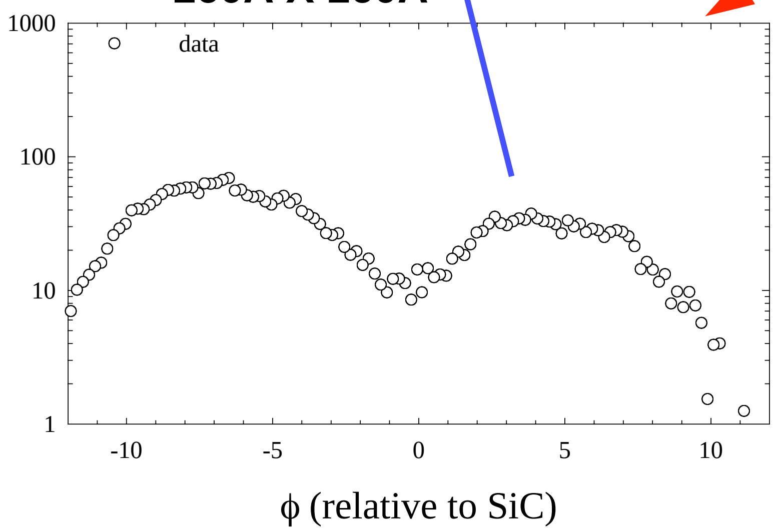
J. Hass, et al. Phys. Rev. Lett **100** 125504 (2008)

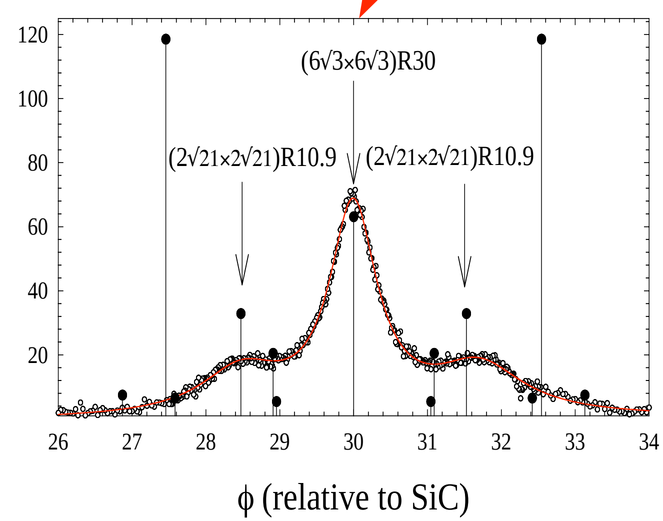
Substrate induced rotations

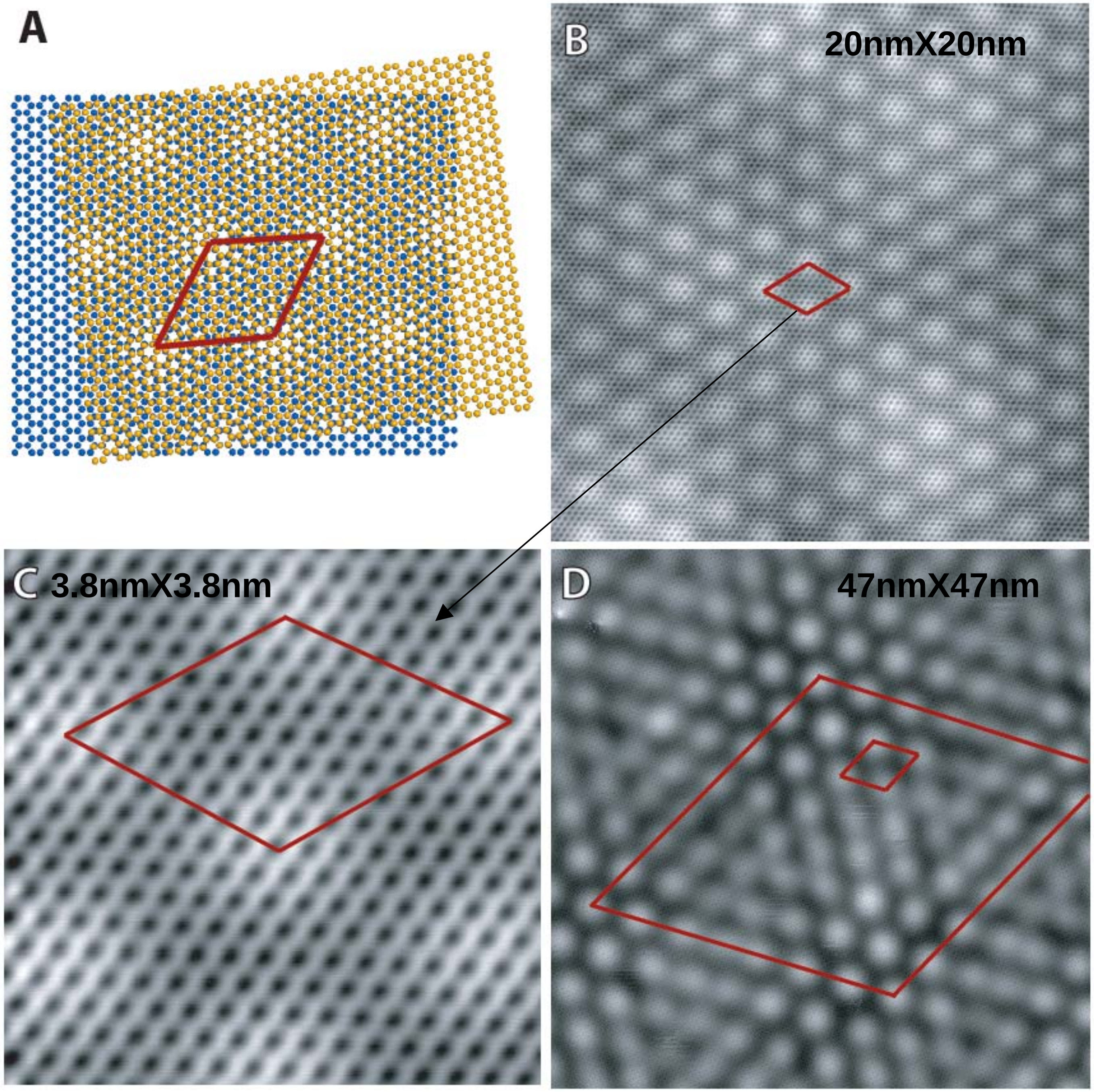


160Å X 160Å





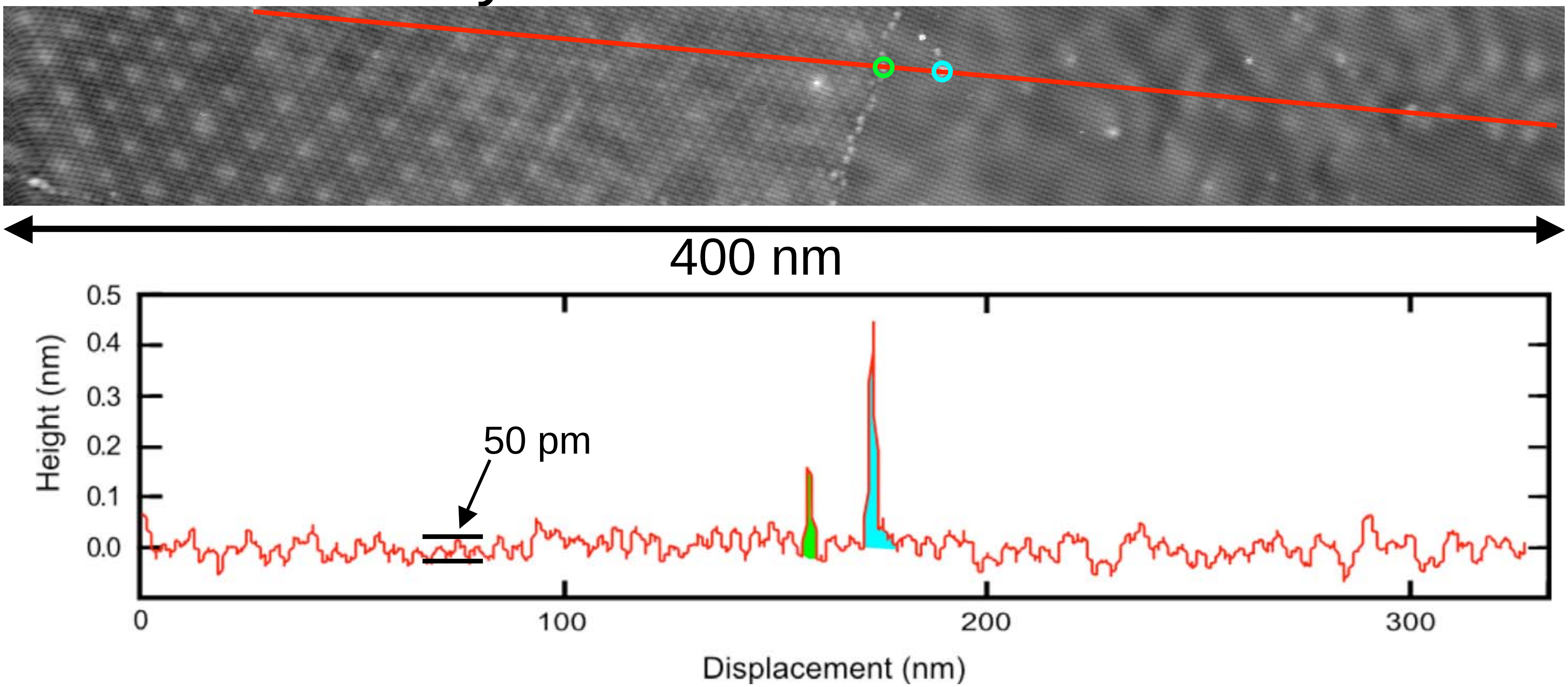




Miller et al
Science, In print

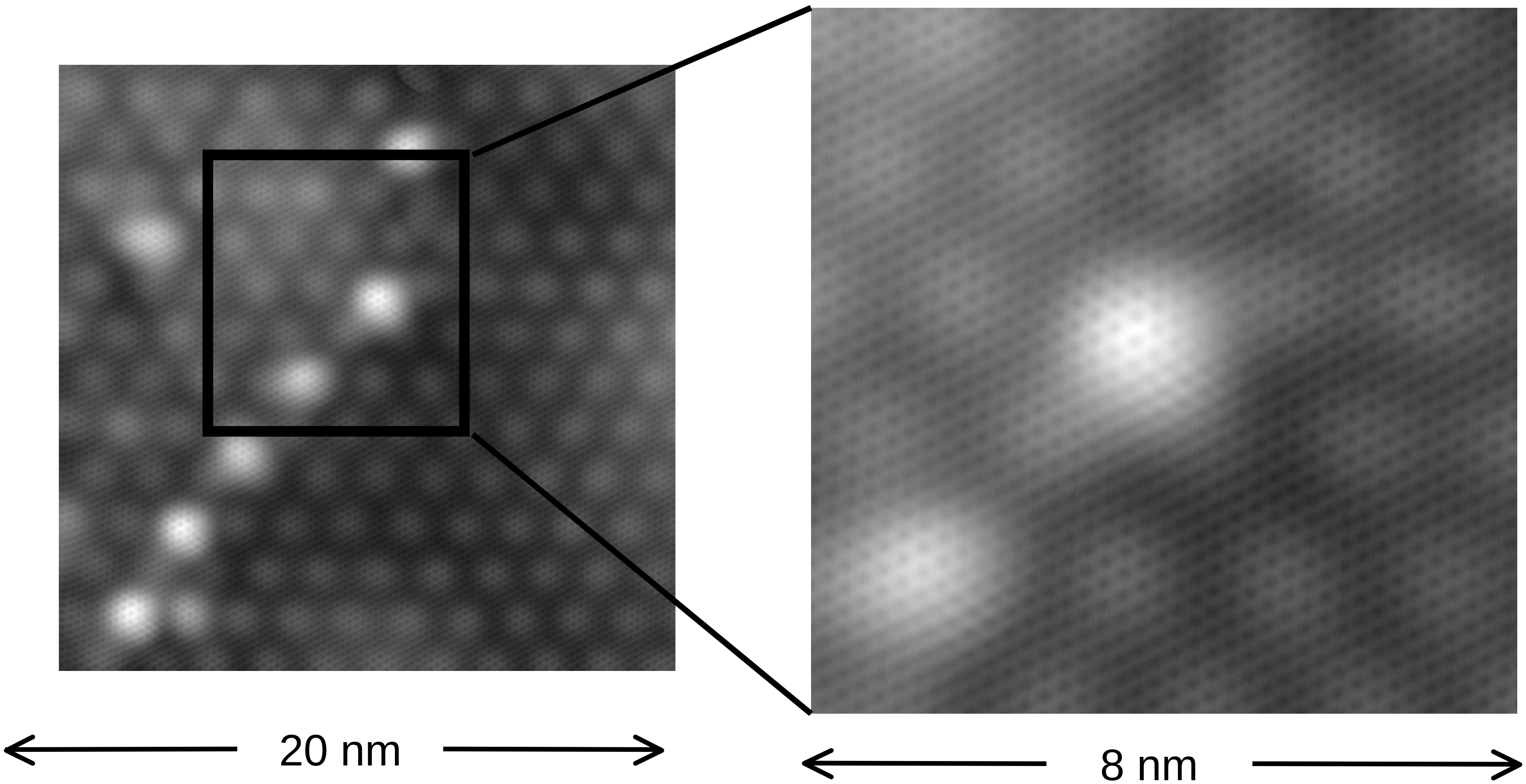
Rotational Domain Boundaries

- Atomically flat and continuous across



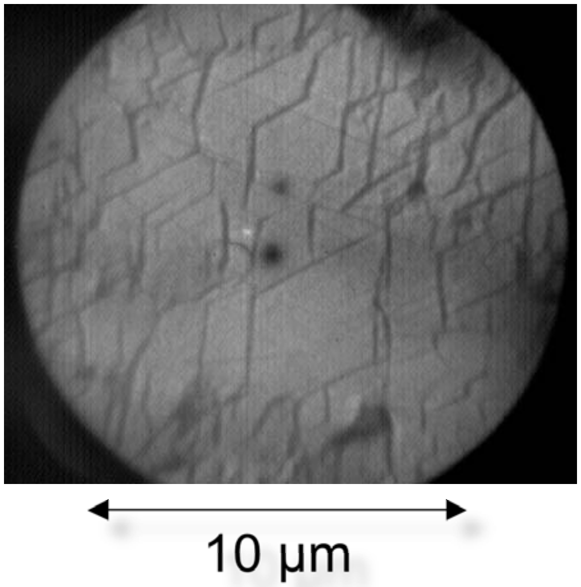
Joseph A. Stroscio email: joseph.stroscio@nist.gov

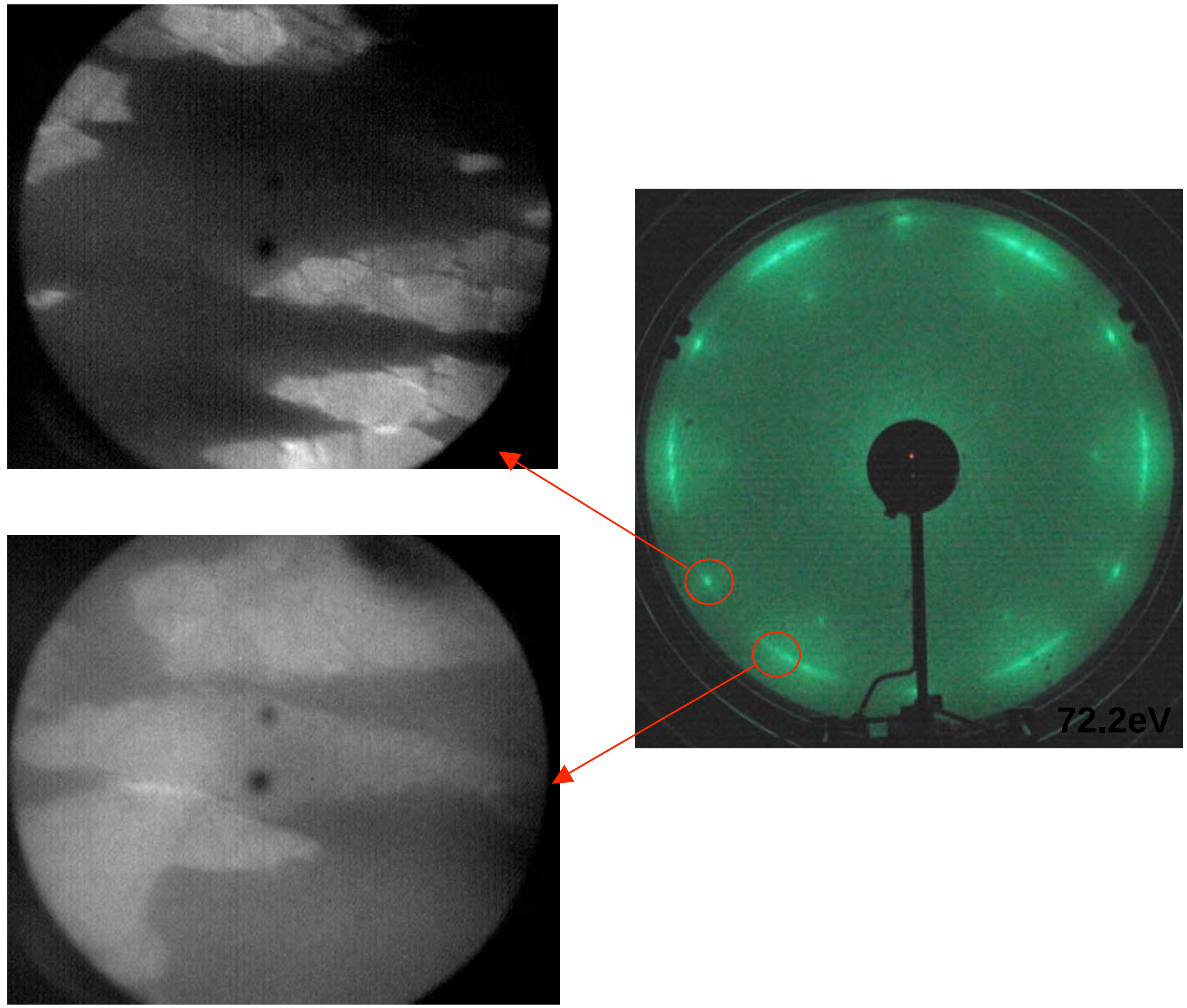
Rotational Domain Boundaries

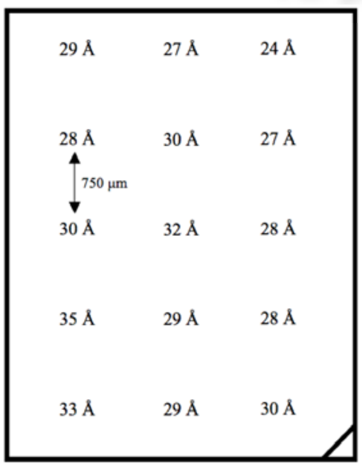


Joseph A. Stroscio email: joseph.stroscio@nist.gov

Rotational domains (LEEM)







Ellipsometery thickness map:
10±1 layer

E.Conrad, M.Sprinkle

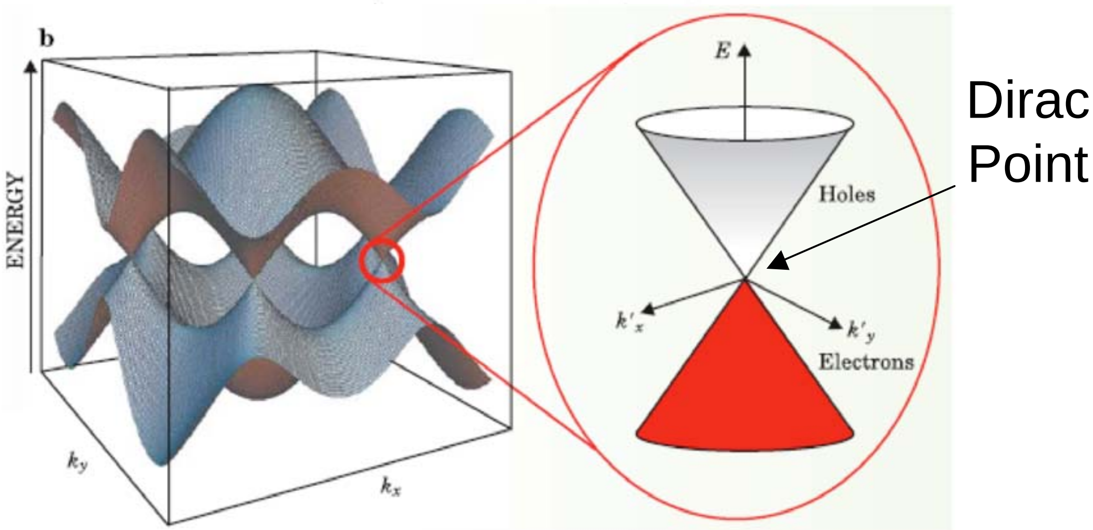
The Dirac cone

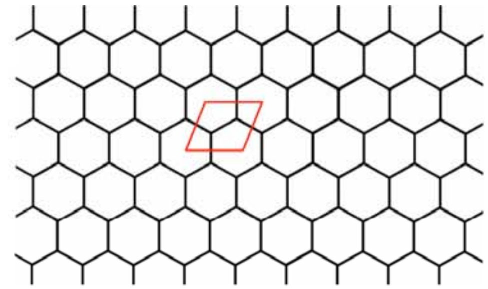
Graphene band structure

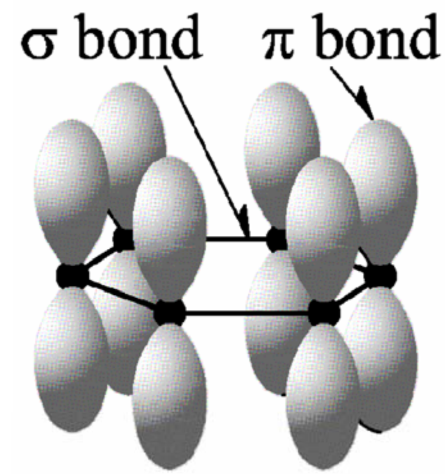
PHYSICAL REVIEW VOLUME 71, NUMBER 9 MAY 1, 1947

The Band Theory of Graphite

P. R. WALLACE*
National Research Council of Canada, Chalk River Laboratory, Chalk River, Ontario
(Received December 19, 1946)







$$H = v_F \cdot \hat{\sigma} \cdot p$$

$$\hat{\sigma} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

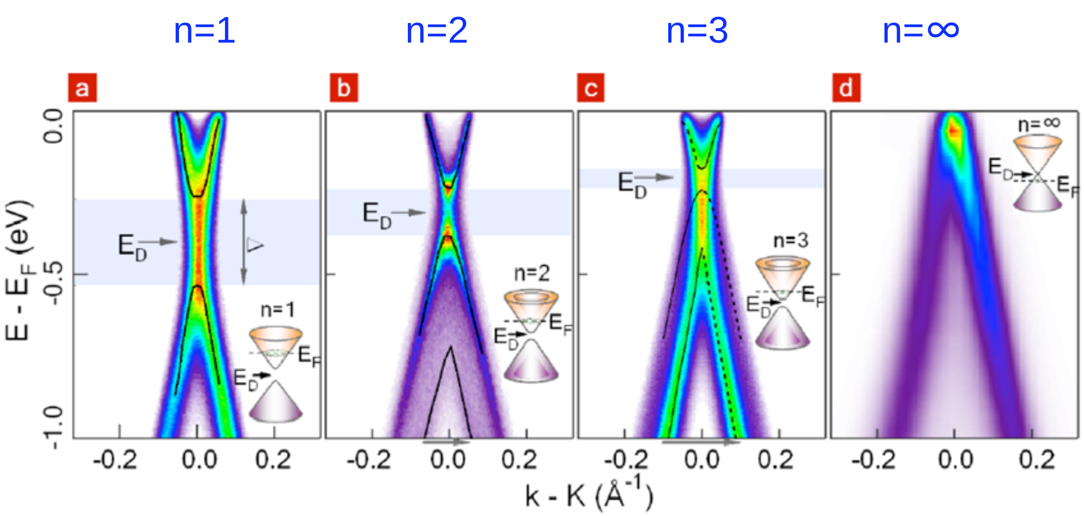
Velocity is constant

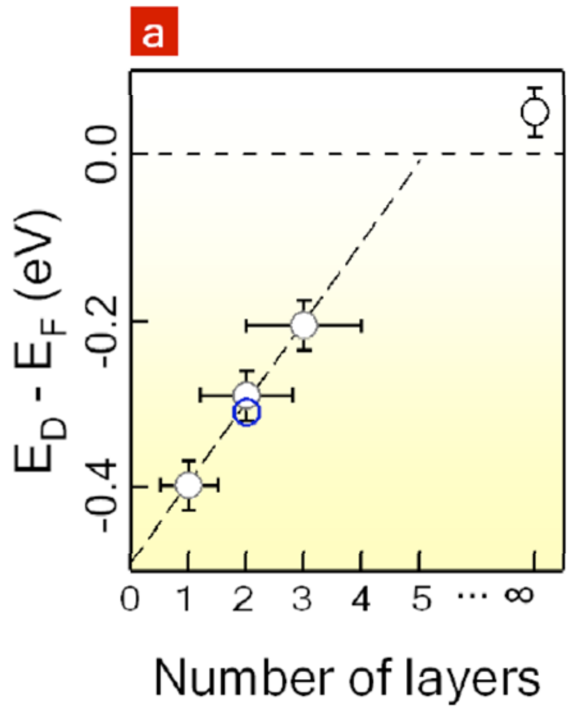
$$E = \pm v_F |p|$$

Neutrino-like dispersion

Substrate-induced band gap in Si-face EG

Zhou, Gweon, Fedorov, First, de Heer, Lee, Guinea,. Castro Neto, Lanzara
*Nature Materials **6,** 770-775 (2007)*





Graphene on Si-face: gap is observed;
Gap closes as the number of layers increases.

Rotations preserve sublattice symmetry

PRL 100, 125504 (2008) PHYSICAL REVIEW LETTERS week ending 28 MARCH 2008

Why Multilayer Graphene on 4*H*-SiC(000$\bar{1}$) Behaves Like a Single Sheet of Graphene

J. Hass,[1] F. Varchon,[2] J. E. Millán-Otoya,[1] M. Sprinkle,[1] N. Sharma,[1] W. A. de Heer,[1] C. Berger,[1,2] P. N. First,[1] L. Magaud,[2] and E. H. Conrad[1]

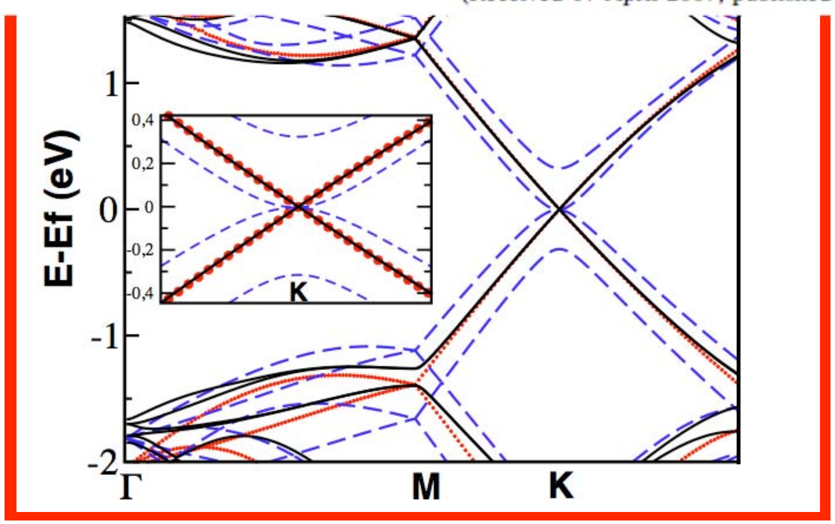
[1]*The Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA*
[2]*Institut Néel/CNRS-UJF BP166, 38042 Grenoble Cedex 9, France*
(Received 13 June 2007; published 28 March 2008)

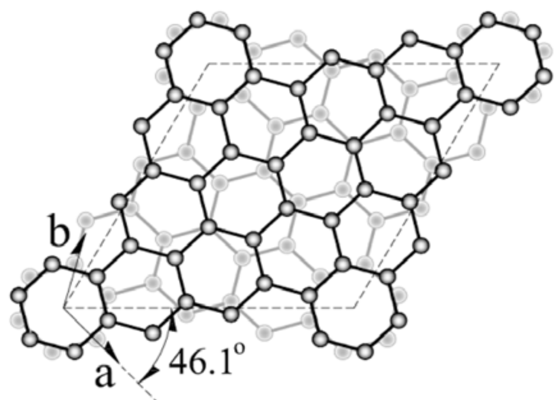
PRL 99, 256802 (2007) PHYSICAL REVIEW LETTERS week ending 21 DECEMBER 2007

Graphene Bilayer with a Twist: Electronic Structure

J. M. B. Lopes dos Santos,[1] N. M. R. Peres,[2] and A. H. Castro Neto[3]

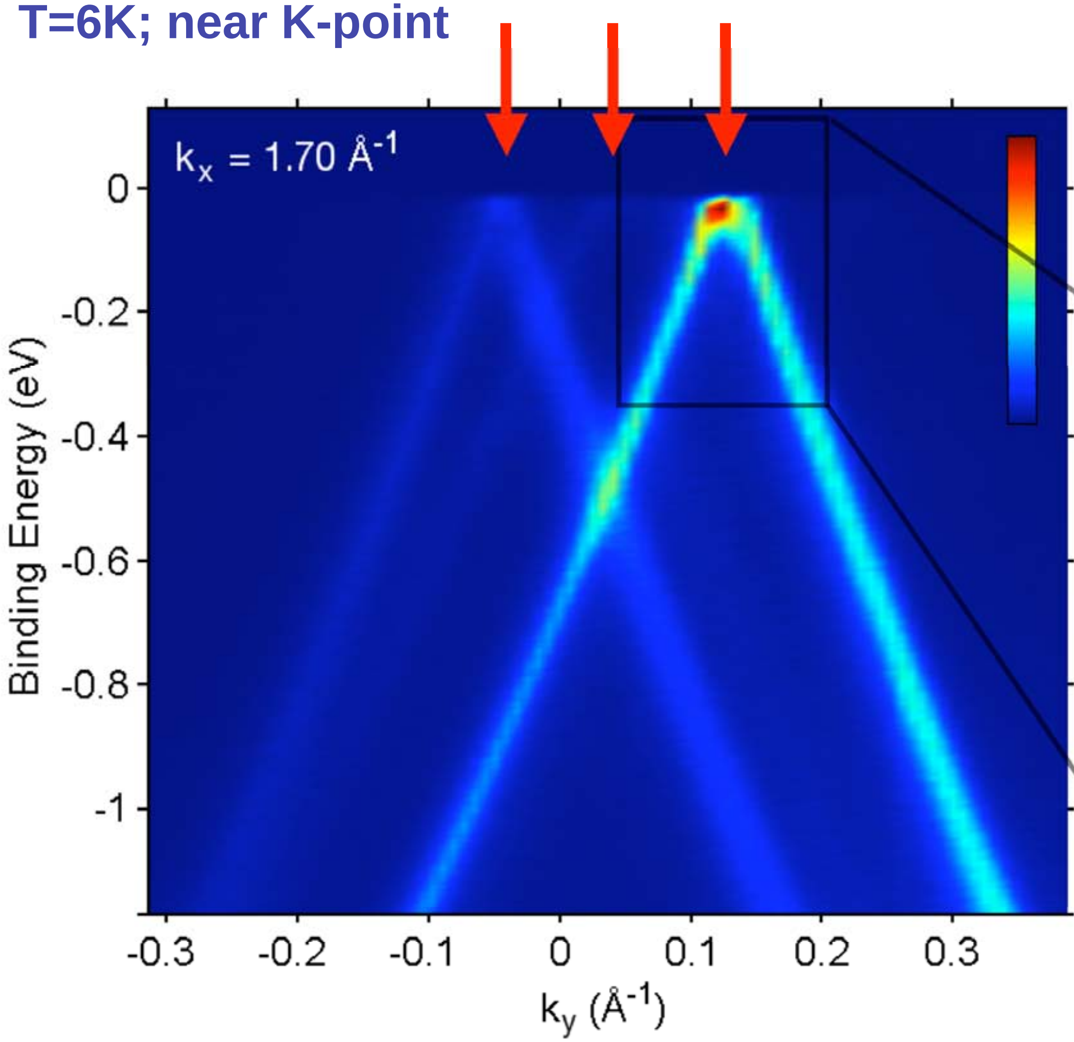
[1]*CFP and Departamento de Física, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal*
[2]*Centro de Física and Departamento de Física, Universidade do Minho, P-4710-057 Braga, Portugal*
[3]*Department of Physics, Boston University, 590 Commonwealth Avenue, Boston, Massachusetts 02215, USA*
(Received 17 April 2007; published 19 December 2007)

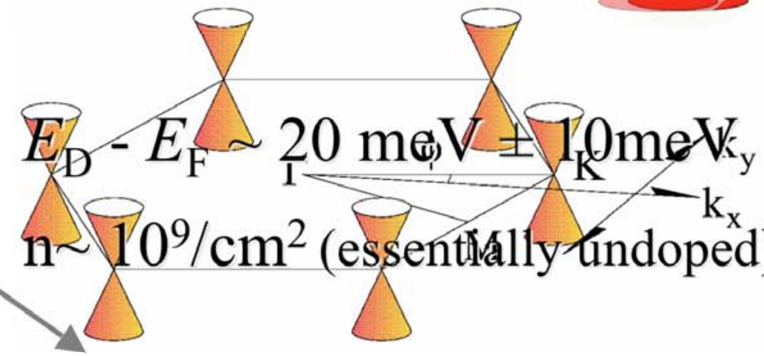




ARPES: MEG (C-face)

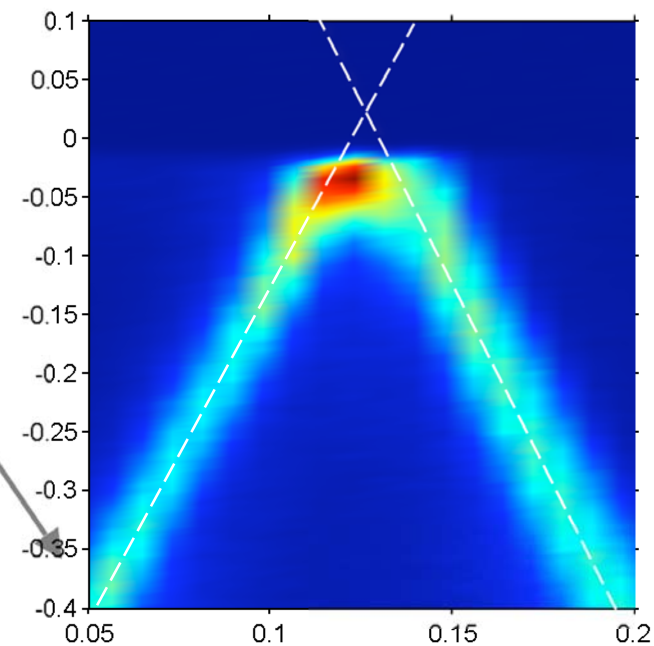
T=6K; near K-point





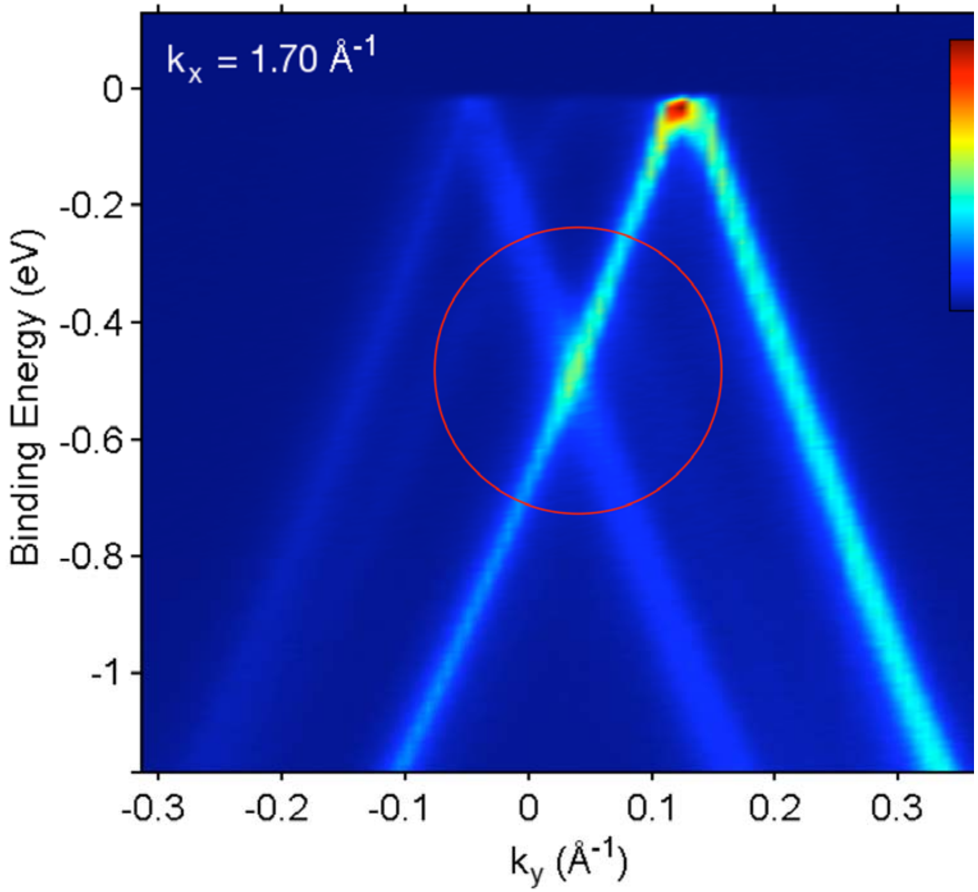
E_D - E_F ~ 20 meV ± 10meV

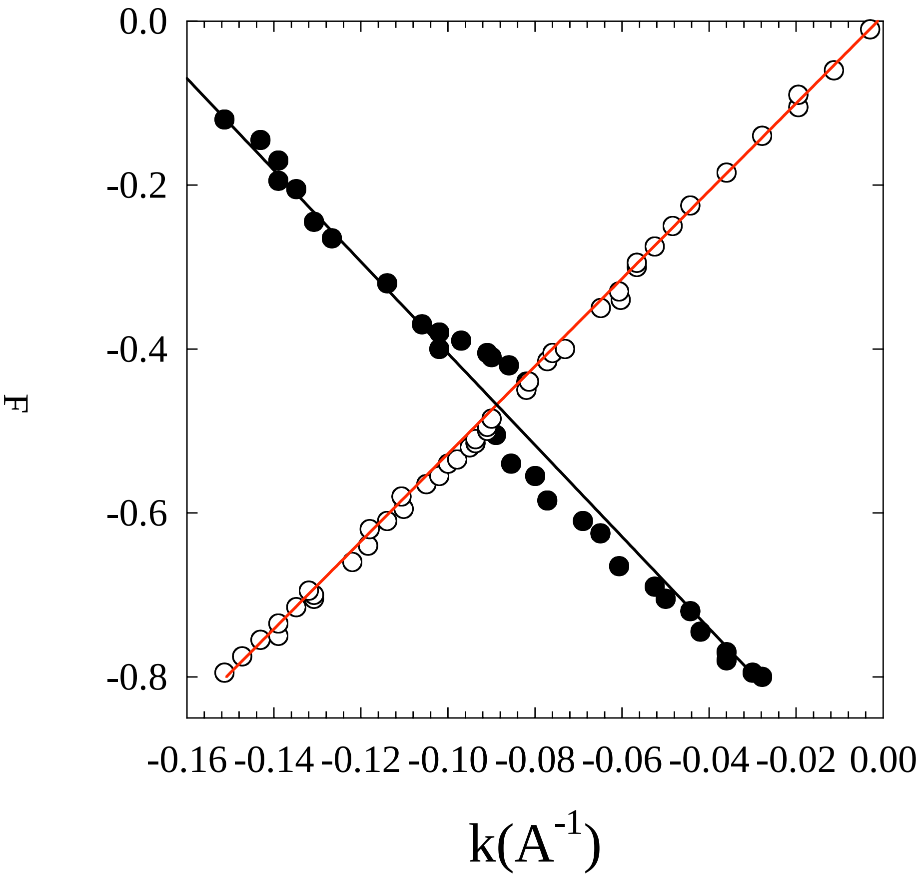
n~ 10^9/cm^2 (essentially undoped)



Each rotated sheet displays linear dispersion!

Layer Interactions (MEG)

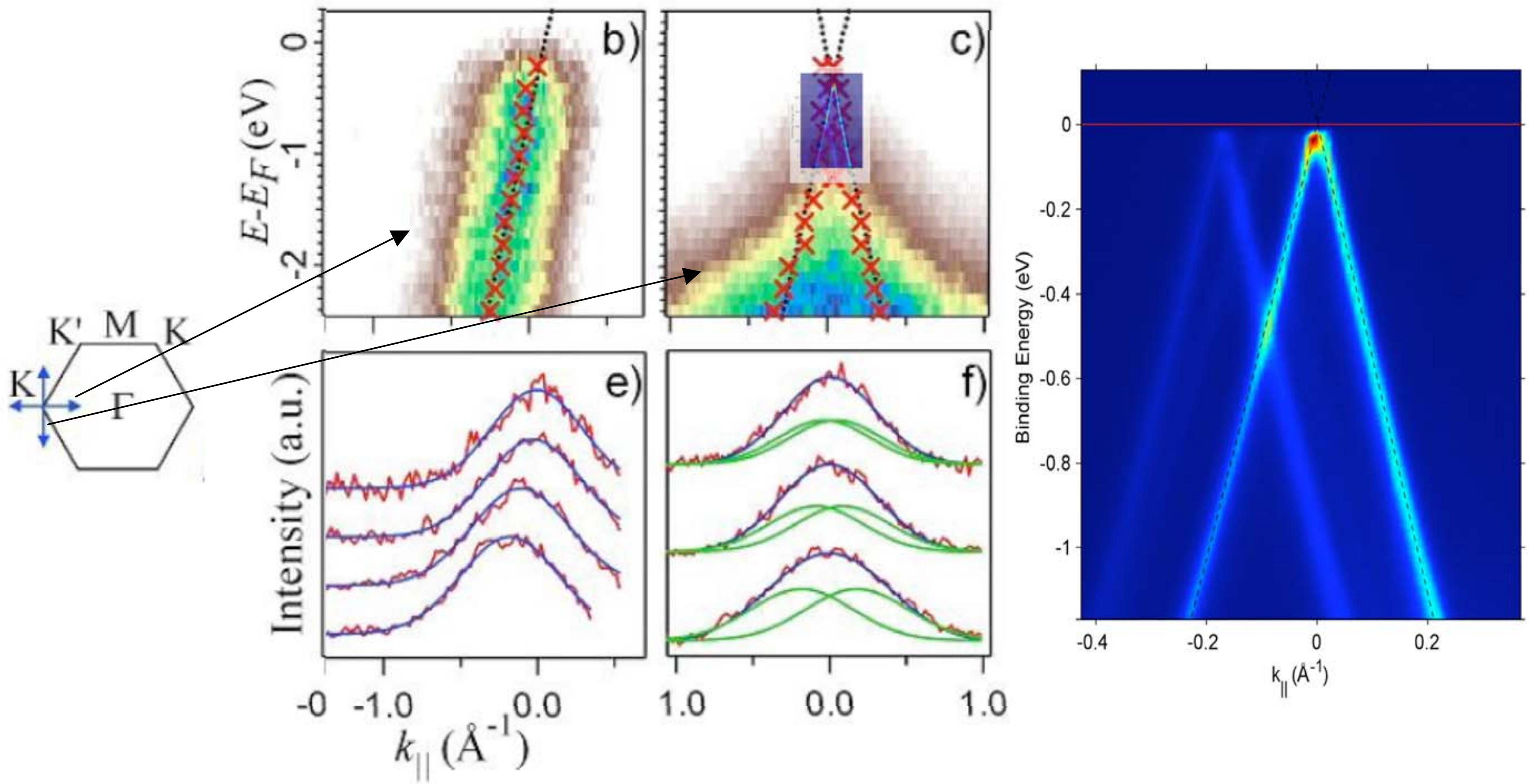




These two sheets are ~3 - 4Å apart

Spectro-microscopy of single and multi-layer graphene supported by a weakly interacting substrate

Knox, Wang, Morgante, Cvetko, Locatelli, Onur Mentes, Angel Ni, Philip Kim, Osgood



ARPES of exfoliated graphene: does it have a Dirac point?

Scanning tunneling spectroscopy of Landau levels

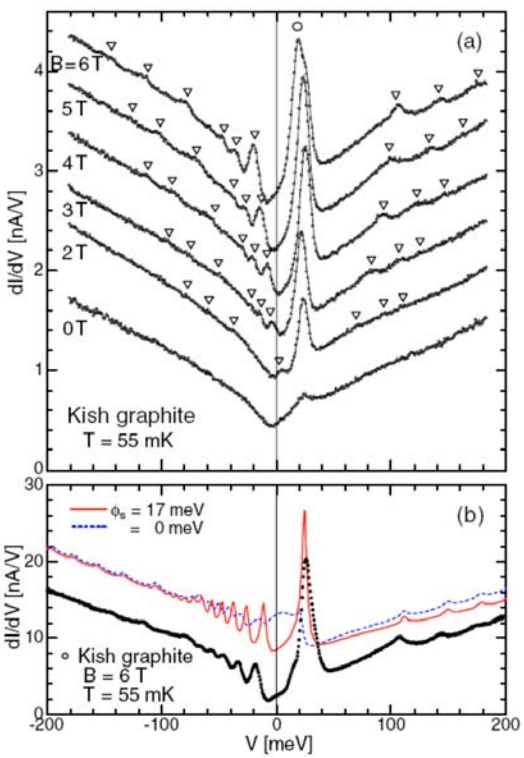
Observing the Quantization of Zero Mass Carriers in (Multilayer Epitaxial) Graphene

Science In Press

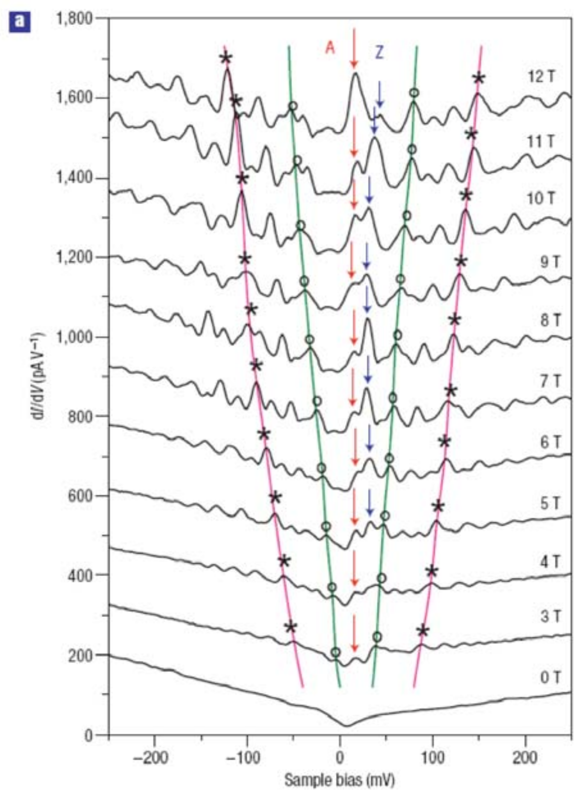
D.L. Miller, K. D. Kubista, G. M. Rutter, M.Ruan, Walt A. de Heer, P. N. First, J. A. Stroscio

(NIST, GIT)

Previous STS Measurements on Graphite Surfaces



T. Matsui et al. PRL (2005)

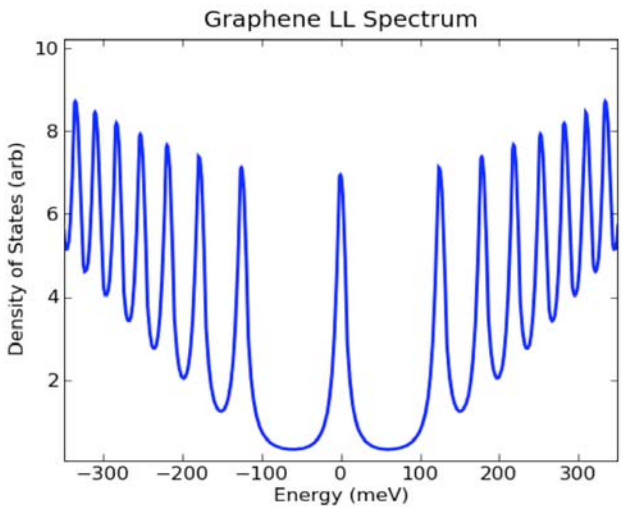


G. Li and E. Andrei
Nature Phys. (2007)

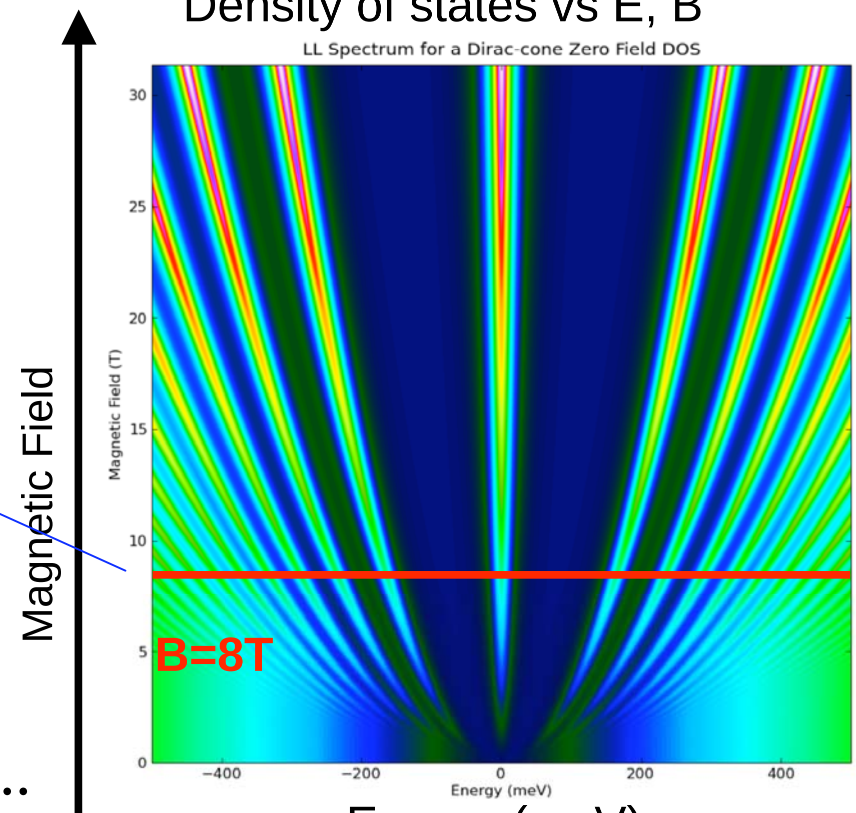
- Complex spectra
- Mixture of peaks of linear and non-linear in *B*

Courtesy Joe Stroscio

Landau Levels in Graphene



Density of states vs E, B



Energy (meV)

$$E_n = \mathrm{sgn}(n)\sqrt{2e\hbar\tilde{c}^2\,|n|\,B} \quad \mathrm{n{=}0, \pm 1\ldots}$$

Graphene

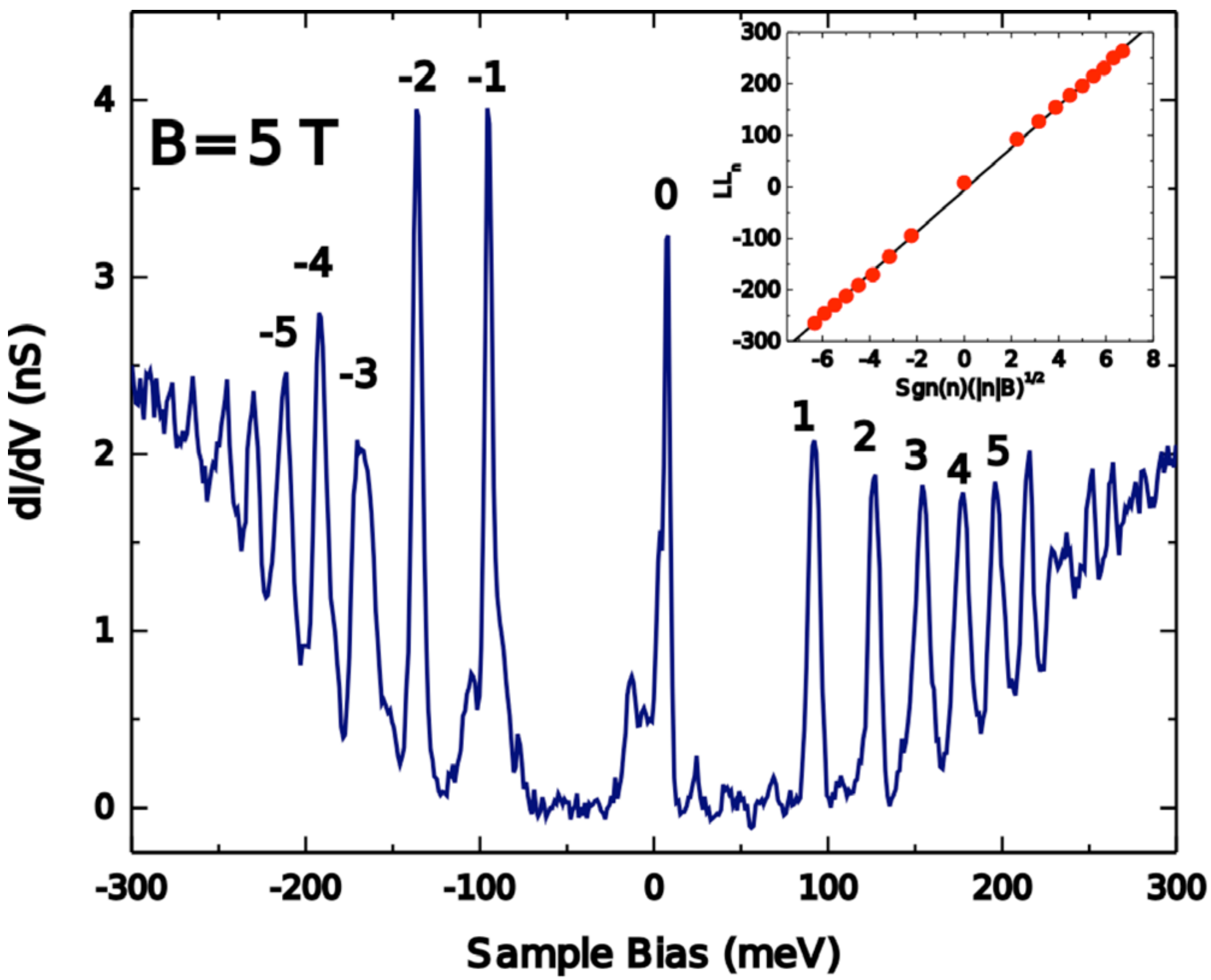
$$E_n = \frac{\hbar e B}{m^*}(n+1/2) \quad n \geq 0$$

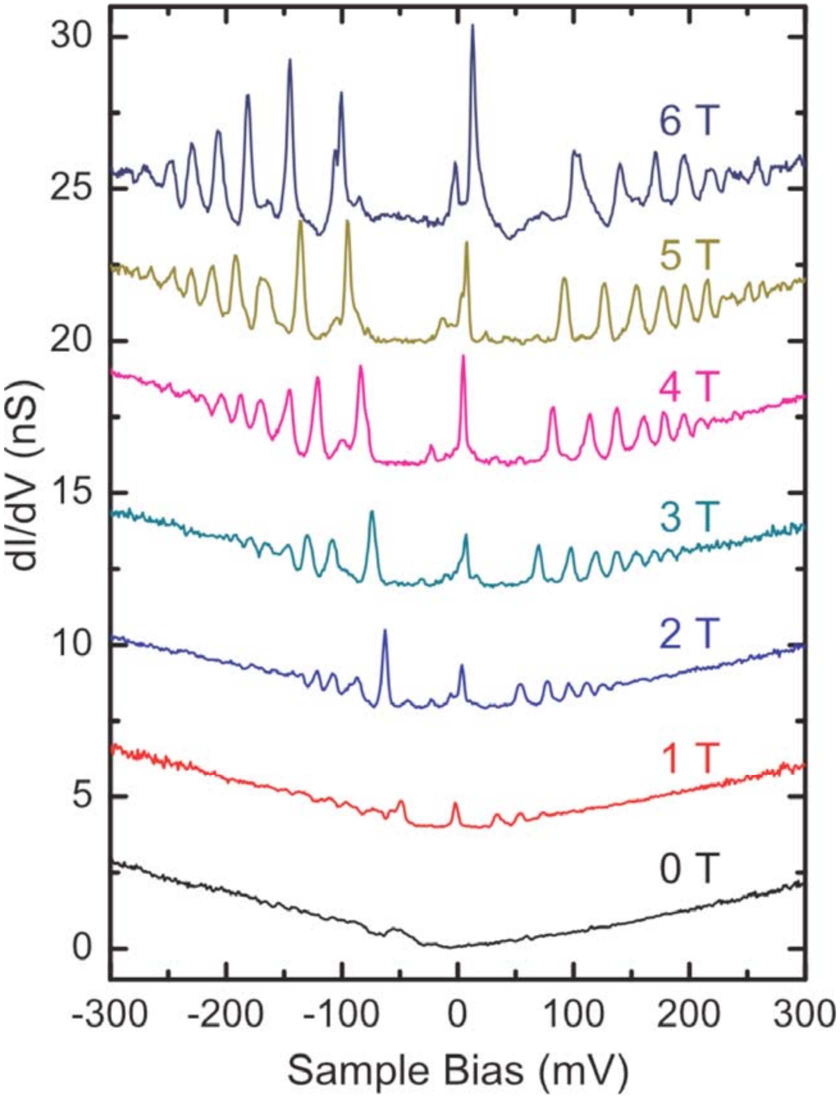
Standard 2DEG

Courtesy P.N.FIrst

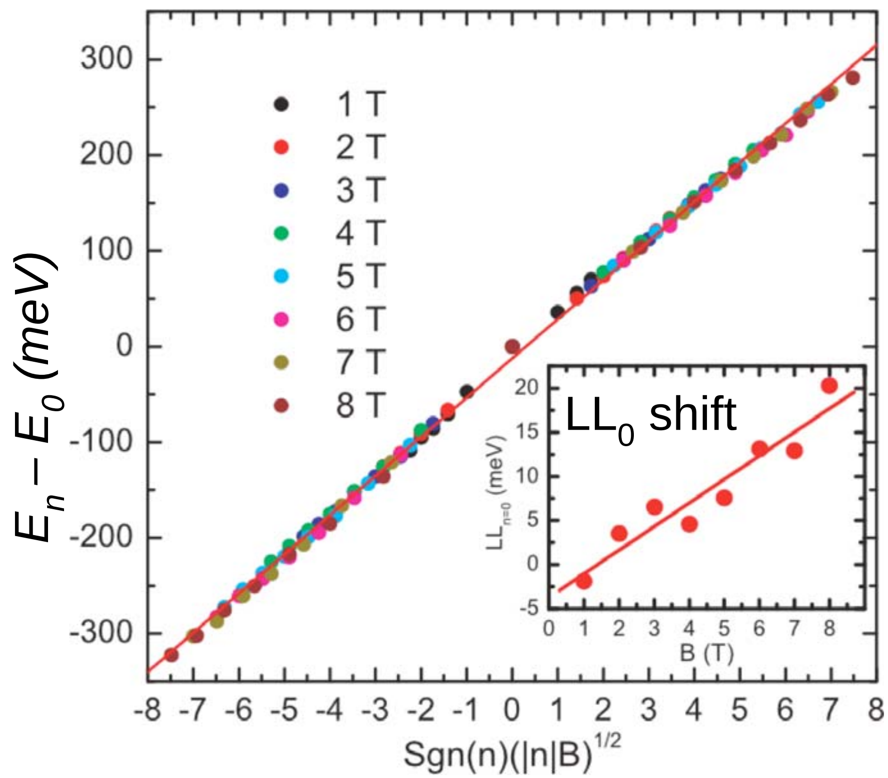
STS

Multilayer Epitaxial Graphene: Landau Levels





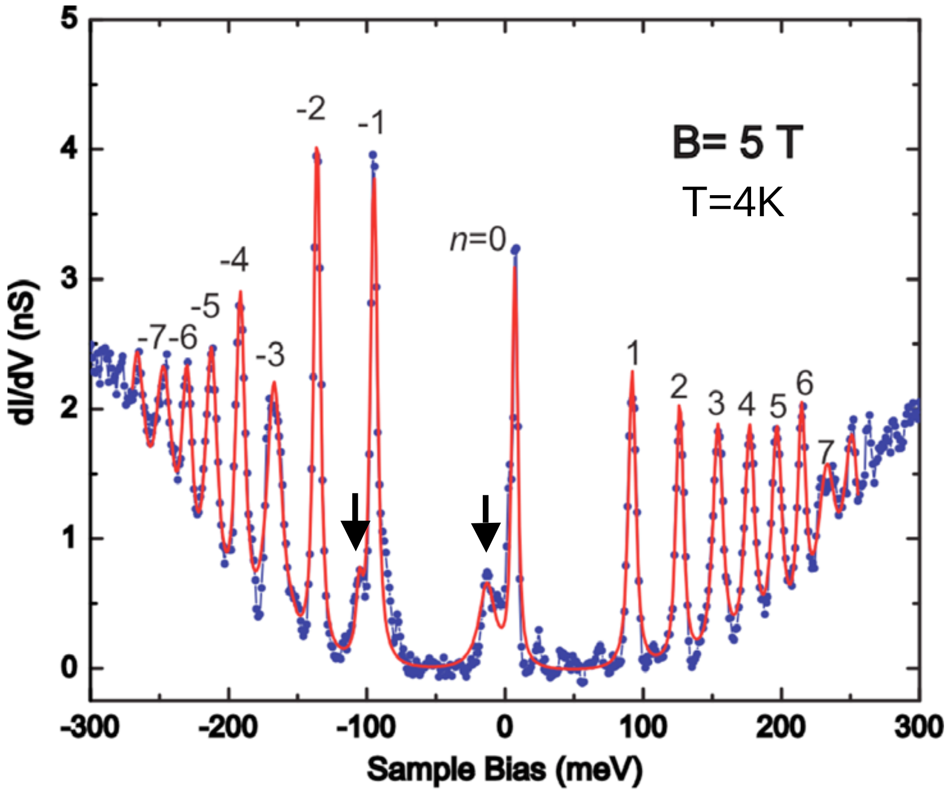
dI/dV (nS)
Sample Bias (mV)
6 T
5 T
4 T
3 T
2 T
1 T
0 T



$E_n - E_0$ (meV)
Sgn(n)(|n|B)$^{1/2}$
1 T
2 T
3 T
4 T
5 T
6 T
7 T
8 T
LL_0 shift
$LL_{n=0}$ (meV)
B (T)

c* = 1.13 x 10^6 m/s

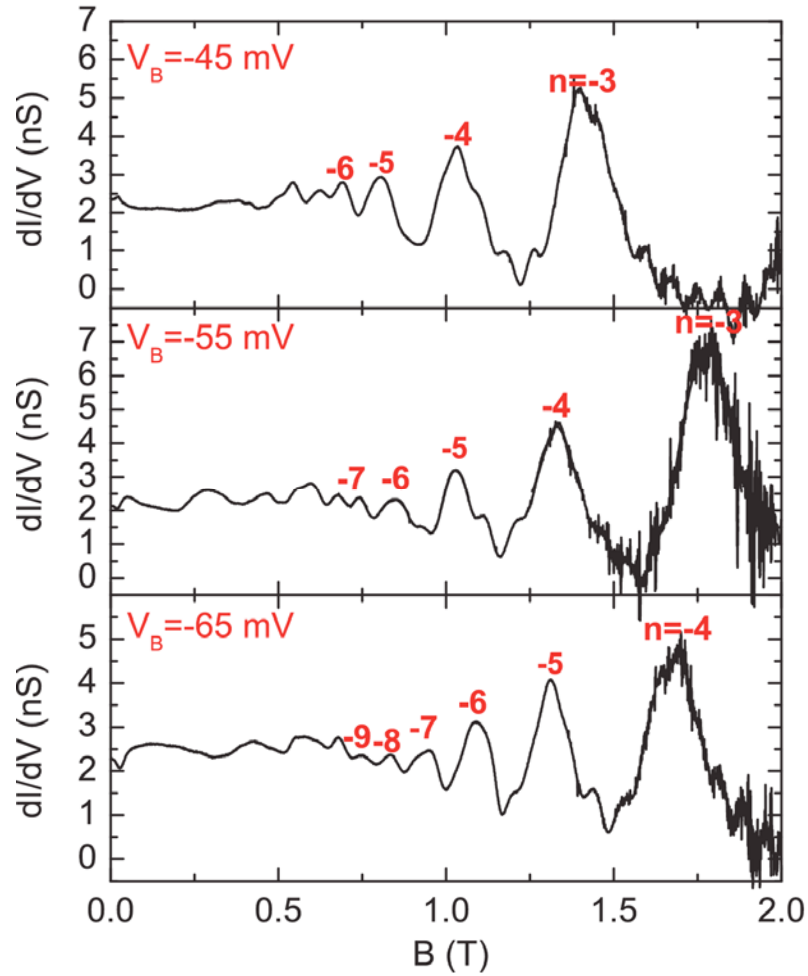
Landau Level Fit

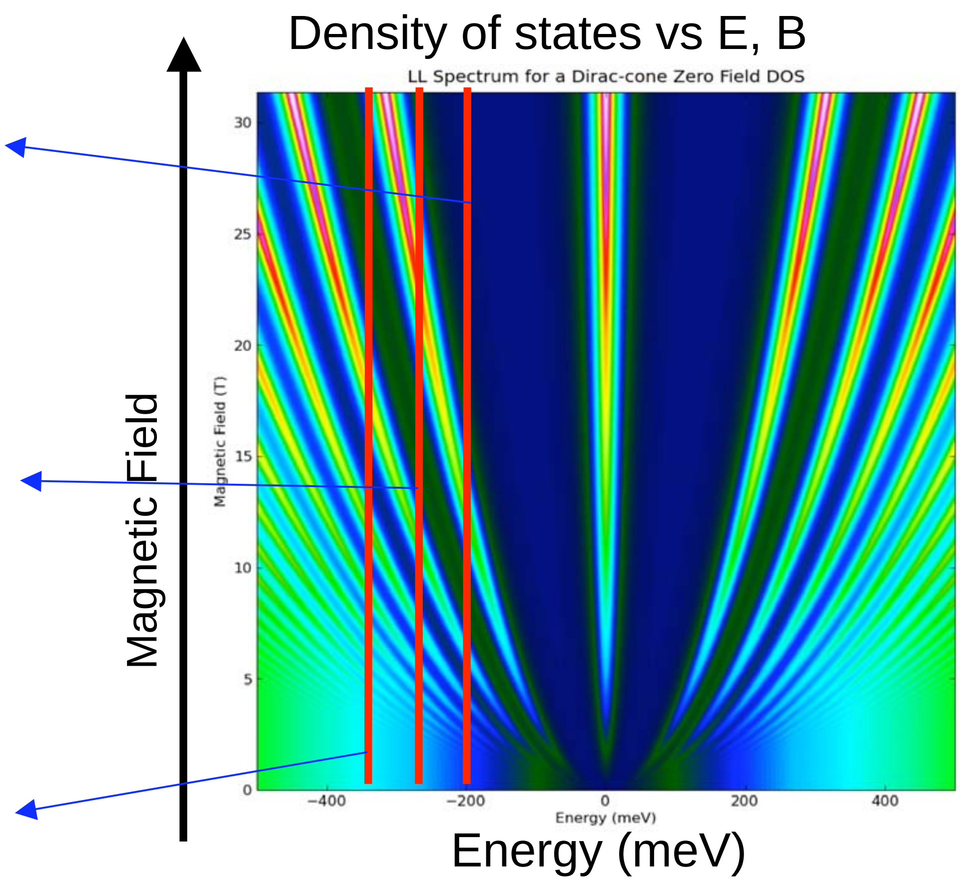


- Simple sum of Voigt functions (Gaussian, Lorentzian convolution)
- Gaussian: 2.8 meV (instrument function + thermal broadening; *fixed*)
- LL_0 Lorentzian: 1.5 meV (0.4 ps lifetime: lower limit to momentum relaxation time)

Tunneling Magnetoconductance Oscillations

(~SdH oscillations, but not restricted to E_F)

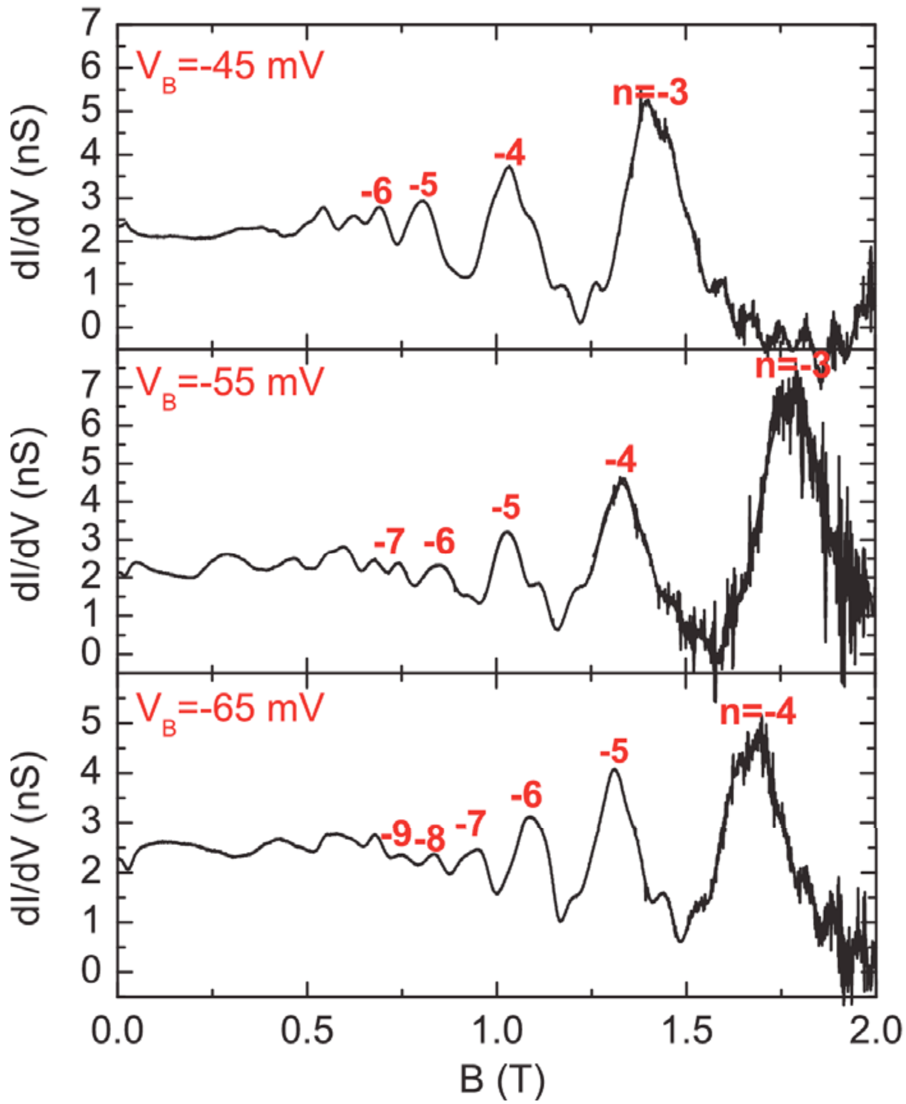


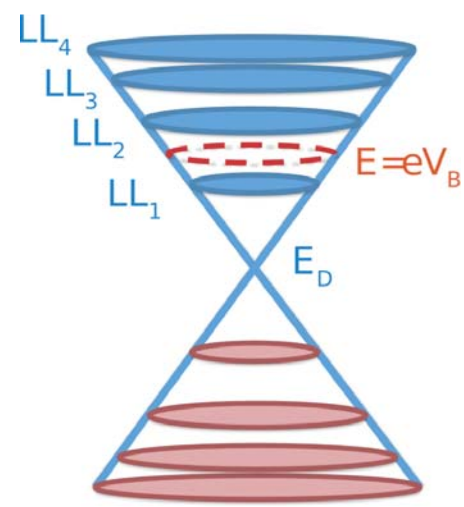


Courtesy P.N.FIrst

Tunneling Magnetoconductance Oscillations

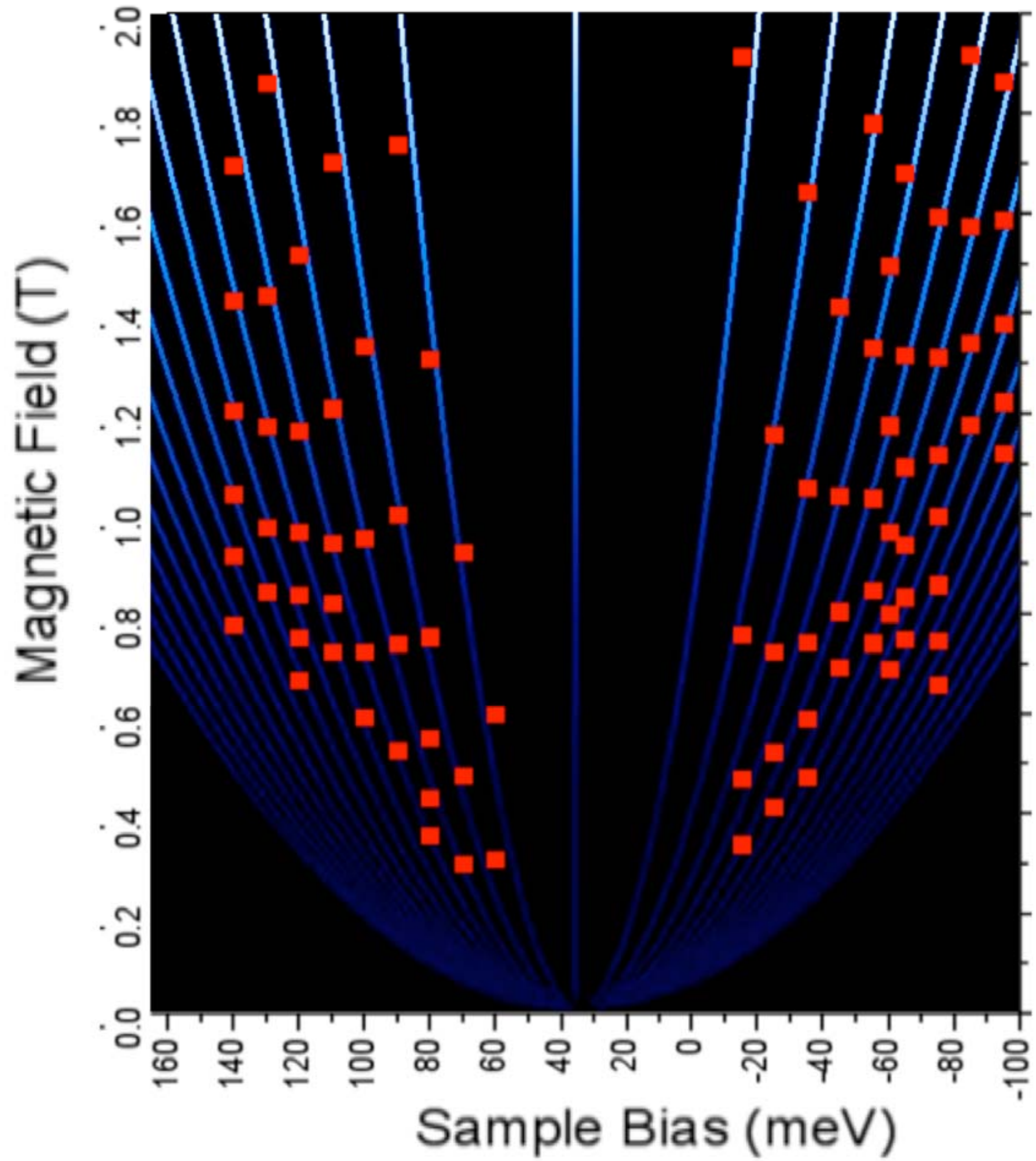
Analogous to SdH oscillations



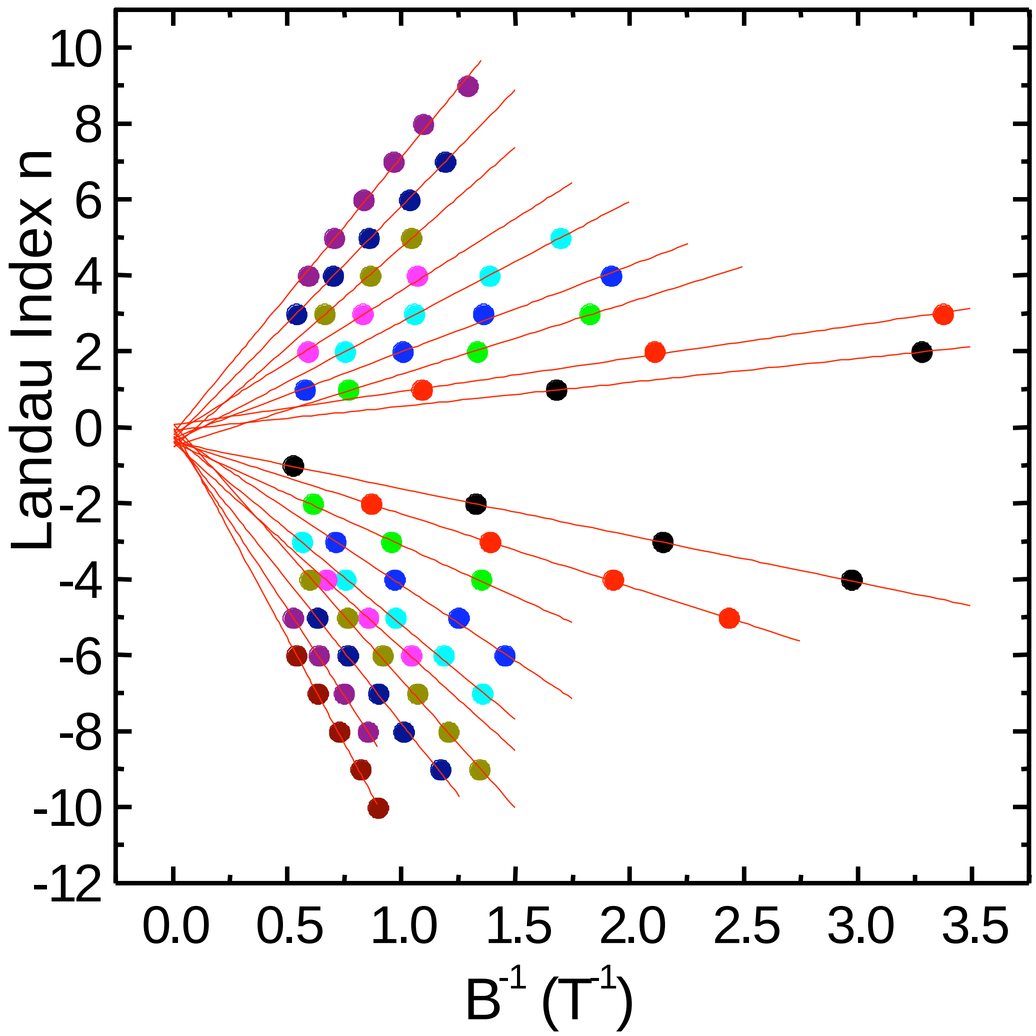


E vs B

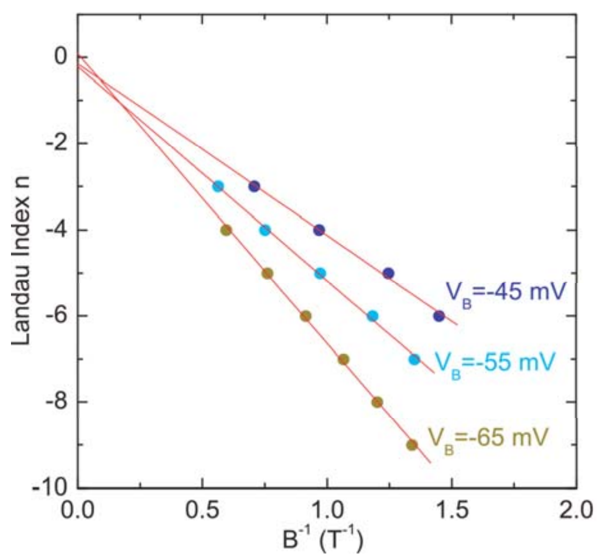
Fit with v= 1.07*10^6,



Fan Plots

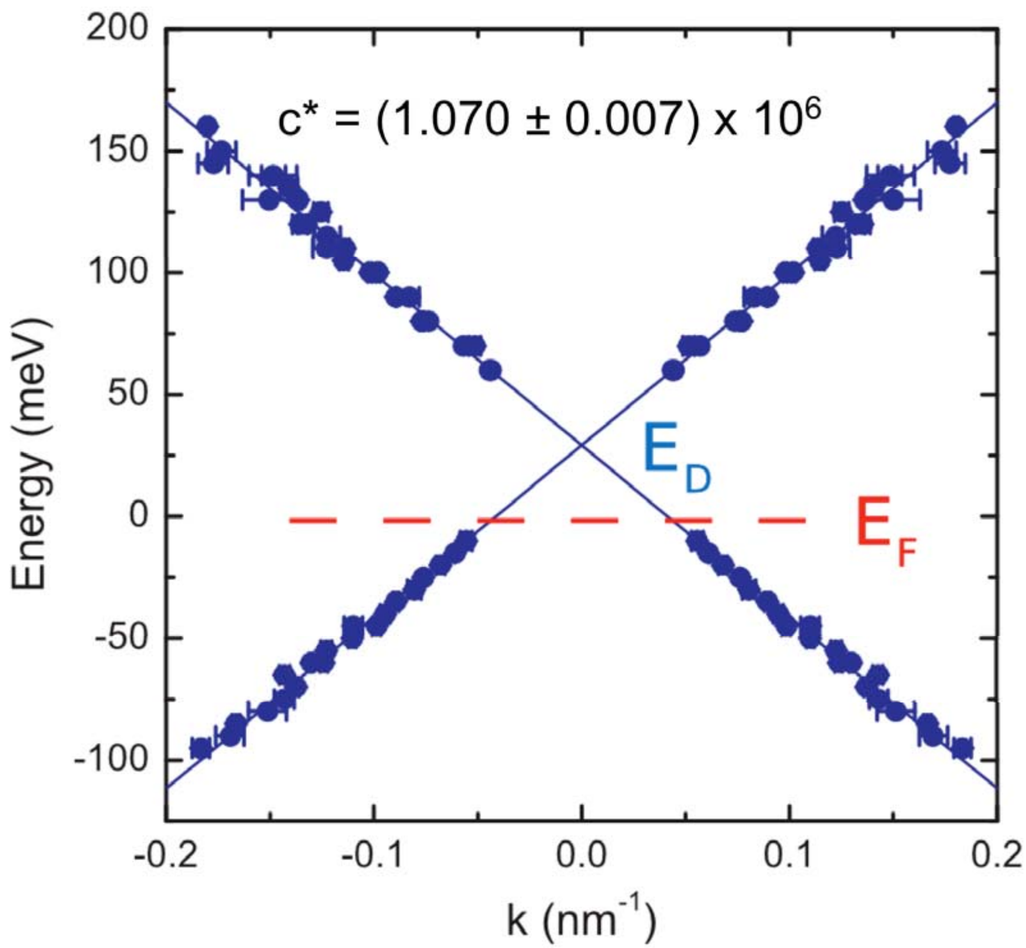


LL index vs 1/B for different energies



$$E_n = \text{sgn}(n)\sqrt{2e\hbar\tilde{c}^2 |n| B} \quad \text{n=0,} \pm 1\ldots$$

Dispersion E(k)



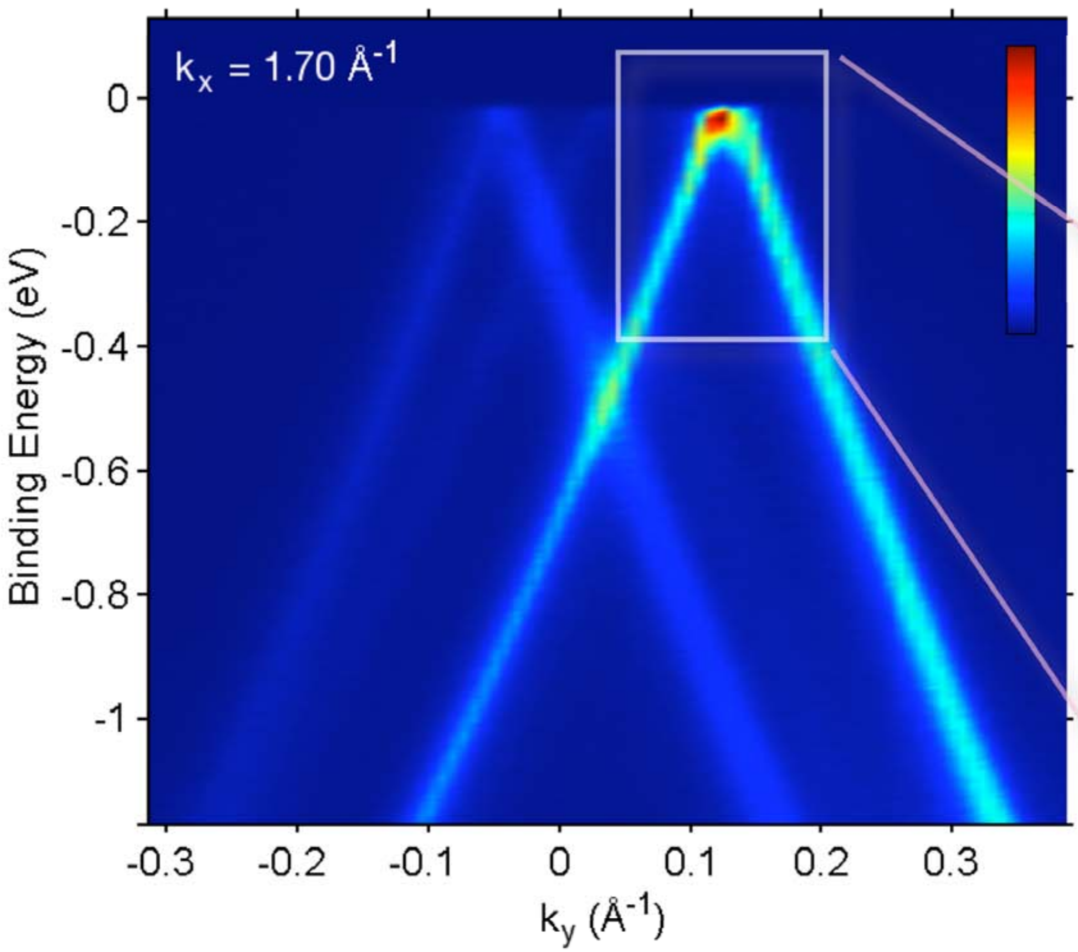
Slight asymmetry

$c^* = (1.044 \pm 0.004) \text{ x } 10^6 \text{ ms}^{-1}$

$c^* = (1.189 \pm 0.007) \text{ x } 10^6 \text{ ms}^{-1}$

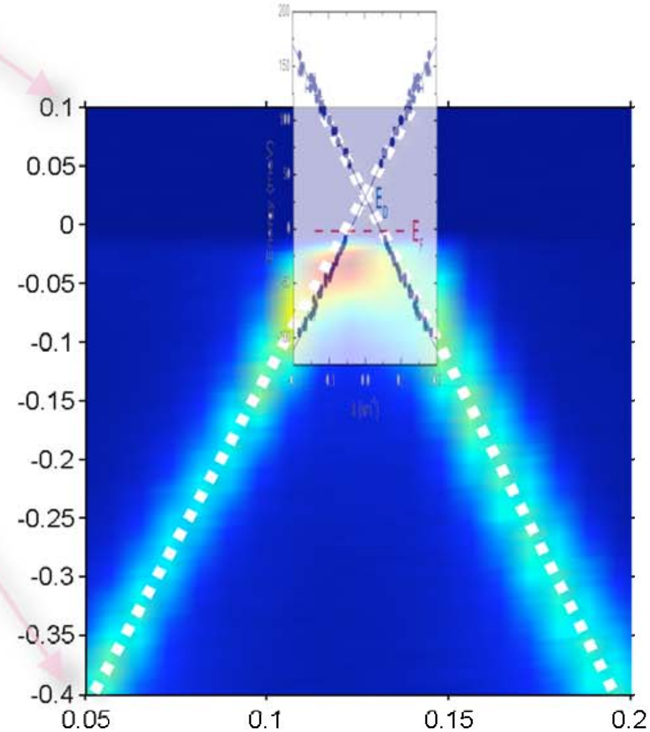
$$E_n = \text{sgn}(n)\sqrt{2e\hbar\tilde{c}^2 \left|n\right| B} \quad \text{n=0, } \pm 1\ldots \quad = \hbar\tilde{c}k$$

ARPES: C-face MEG

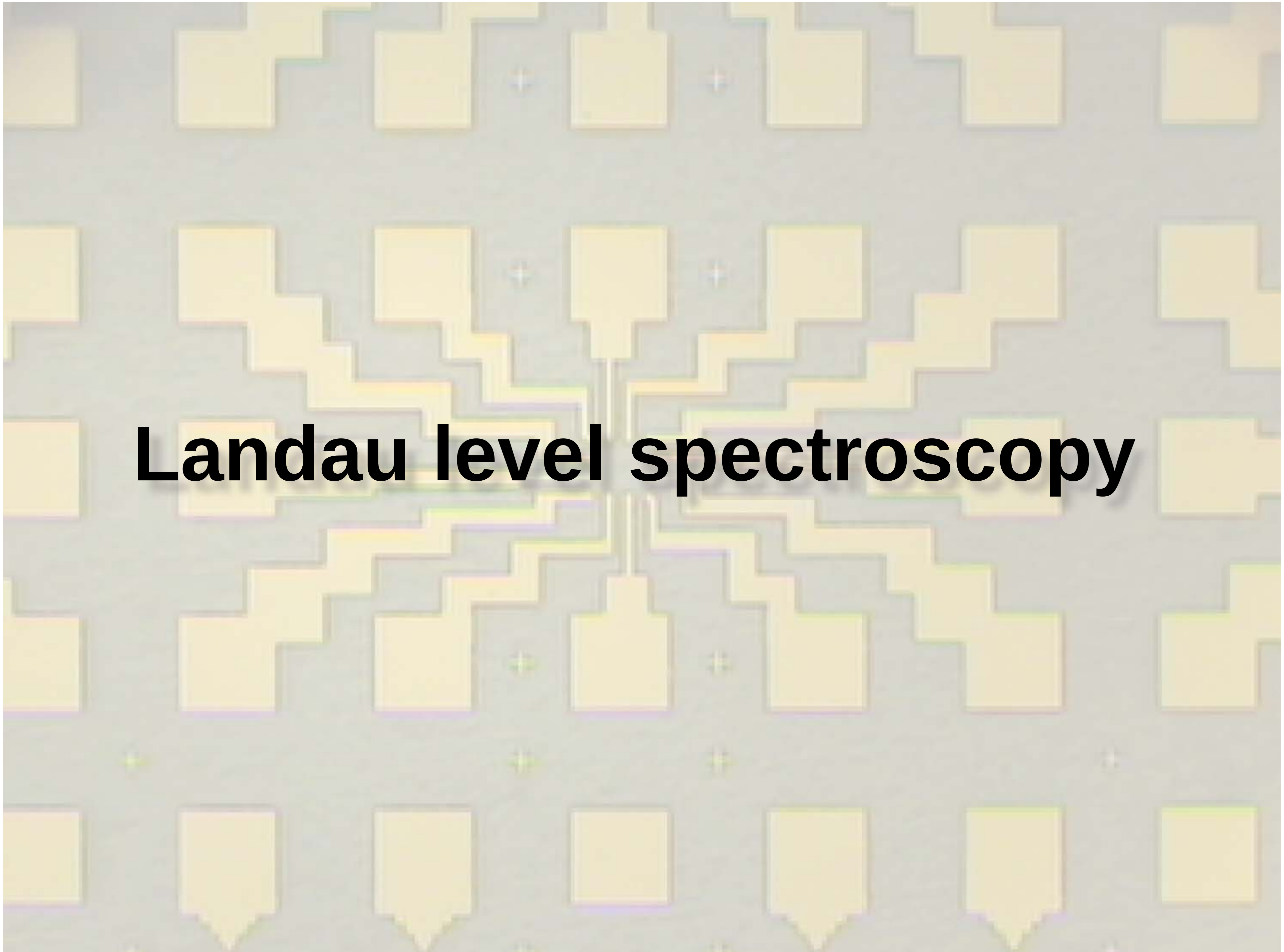


$v_F = 0.87 \pm .02 \times 10^6$ m/s

$E_D - E_F \sim 20 \pm 10$ meV



Landau level spectroscopy



Magneto spectroscopy and Raman scattering of C-face multi layer epitaxial graphene

C. Faugeras, M. Orlita, P. Plochocka, P. Neugebauer, M. Amado Montero, P. Kossacki, A.L. Barra, M.L. Sadowski, D.K. Maude, G. Martinez, M. Potemski

LNCMI

LNCMI-CNRS, Grenoble

cnrs

advancing the frontiers

C. Berger, W.A. de Heer

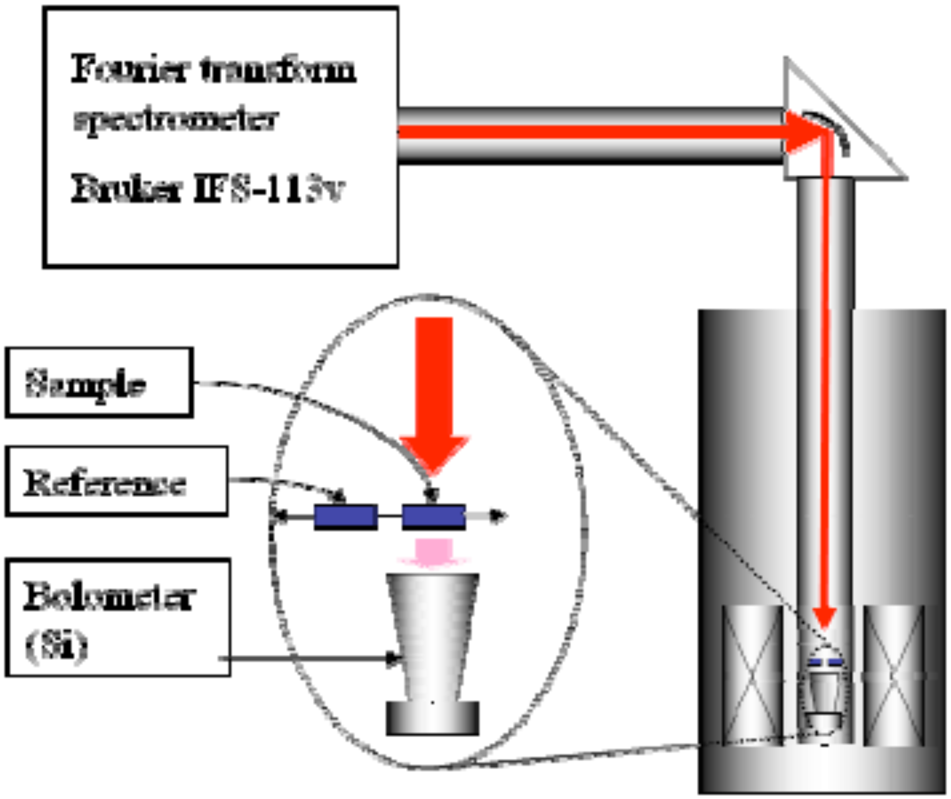
Georgia Tech, Atlanta

Georgia Institute of Technology

Courtesy C. Faugeras

FIR and MIR Experimental setup

Far and middle infrared transmission (FIR and MIR) spectroscopy in magnetic fields
= Landau level spectroscopy



Relative change of the sample transmission at finite magnetic field:

$$\frac{T(B)}{T(B=0)}$$

Magnetic field up to

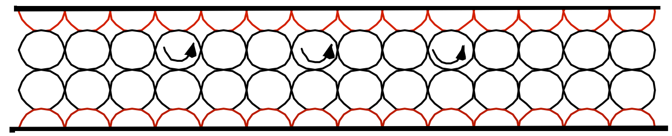
$$B = 34\ \mathrm{T}$$

Possibility to perform <u>absolute transmission measurement</u>

Bands in a magnetic field : Landau level

Energy quantization $2\pi r_c \equiv n\lambda_F$

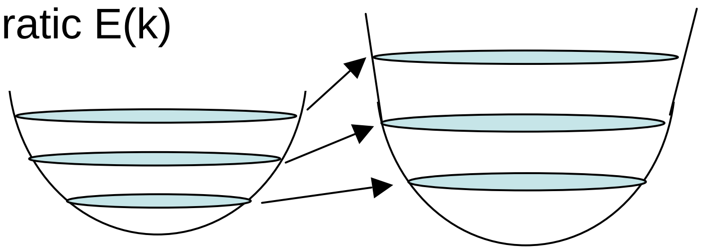
$r_c = p/eB \quad \lambda_F = 2\pi / k_F$

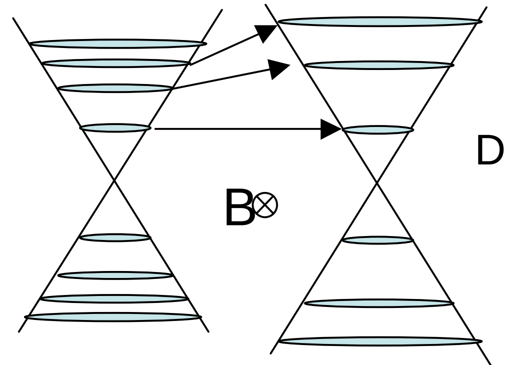


⊙ B

Normal electrons:
quadratic E(k)

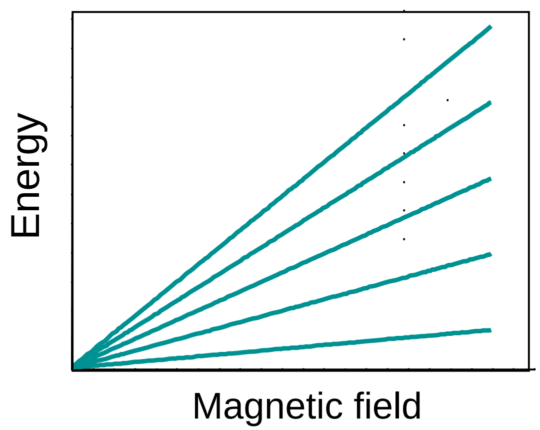
B⊗



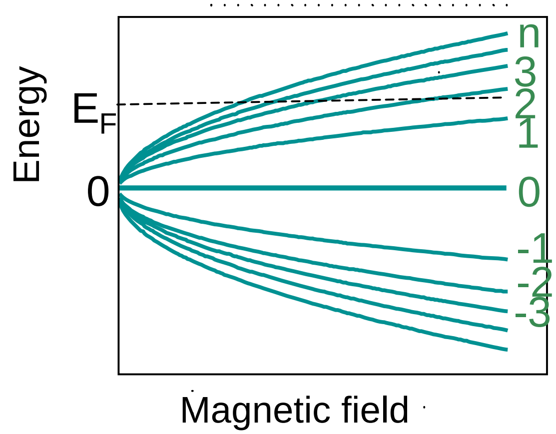


B⊗

Dirac particles:
linear E(k)

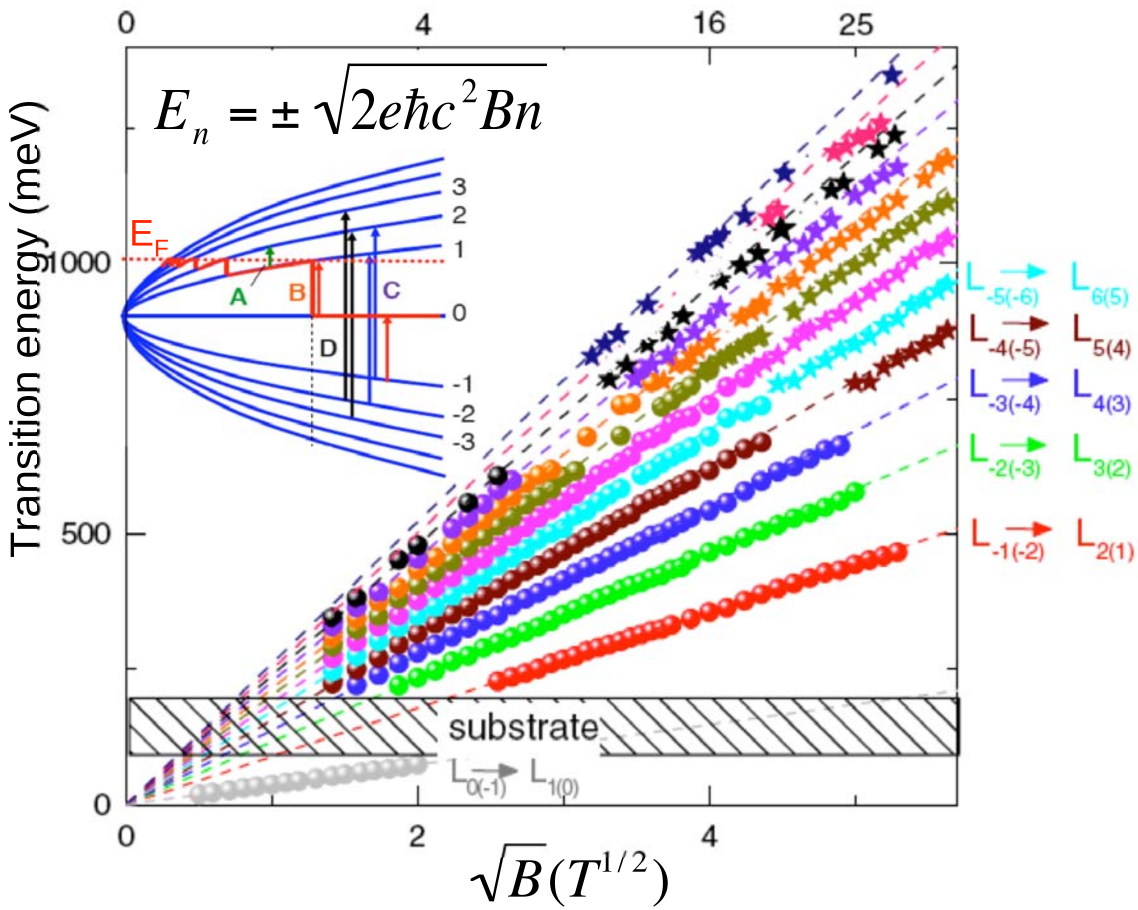


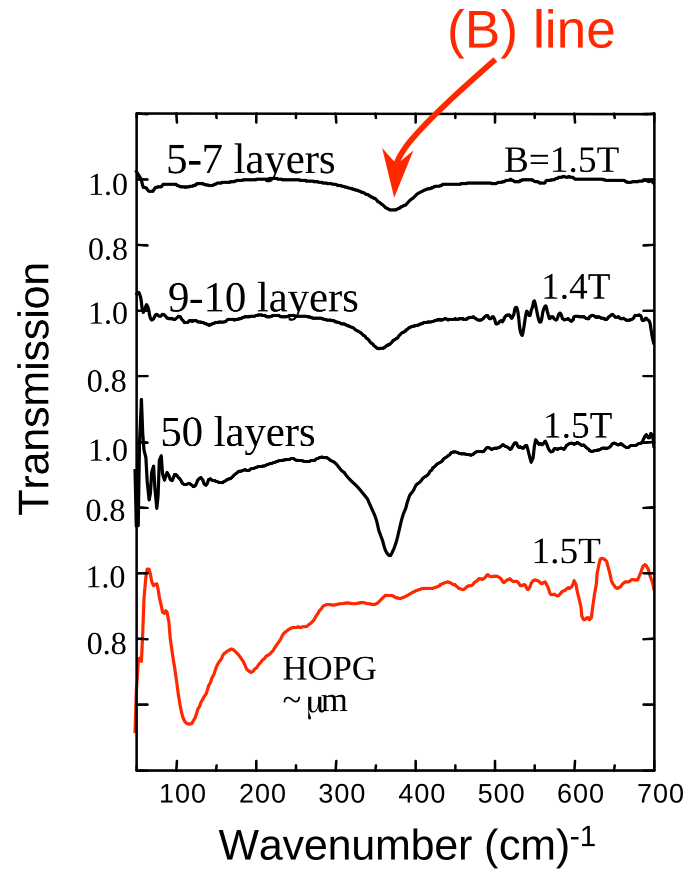
$$E_n = (n + \frac{1}{2})\frac{\hbar eB}{m^*}$$



$$E_n = \pm\sqrt{2e\hbar c^2 Bn}$$

Landau Spectra of C-face Graphene



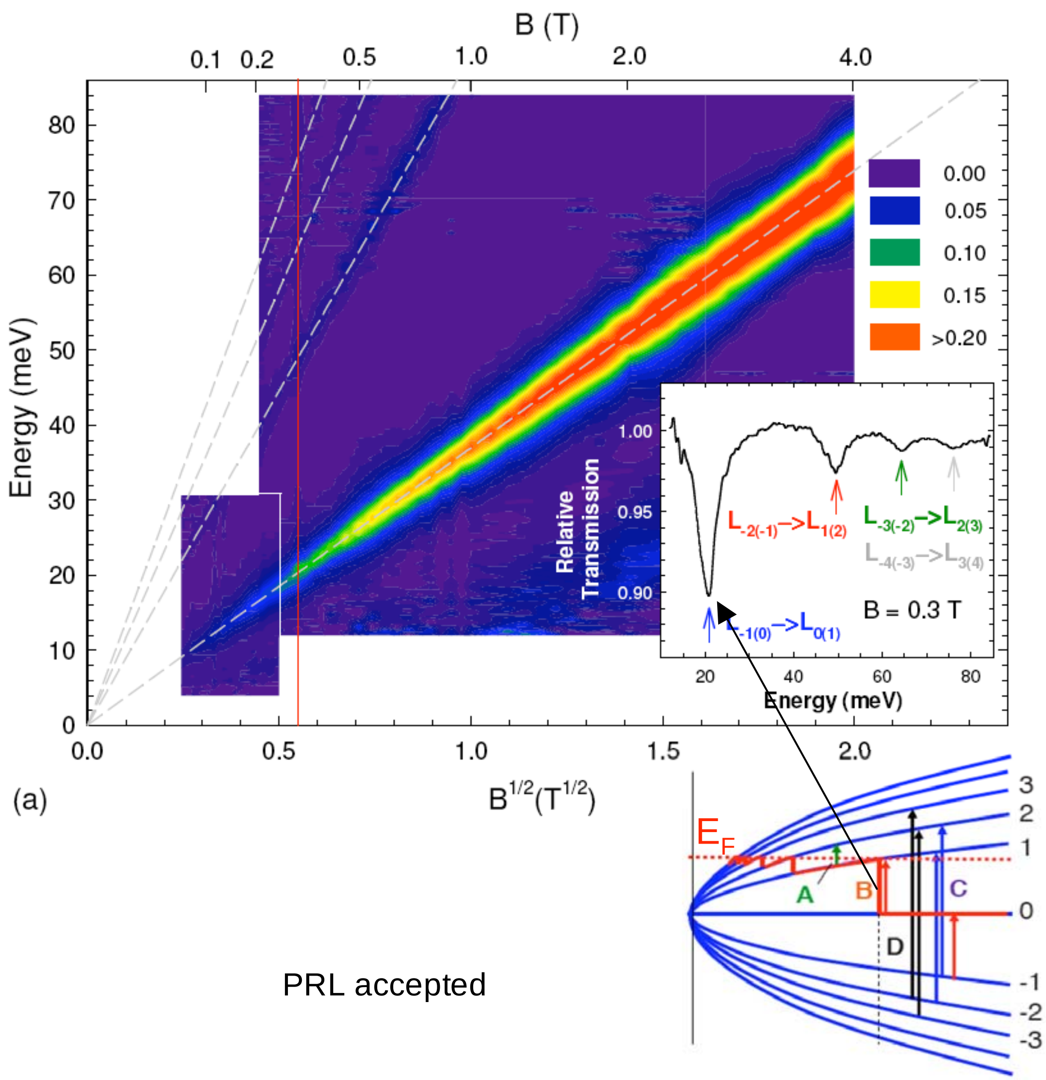


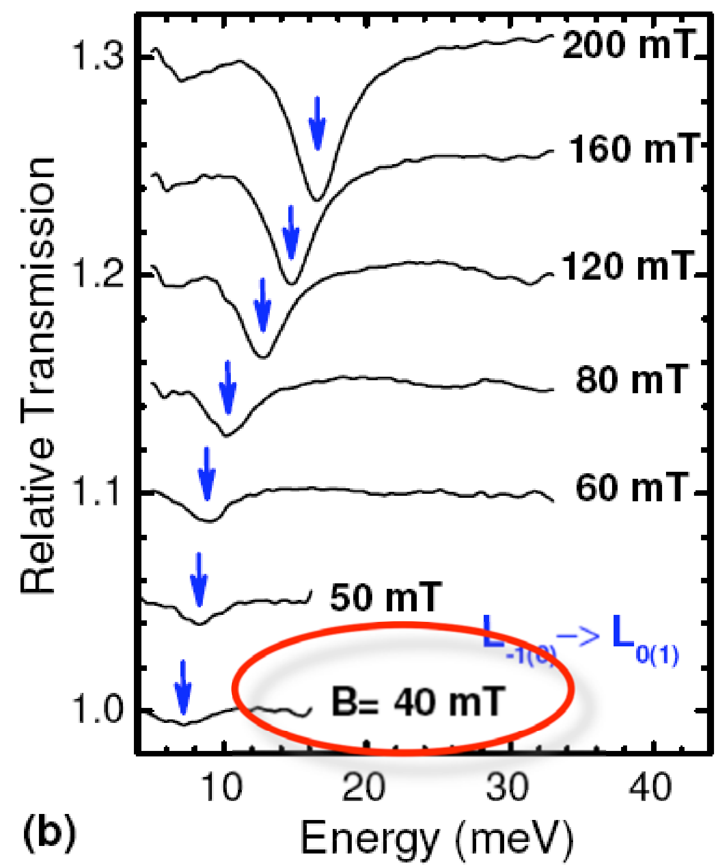
M. Potemski, G.Martinez, CNRS-LCMI

IR cyclotron resonance spectroscopy

Approaching the Dirac point in high mobility multilayer epitaxial graphene

M. Orlita,[1,2,3,*] C. Faugeras,[1] P. Plochocka,[1] P. Neugebauer,[1] G. Martinez,[1] D. K. Maude,[1] A.-L. Barra,[1] M. Sprinkle,[4] C. Berger,[4,5] W. A. de Heer,[4] and M. Potemski[1]

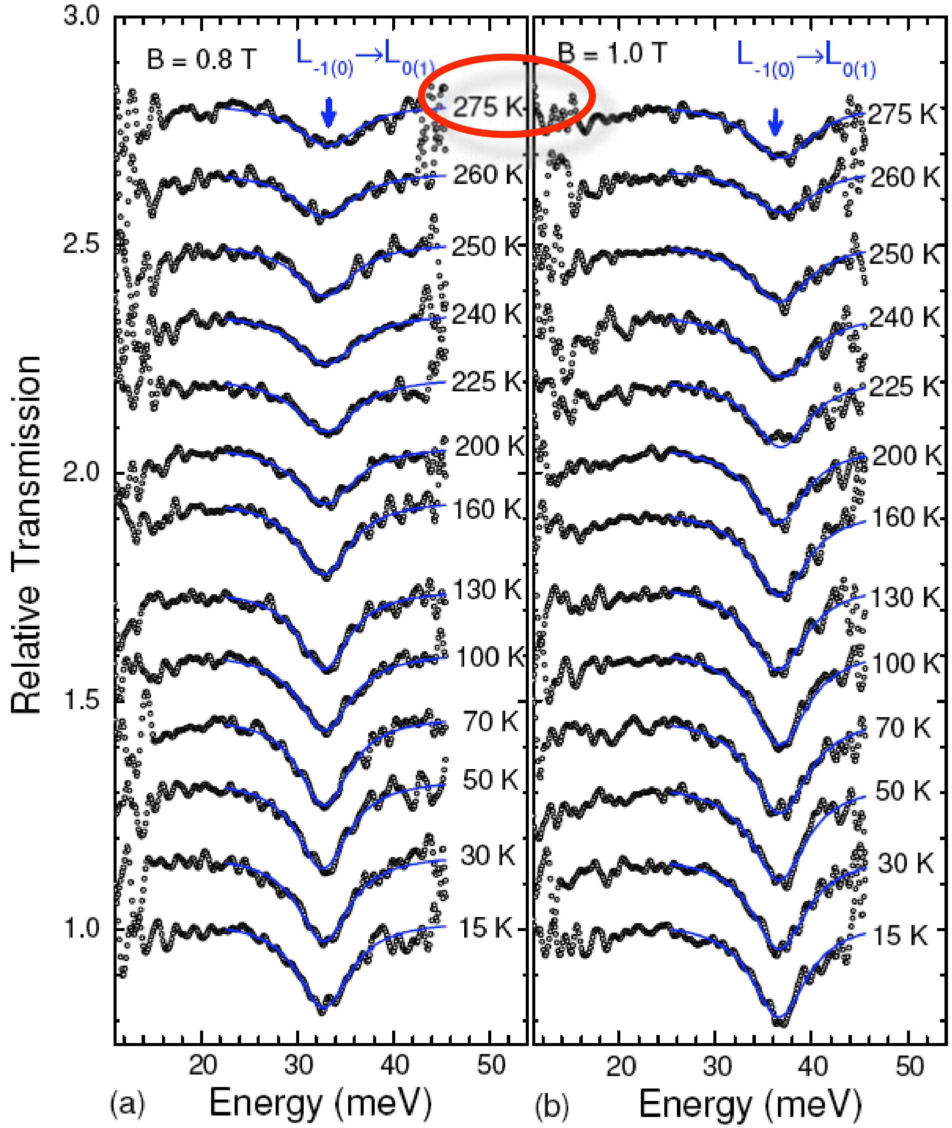




PRL accepted

μ>250,000

IR cyclotron resonance spectroscopy



LL's visible at RT below 1T.

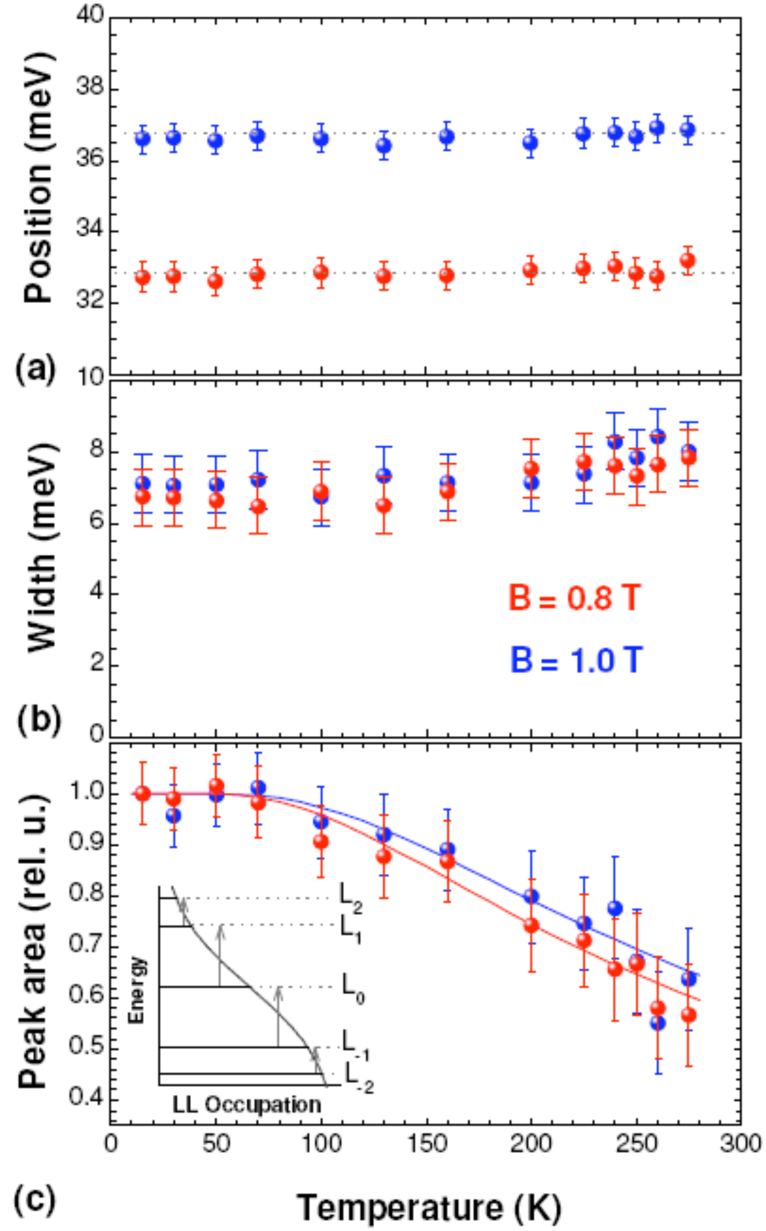
MEG Landau Levels

Temperature Independent LL's.

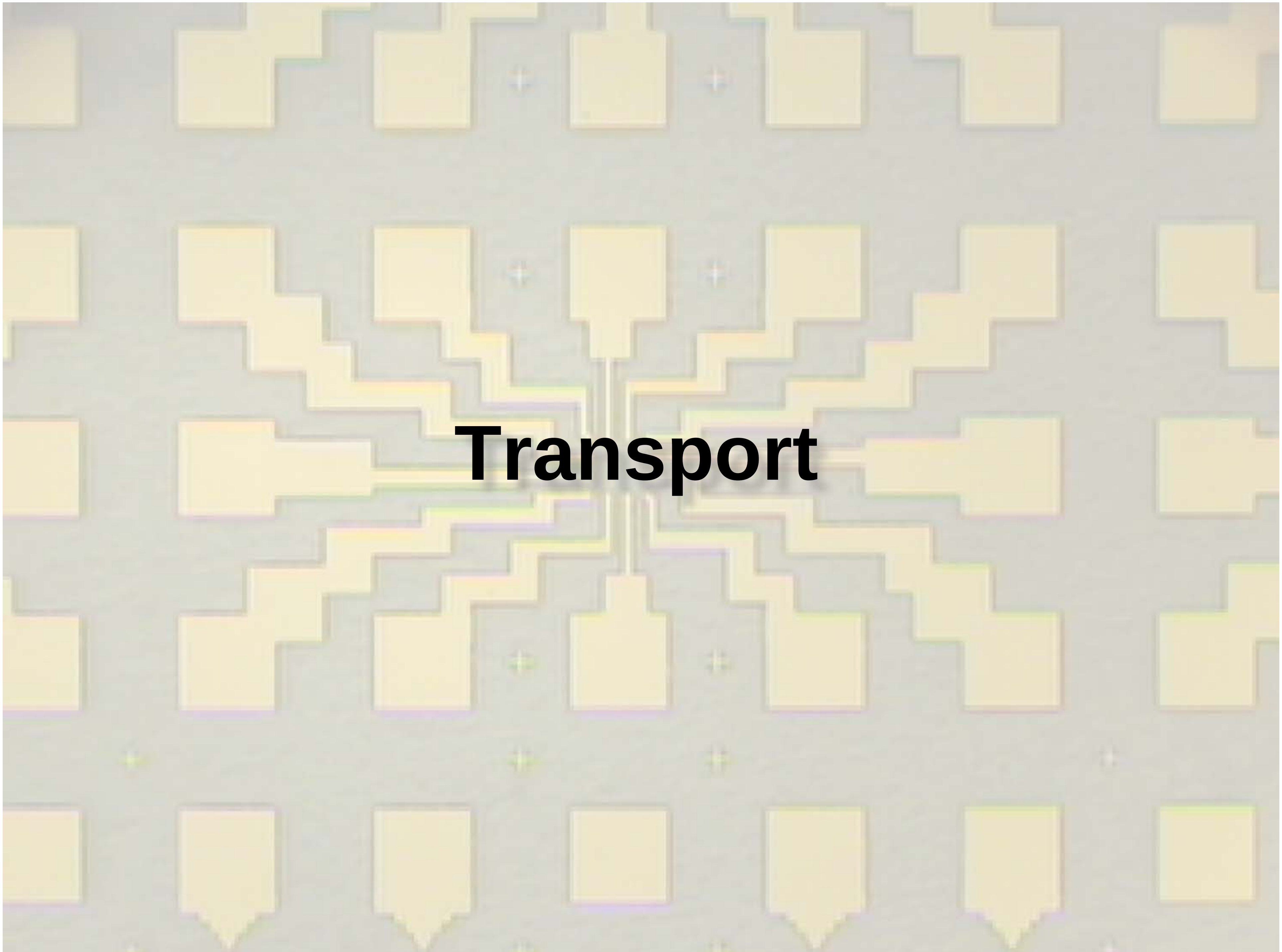
Temperature Independent widths

Boltzmann population of levels

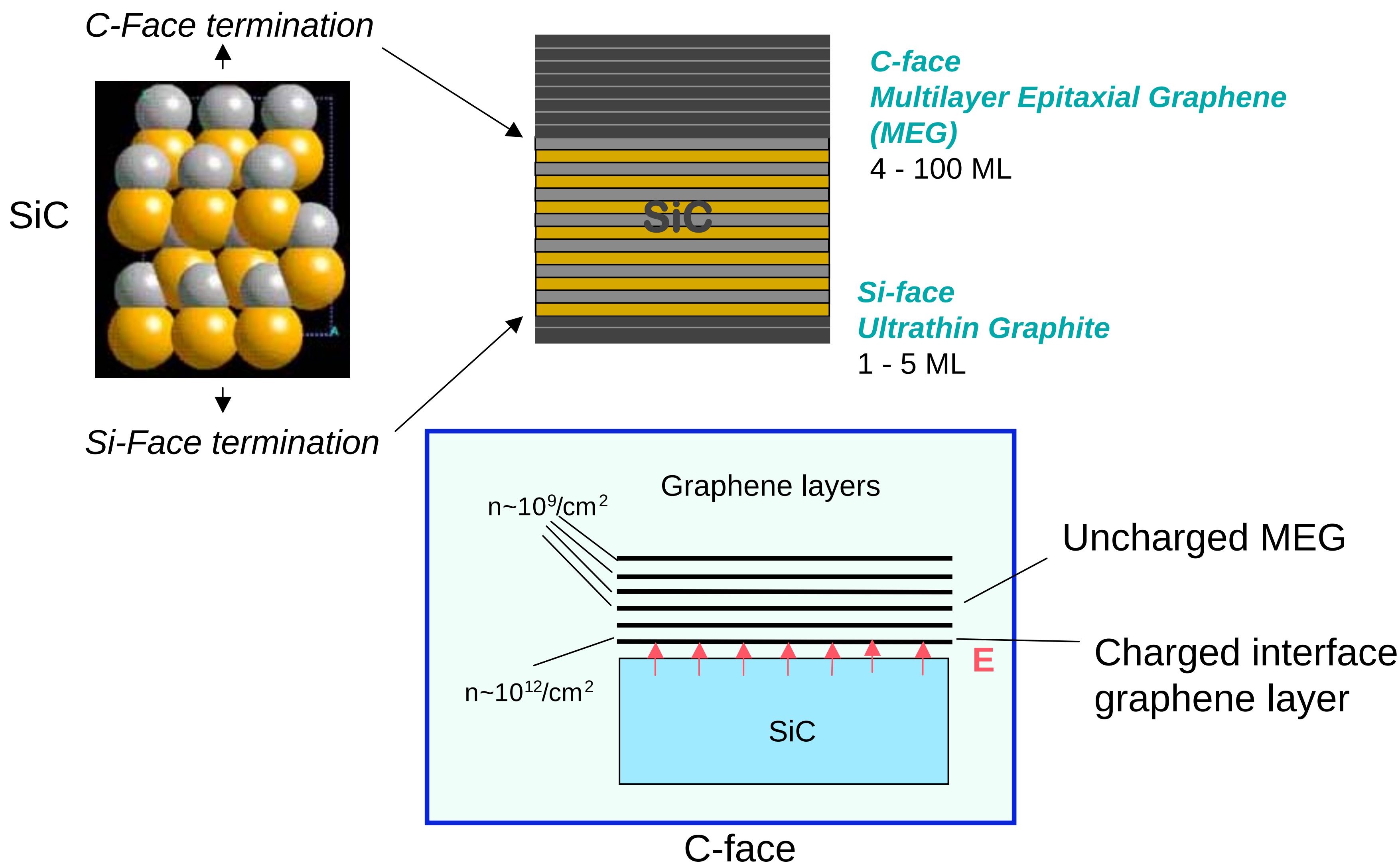
Weak Electron-Phonon Coupling: μ>250,000 at RT



Transport

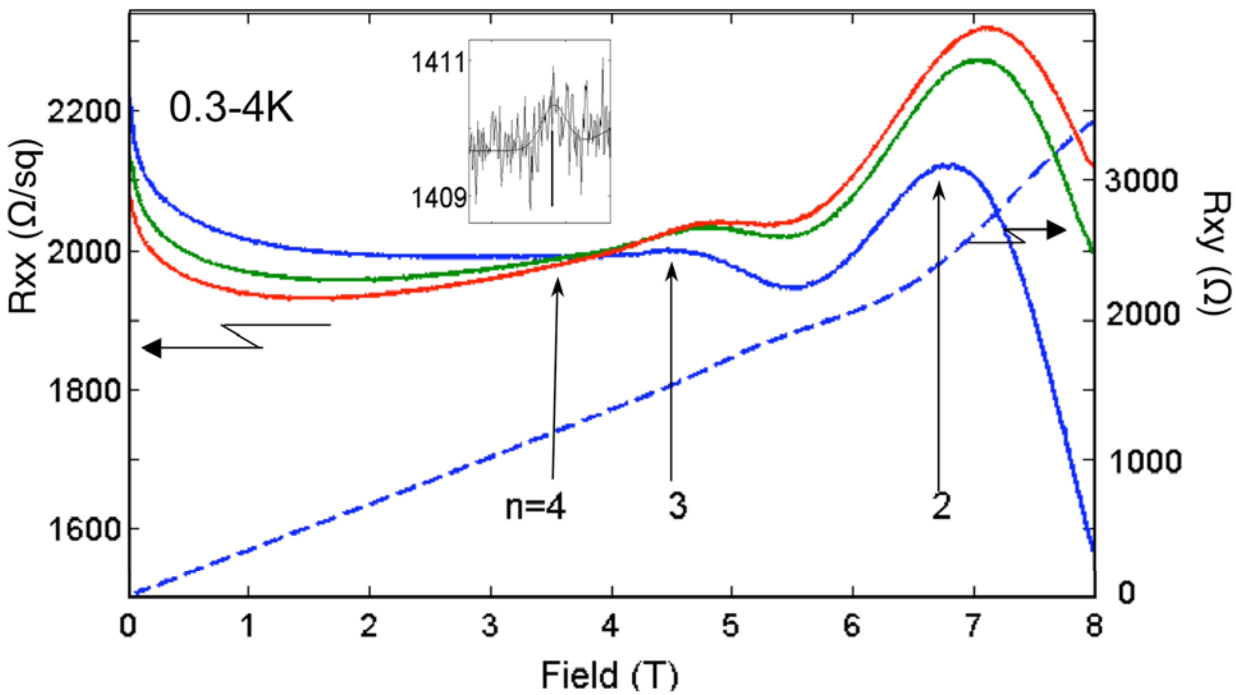


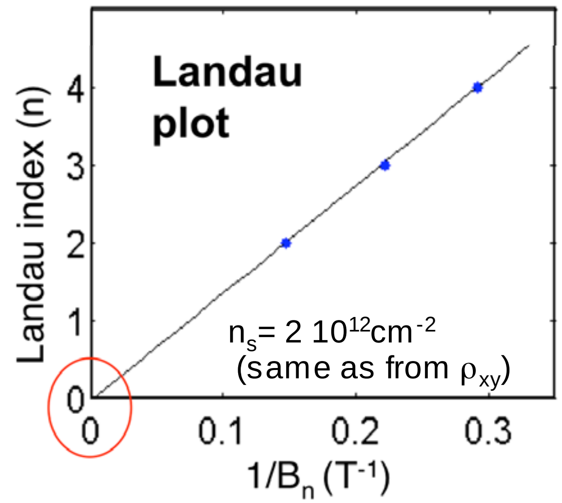
Epitaxial Graphene on 4H-SiC



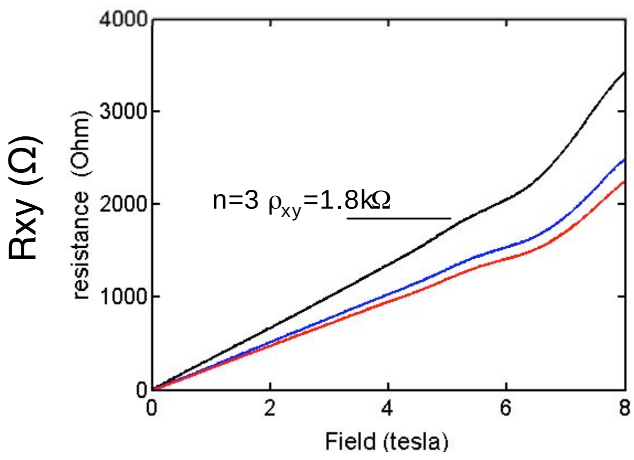
Magneto-transport of 1-2 graphene layers on Si-face

Hall bar 400X800 µm Si-face, UHV grown, µ=1000





Berry's phase=π



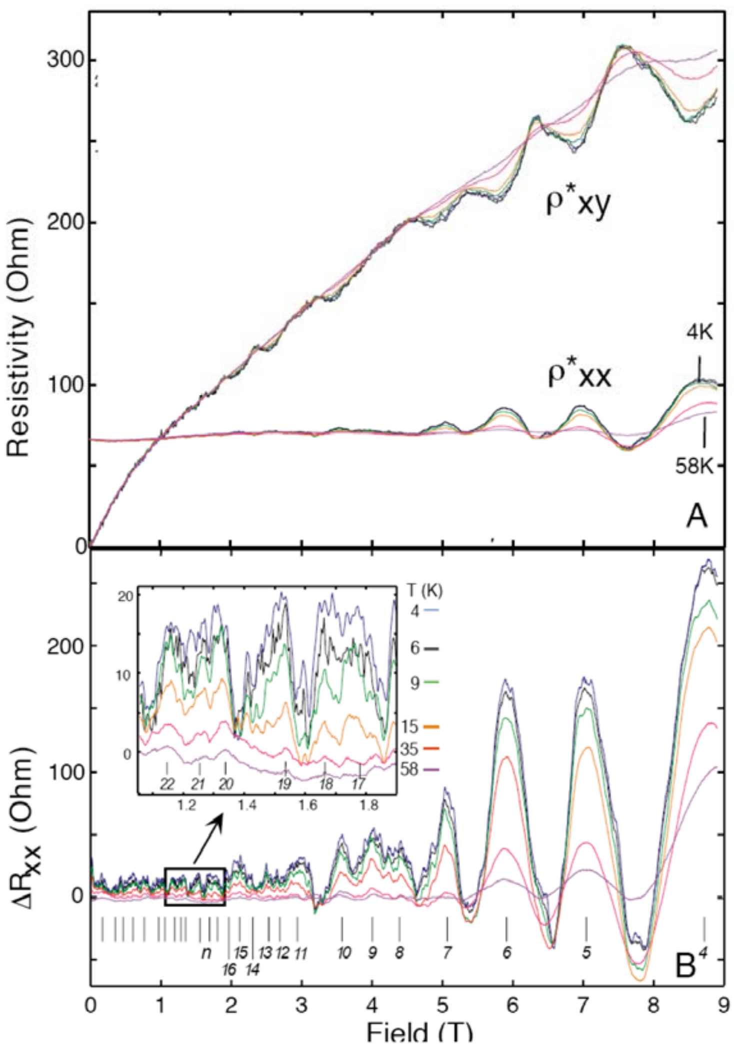
Berger et al. J. Chem. Phys. 2004

Electronic Confinement and Coherence in Patterned Epitaxial Graphene

SCIENCE VOL 312 26 MAY 2006

Claire Berger,[1,2] Zhimin Song,[1] Xuebin Li,[1] Xiaosong Wu,[1] Nate Brown,[1] Cécile Naud,[2] Didier Mayou,[2] Tianbo Li,[1] Joanna Hass,[1] Alexei N. Marchenkov,[1] Edward H. Conrad,[1] Phillip N. First,[1] Walt A. de Heer*

T=4,6, 9, 15, 35 and 58 K; -9 T≤B≤9 T.



C-face

Hall bar

1μmX200 nm

μ^*=27000cm²/Vs.

Landau levels:

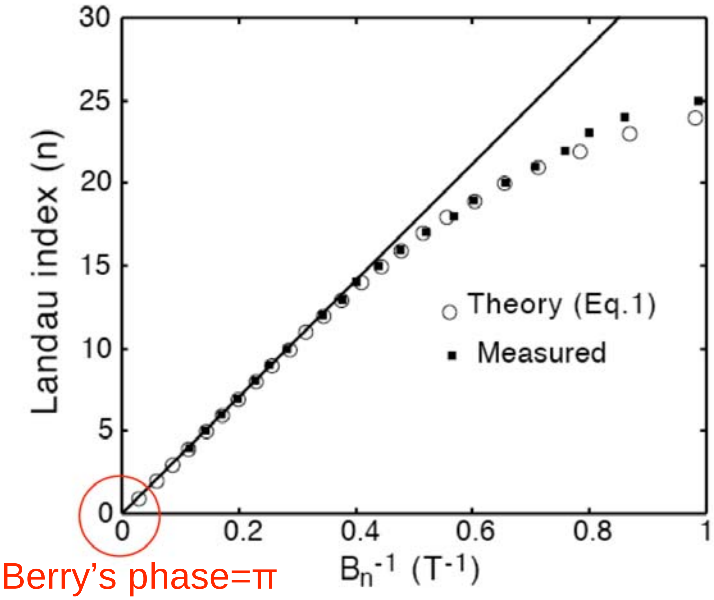
$E_n(B)=\sqrt{(2neBv_0^2)}$

Confinement:

$E_n(W)=n\pi v_0/W$

Confined Landau levels:

$E_n(B,W)\approx [E_n(W)^4+E_n(B)^4]^{1/4}$

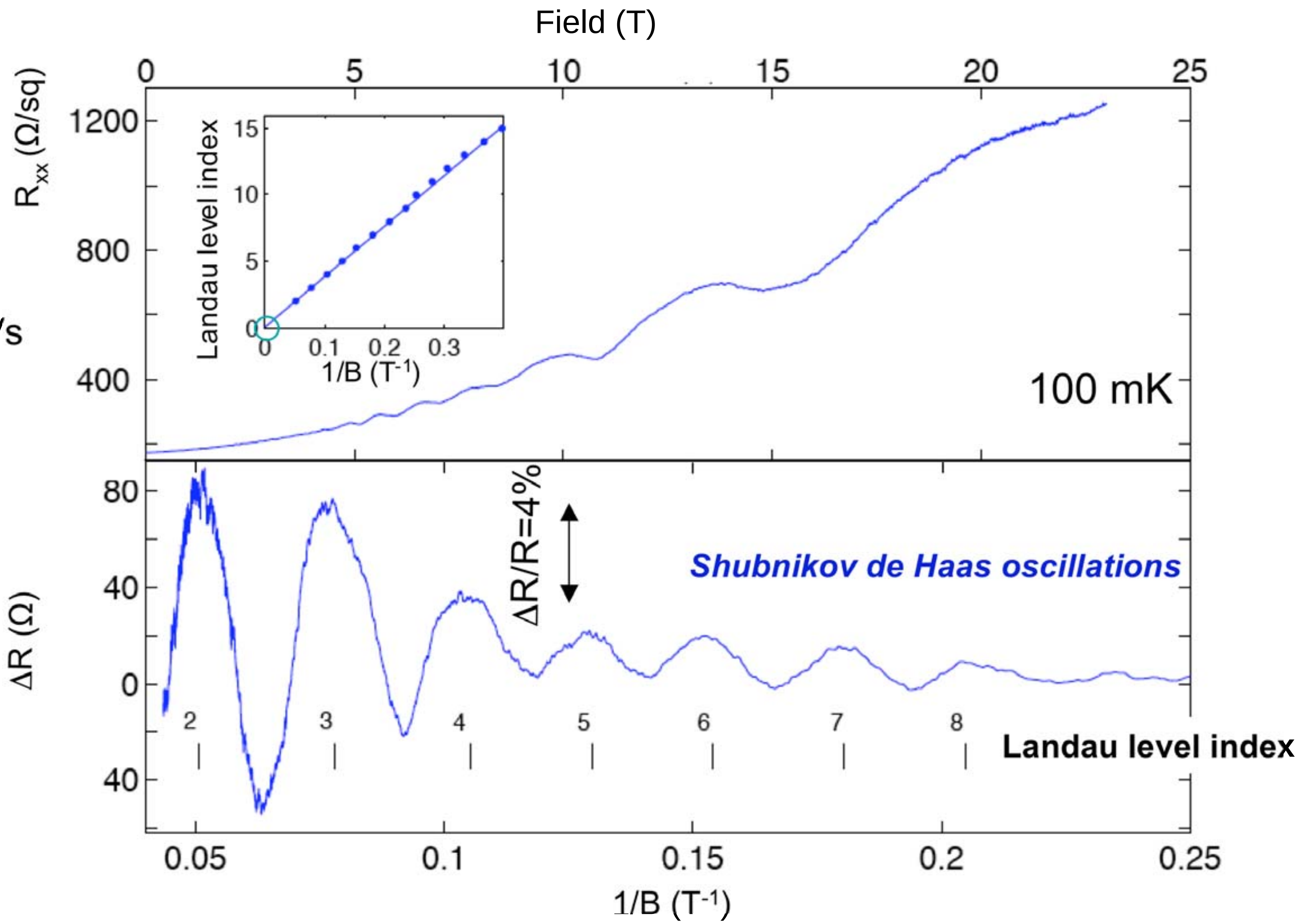


Berry's phase=π

Magnetotransport: graphene like; Berry's phase =π (No QHE)

Hall bar
C-face

1μm x 6.5μm
R= 502 Ω/sq
μ= 10000 cm^2/Vs

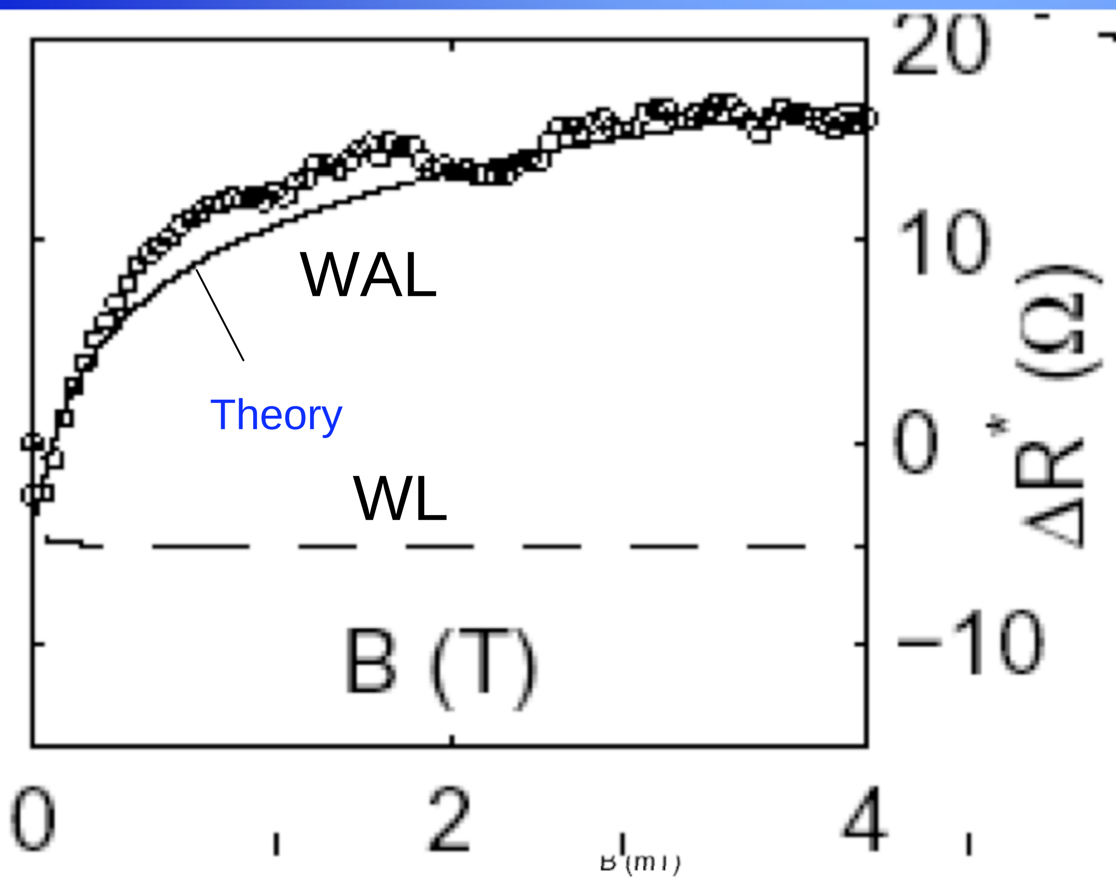


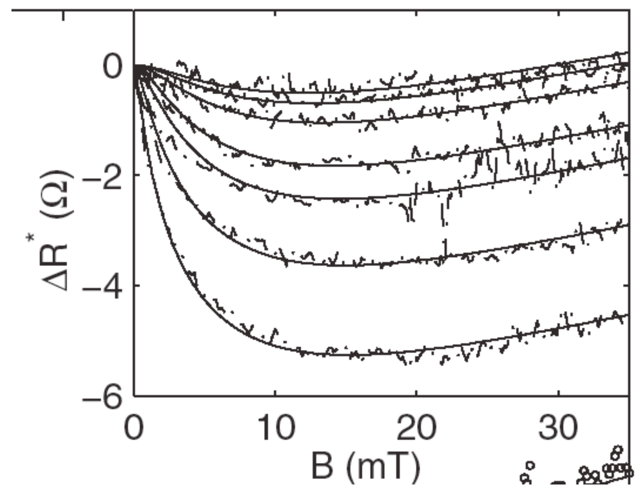
Solid State Com. 2007,Grenoble/GIT collaboration

PRL **98,** 136801 (2007) PHYSICAL REVIEW LETTERS week ending 30 MARCH 2007

Weak Antilocalization in Epitaxial Graphene: Evidence for Chiral Electrons

Xiaosong Wu,[1] Xuebin Li,[1] Zhimin Song,[1] Claire Berger,[1,2] and Walt A. de Heer[1]





C-face Hall bar

τ_ϕ phase coherence time

τ_w warping-induced relaxation time

τ_{iv} intervalley scattering time

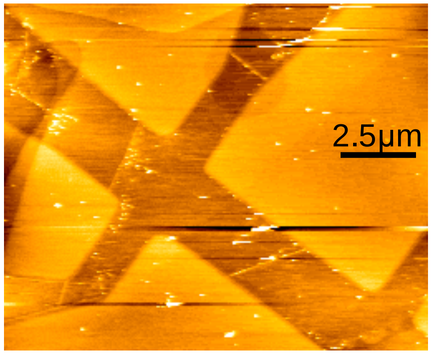
$\tau_B = \hbar/2eDB$

D is the diffusion constant

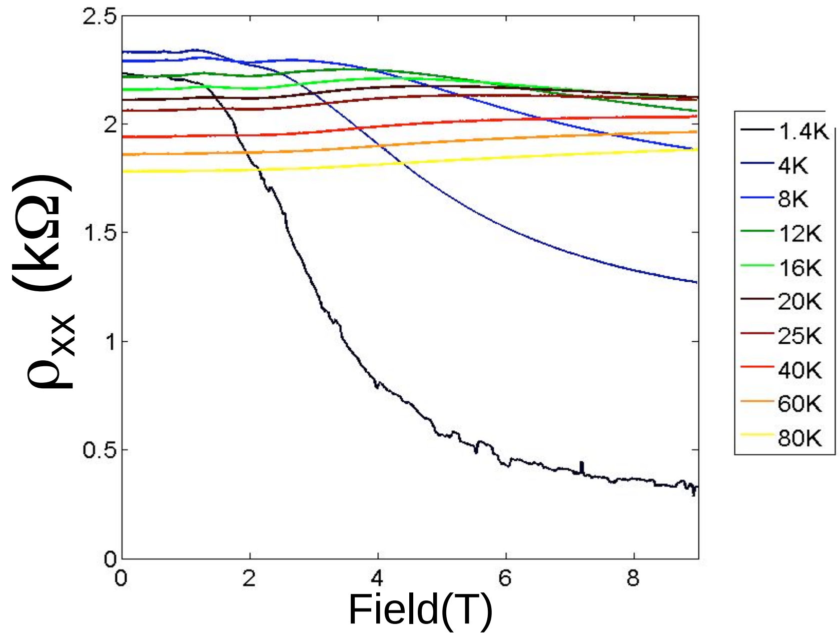
$$\Delta\rho(B) = -\frac{e^2\rho^2}{\pi h}\left[F\left(\frac{2\tau_\phi}{\tau_B}\right) - F\left(\frac{2}{\tau_B(\tau_\phi^{-1} + 2\tau_{iv}^{-1})}\right) - 2F\left(\frac{2}{\tau_B(\tau_\phi^{-1} + \tau_{iv}^{-1} + \tau_w^{-1})}\right)\right]$$

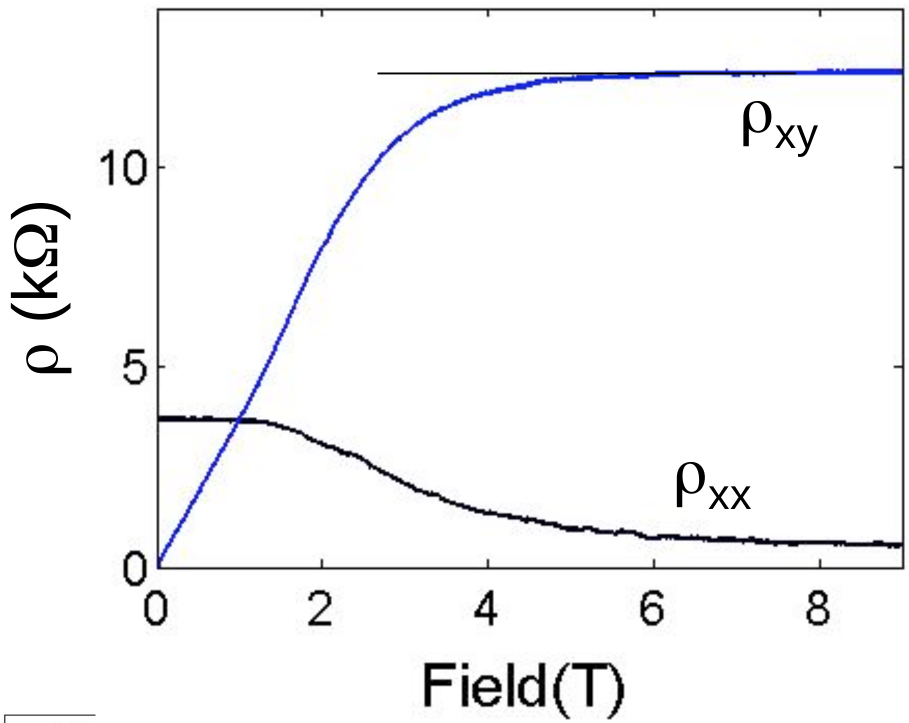
Magnetotransport of ~1 graphene sheet on C-face

Cross etched in a flat terrace



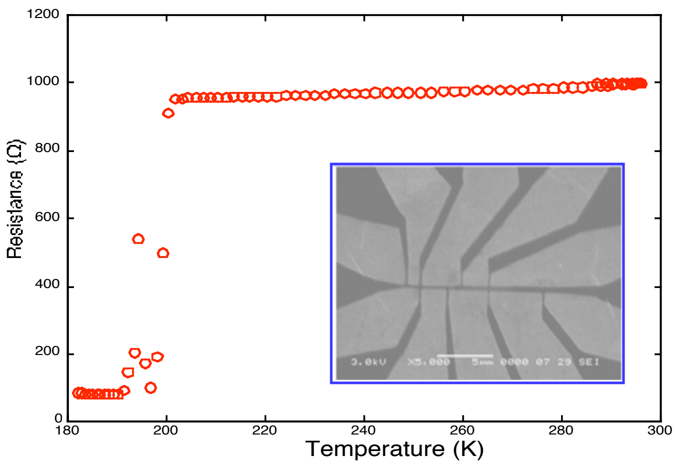
μ~ 9000 cm^2/Vs
n_s=1.6 $10^{11}cm^{-2}$

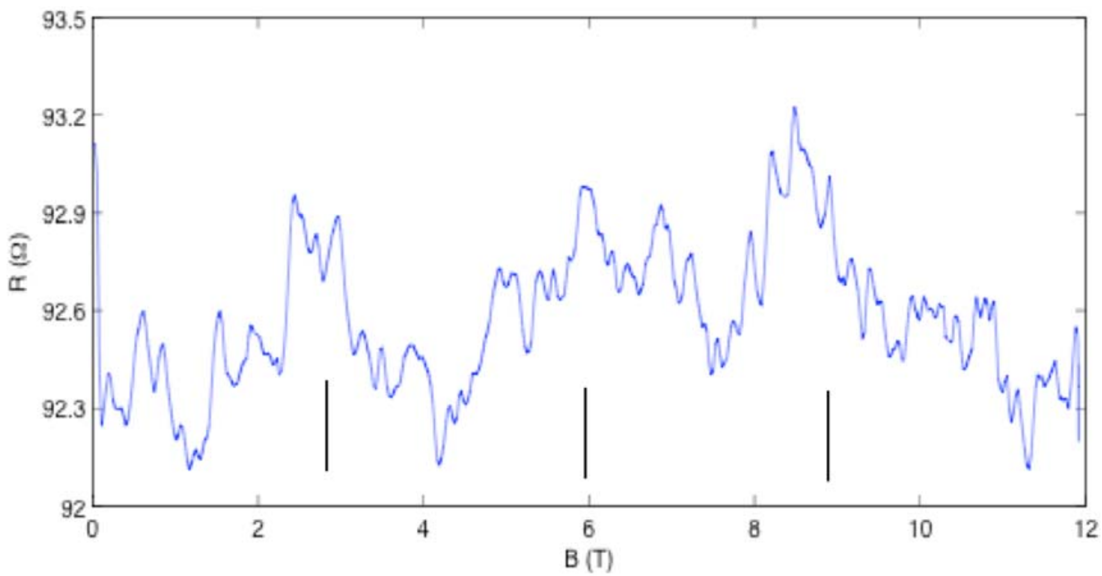




Anomalous Conductance Transition

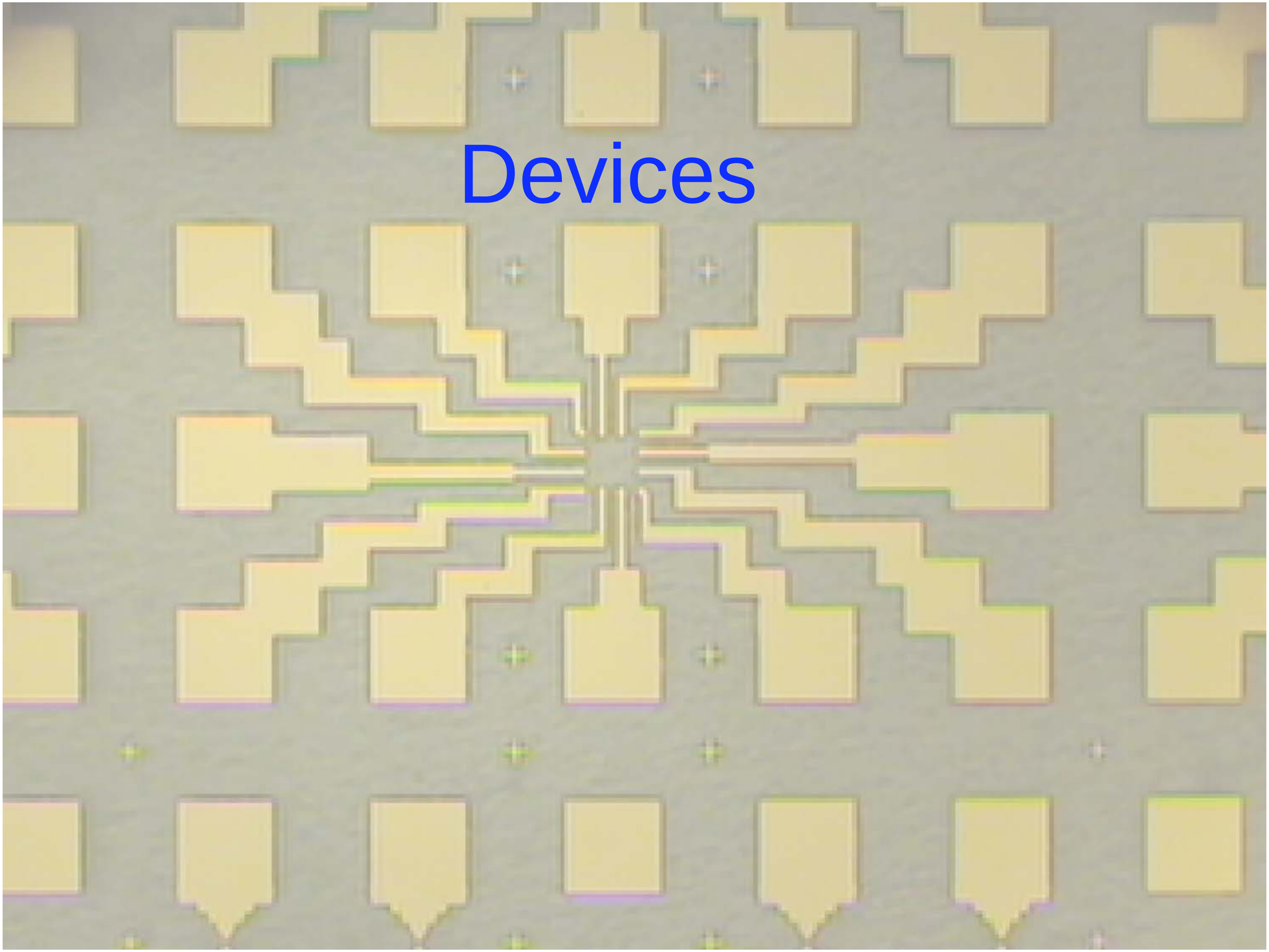
- A reversible, reproducible, drop in the conductivity is observed at 200K.
- The resistance is at its theoretical minimum .
- Transport is <u>phase coherent over the entire structure (0.5X5 μm).</u>
- Resistance is at its theoretical minumum (no boundary scattering!)
- Oscillations periodic in the magnetic field are seen.



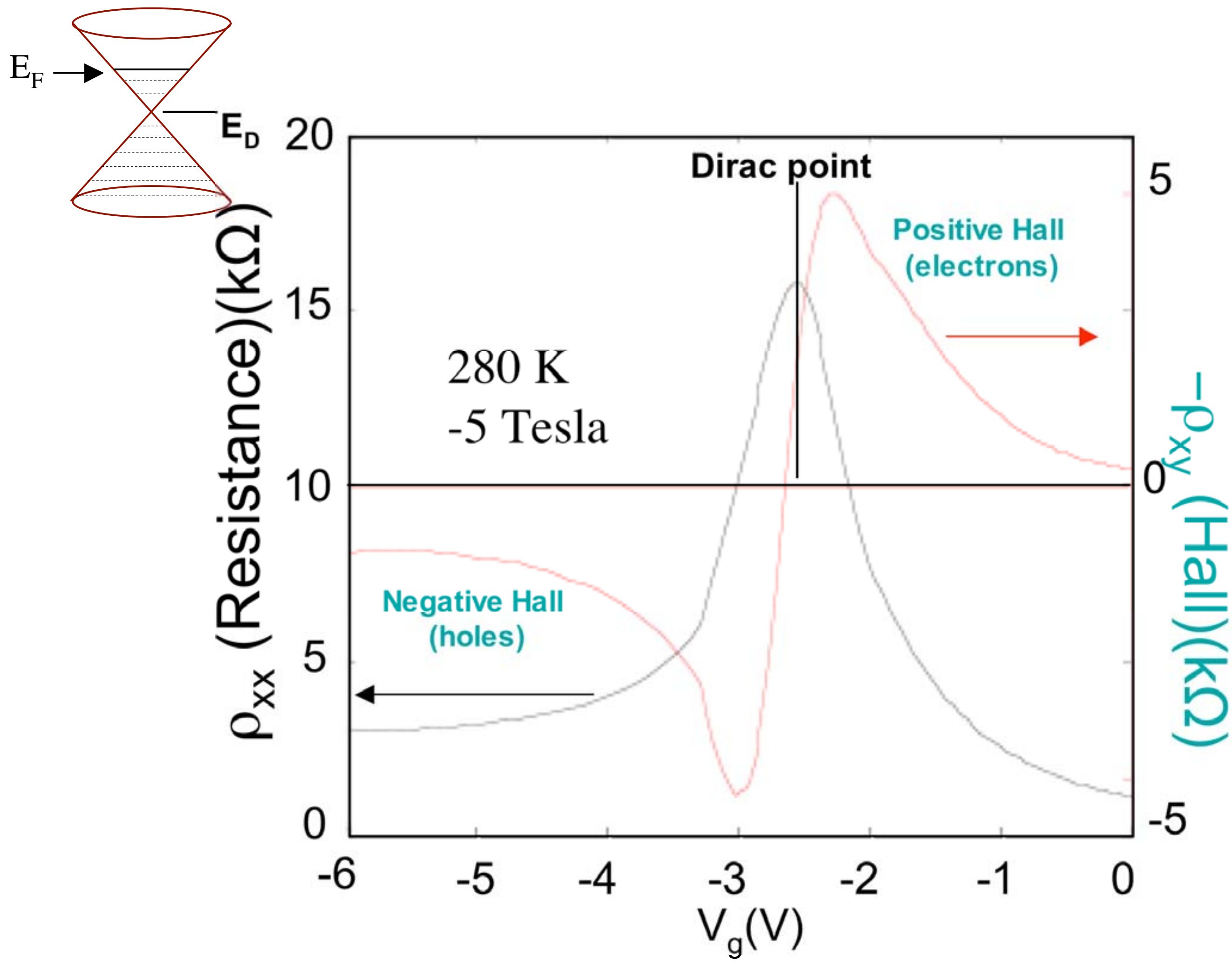


Could this be the Hoffstadter butterfly?
(Moire with a 20 nm lattice constant)

Devices

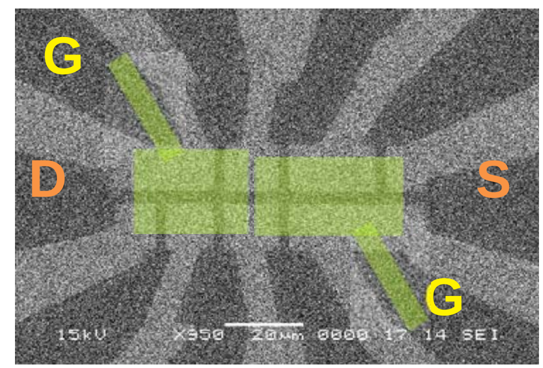


The Dirac point

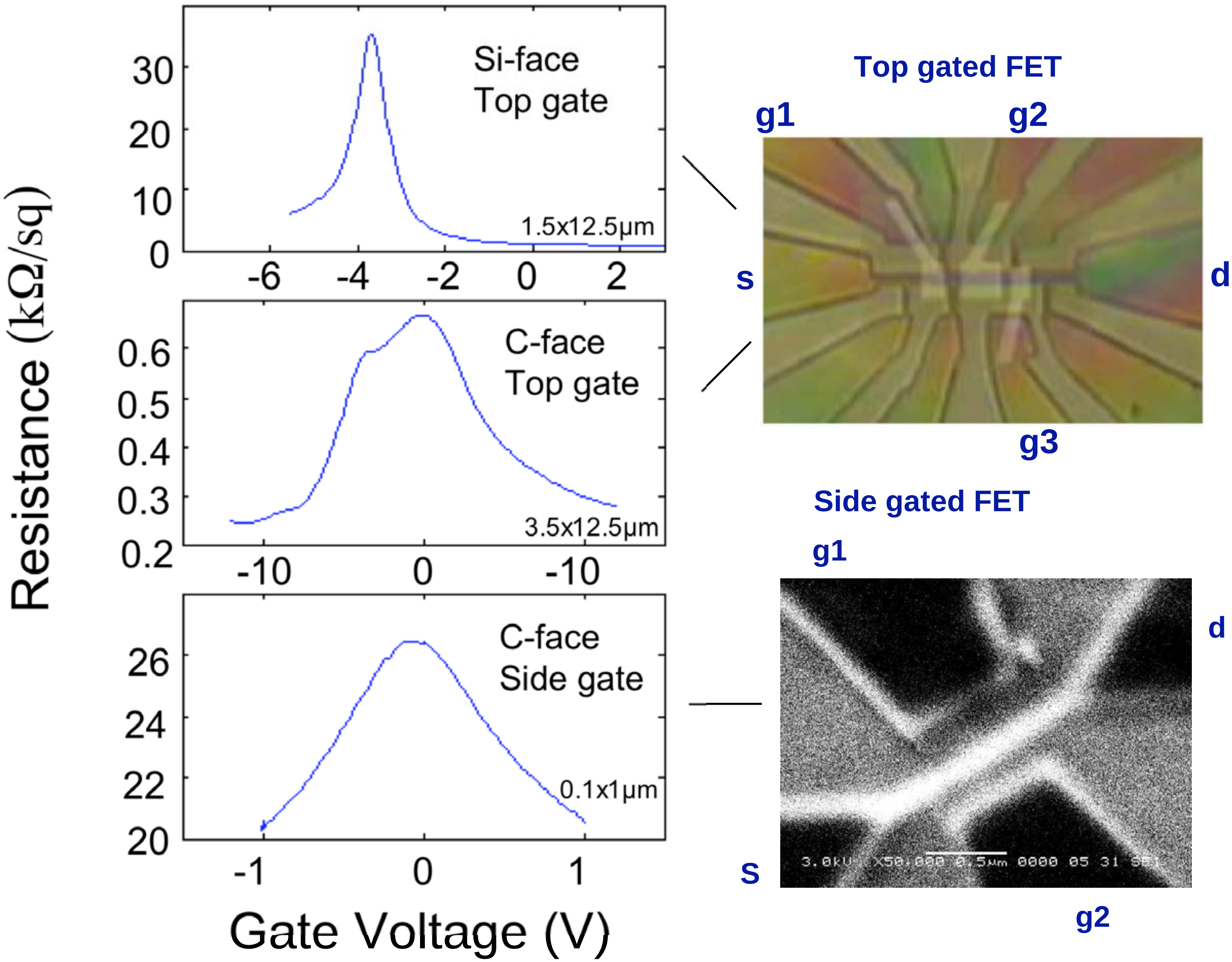


1.5μmx12μm

Top gated Hall bar, Si face

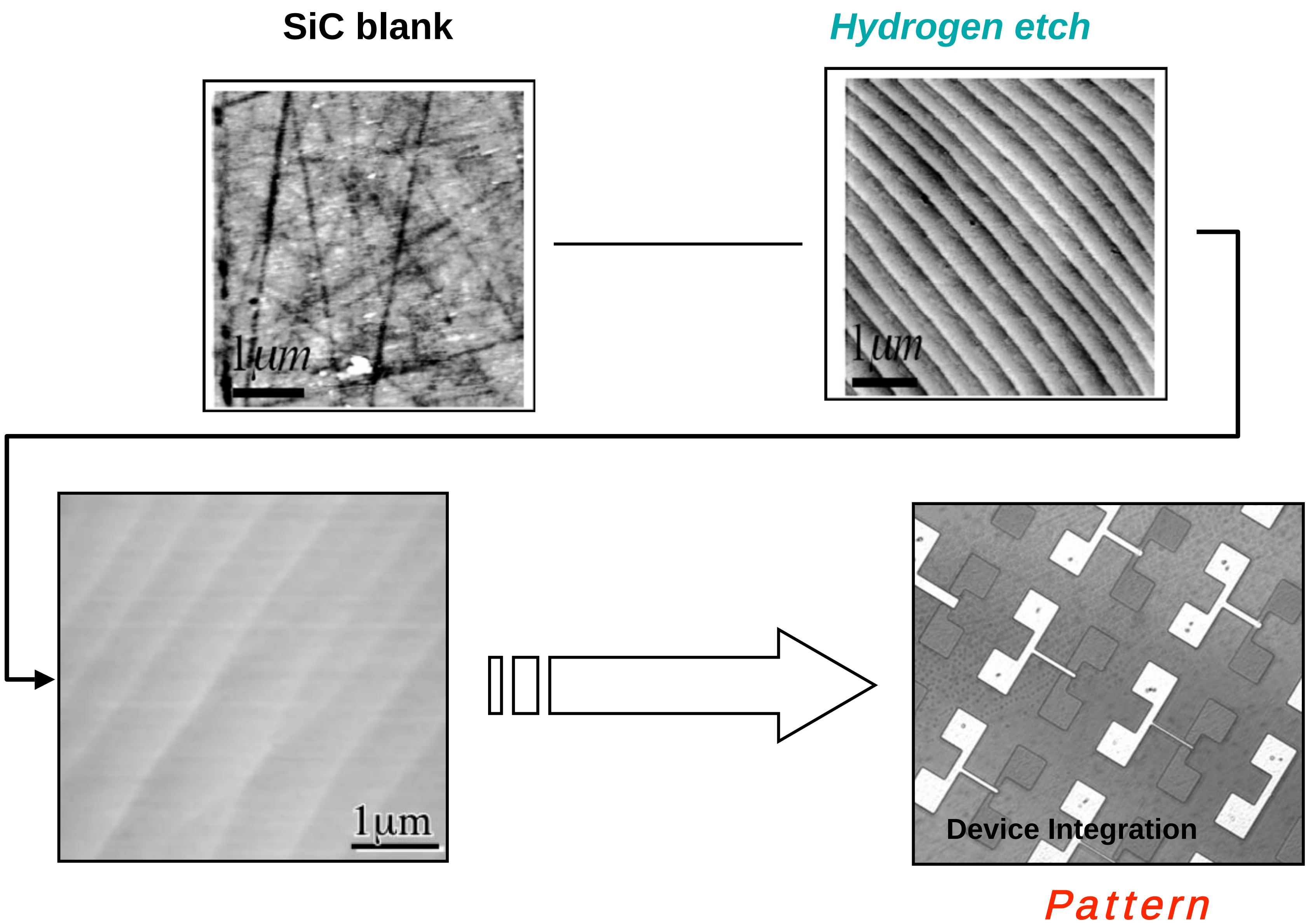


Top and side gated FETs

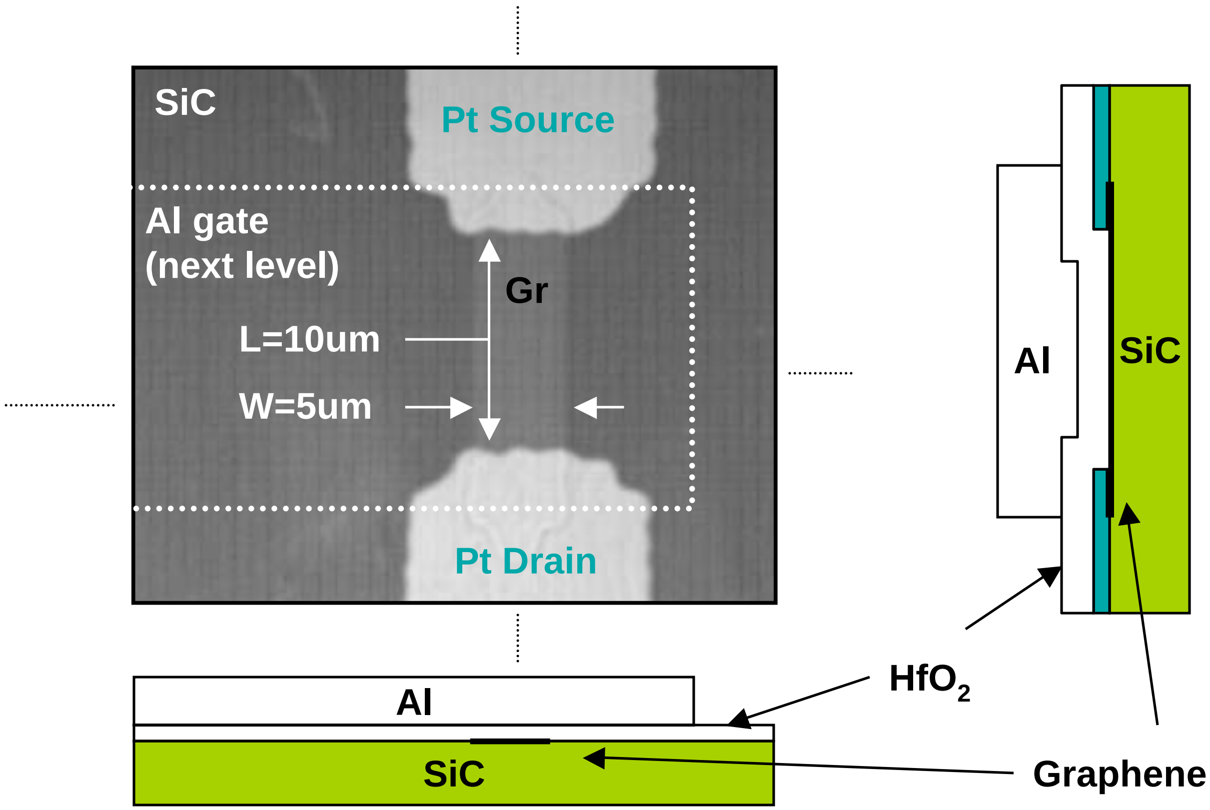


The first epitaxial graphene transistors

Production process



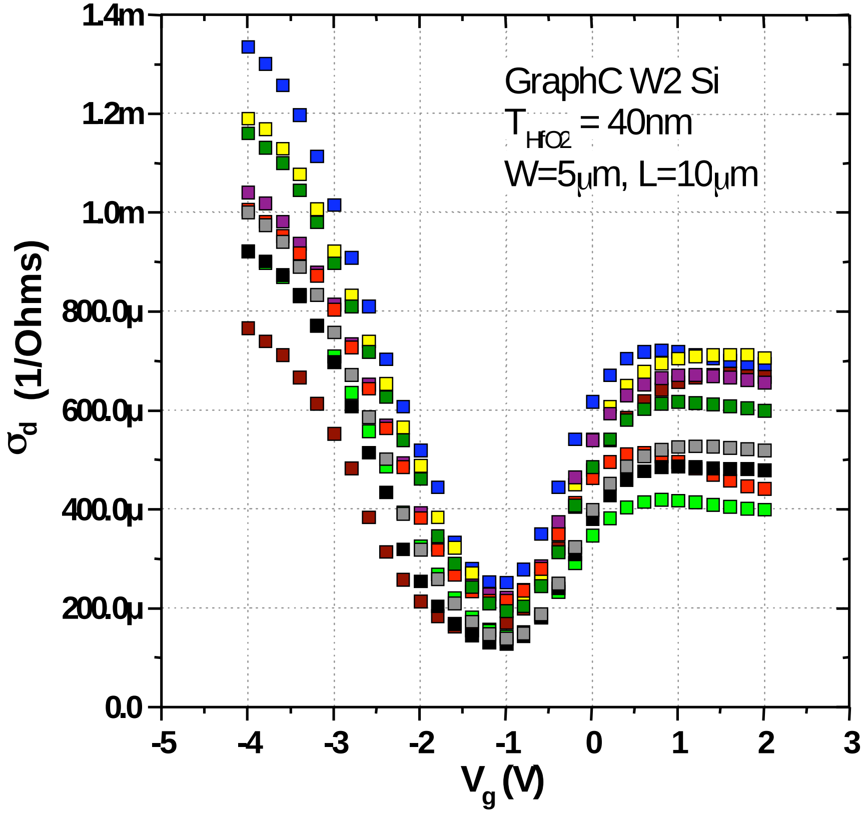
Final Device Geometry



- Device description and cross section
  - Nominal device – Graphene/SiC active layer (C-side), L = 10um, W = 5 um, ridge parallel, 50nm HfO_2 dielectric, Al gate
  - Microscope image shown before gate lift-off

J. Kedzierski, P. L. Hsu , P. Hea ley, P. W. Wyatt, C. L. Keast, M. Sprinkle, C. Berger, W. A. de Heer, *Epitaxial graphene transistors on SIC substrates*,Ieee T Electron Dev **55**, 2078 (2008).

Set of Identical Devices (Si-face)



Drain current vs. gate voltage at V_d = 0.5V

- Minimum conductivity
  - 130uS to 250uS
- Field Effect Mobility values
  - 400-1000 cm^2/Vs
- I_{on}/I_{off} ~ 5

J. Kedzierski, P. L. Hsu, P. Healey, P. W. Wyatt, C. L. Keast, M. Sprinkle, C. Berger, W. A. de Heer, *Epitaxial graphene transistors on SIC substrates*,Ieee T Electron Dev **55**, 2078 (2008).

Lithography

98 ribbons per 3.5 x 4.5 mm chip

Hall bars and 2-point devices