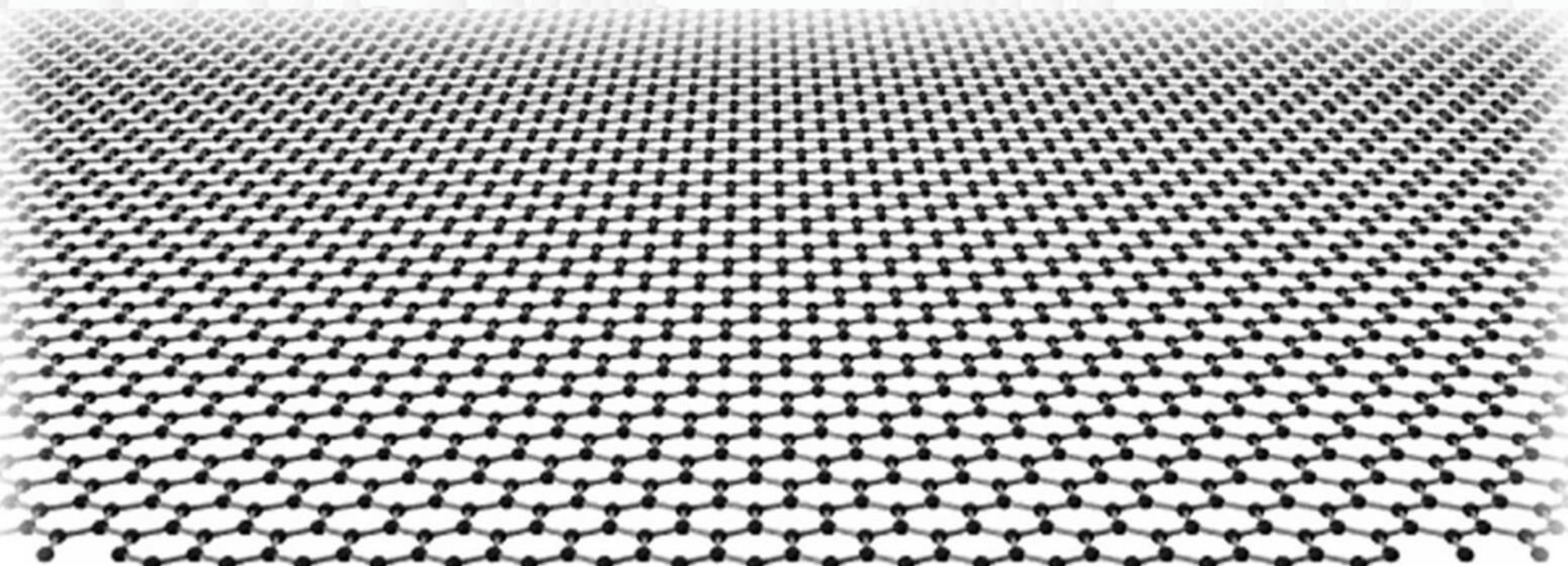
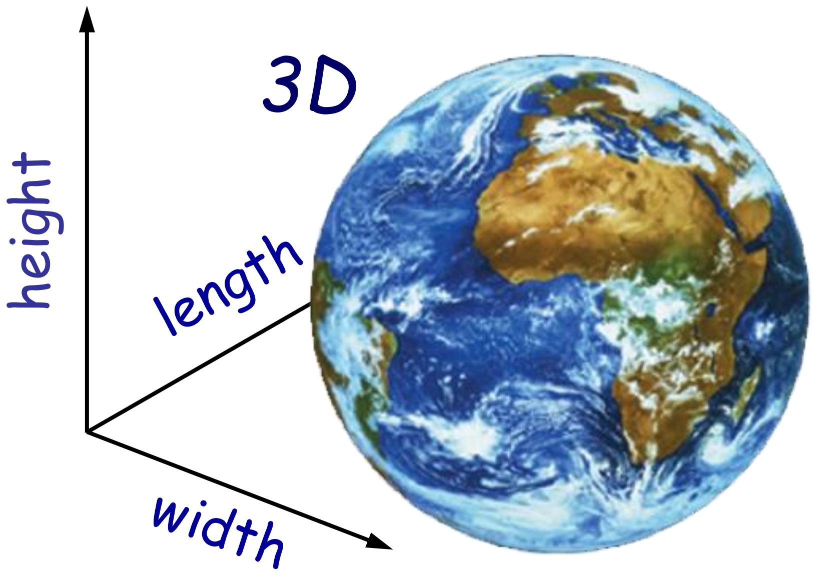
MANCHESTER
1824

The University
of Manchester

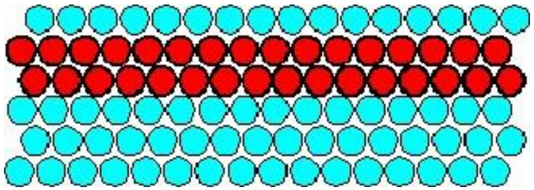
Graphene:
Magic of Flat Carbon



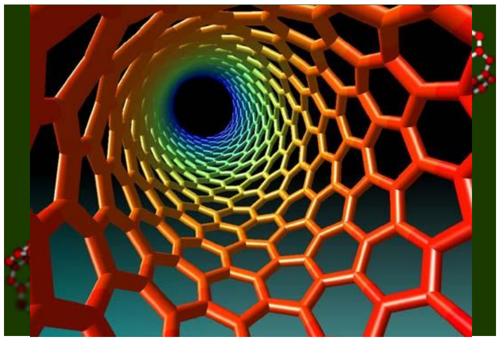
All Natural Materials Are 3D



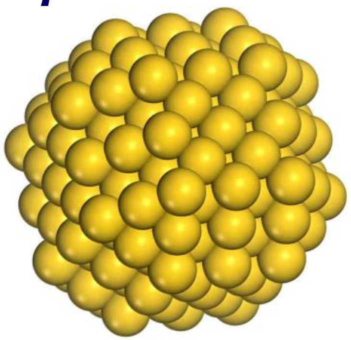
quasi-2D



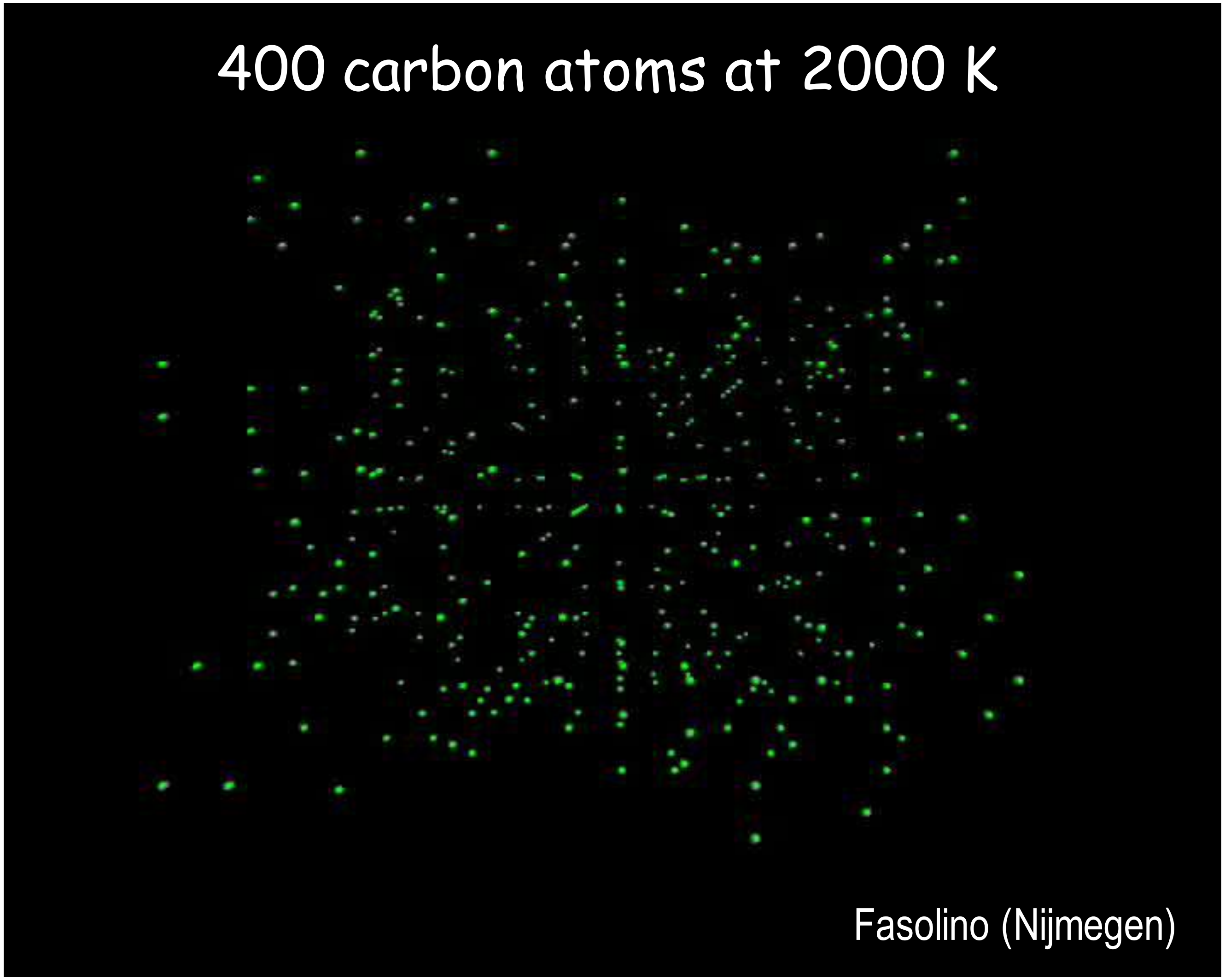
quasi-1D



quasi-0D



Nature Utilizes All Dimensions



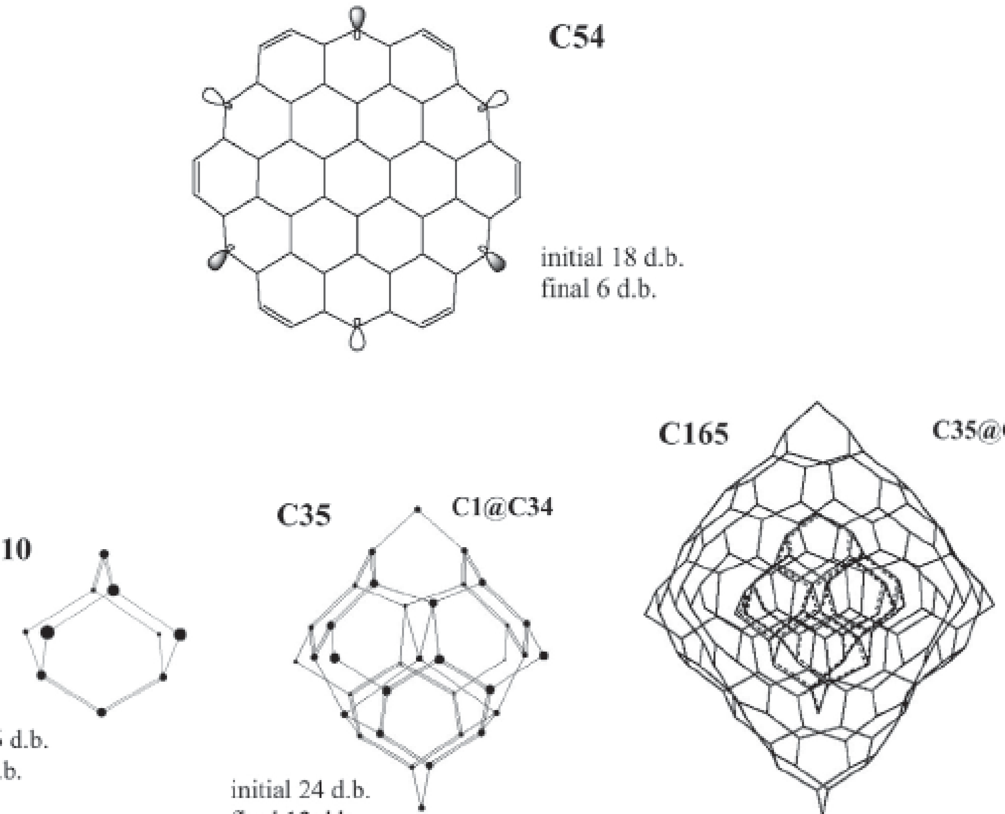
GROWTH
↓
HIGH TEMPERATURES
↓
VIBRATIONS MOST VIOLENT IN LOW D

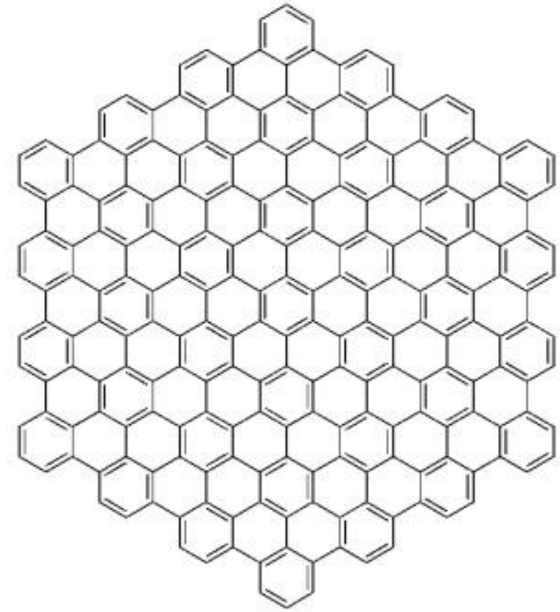
growth of macroscopic 2D objects is <u>strictly</u> forbidden

Peierls; Landau; Mermin-Wagner; …

(only nm-scale flat crystals possible to grow in isolation)

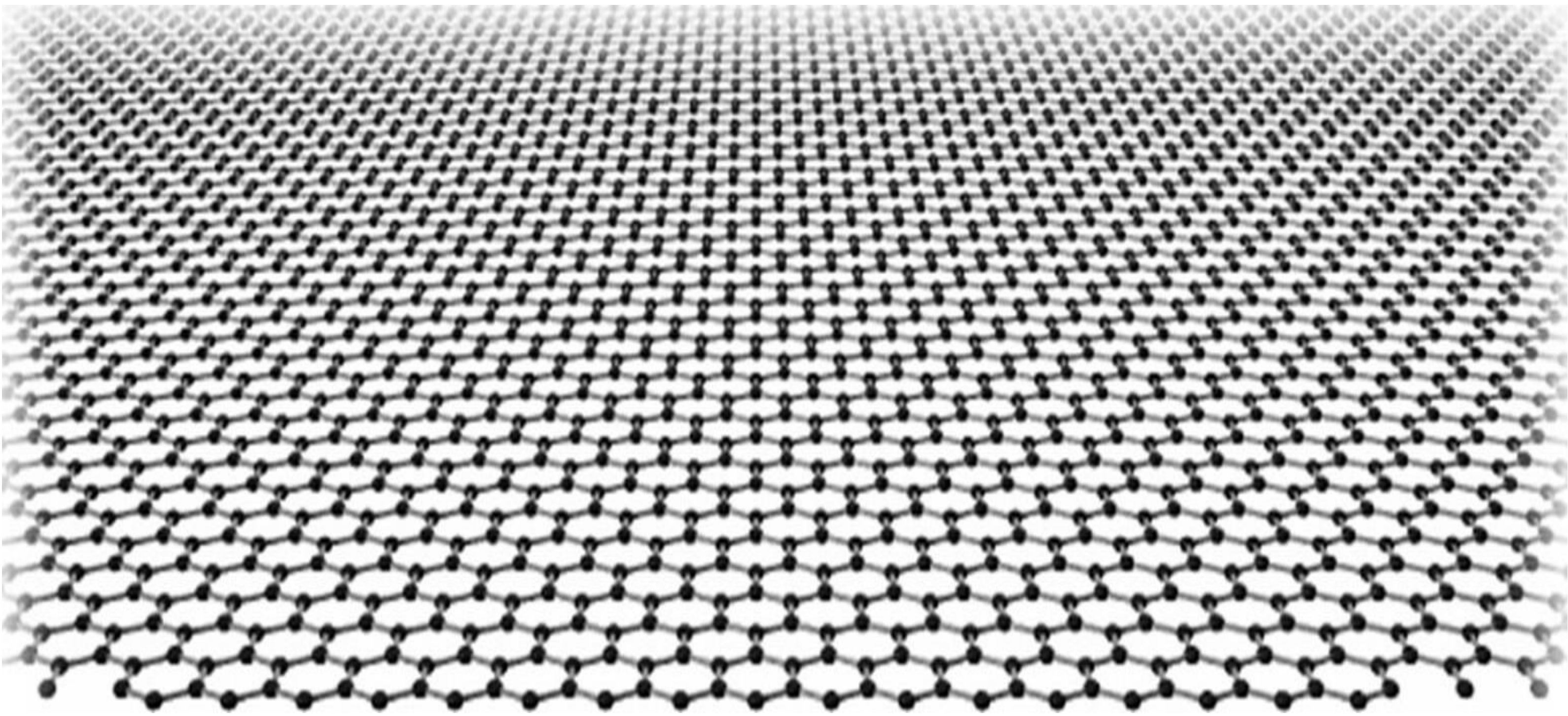
No Bottom-Up for 2D Crystals





largest known
flat hydrocarbon:
222atoms/37rings
(Klaus Müllen 2002)

the FLAT sheet is
least stable configuration
for <24,000 atoms (Don Brenner 2002)

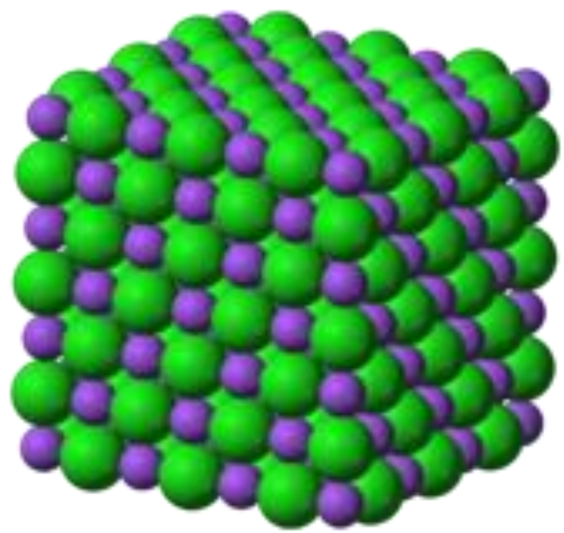


ONE-ATOM-THICK OBJECTS, HUGE MACRO-MACROMOLECULES?

(not only graphene)

Can We Get One-Atom-Thick Materials?

forbidden growth
does not mean cannot be made



just extract
one atomic plane from a bulk crystal

isolating individual atomic planes

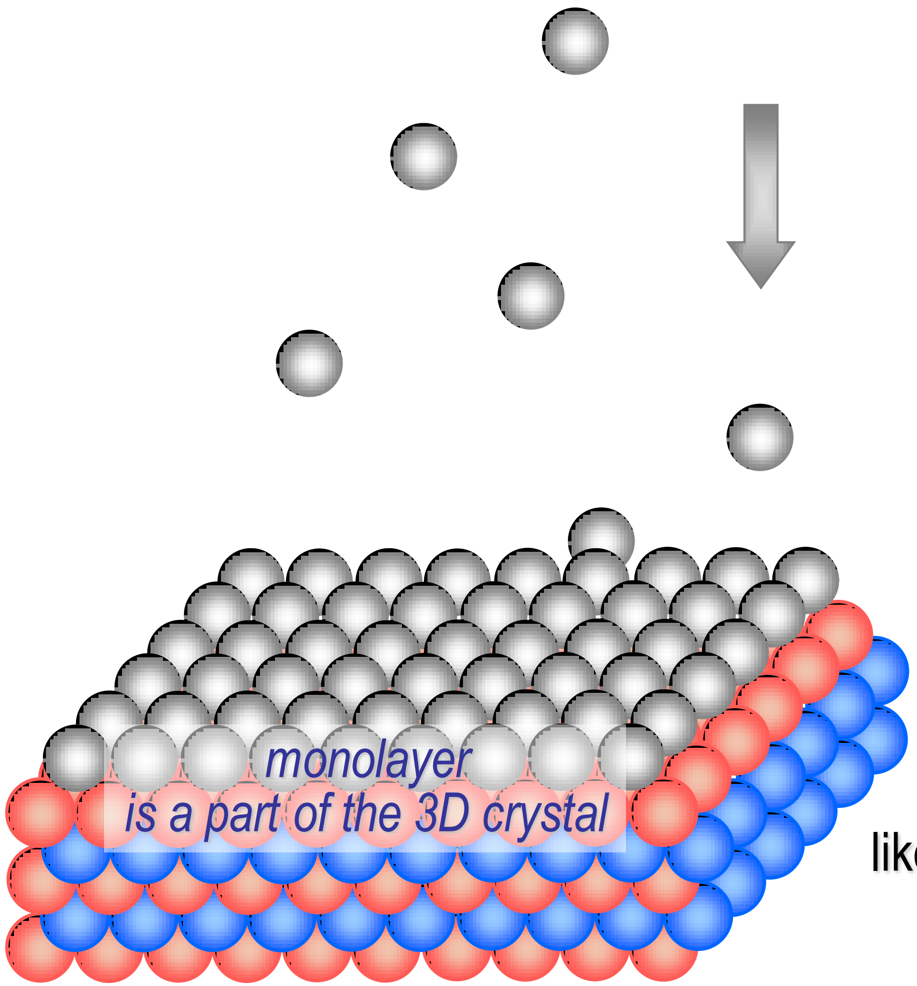
starting point in <<2004
suggested in print: *Nature Mater* 2007

epitaxial growth

MANY MANY DIFFERENT EPITAXIAL SYSTEMS

including graphitic layers

Grant 1970 (on Ru)
Bommel 1975 (SiC)
McConville 1986 (on Ni)
Land *1992* (on Pt)
Nagashima 1993 (on TiC)
Forbeaux 1998 (SiC)
de Heer 2004 (SiC)
... ...



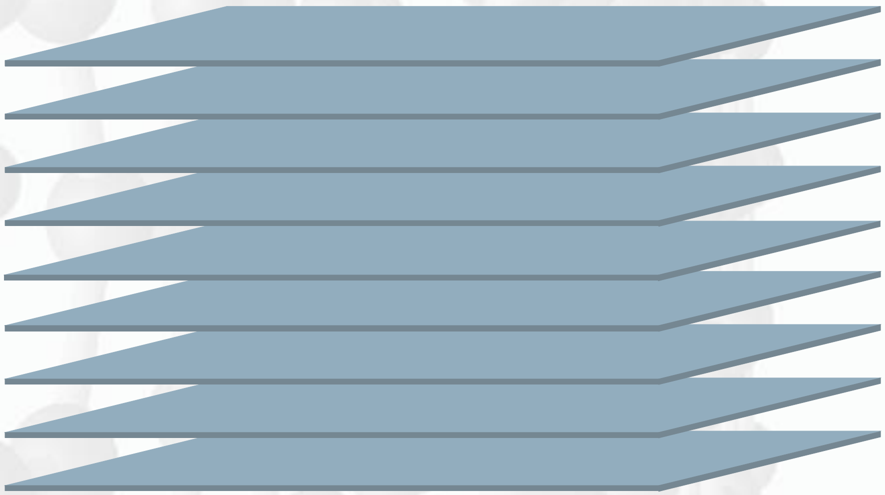
let us remove the substrate chemically,
like SiN or αC membranes

GOAL: NOT EPITAXIAL LAYERS
but rather
MACROMOLECULES, ISOLATED ATOMIC PLANES

extracting individual atomic planes

3D LAYERED MATERIAL

extract individual planes

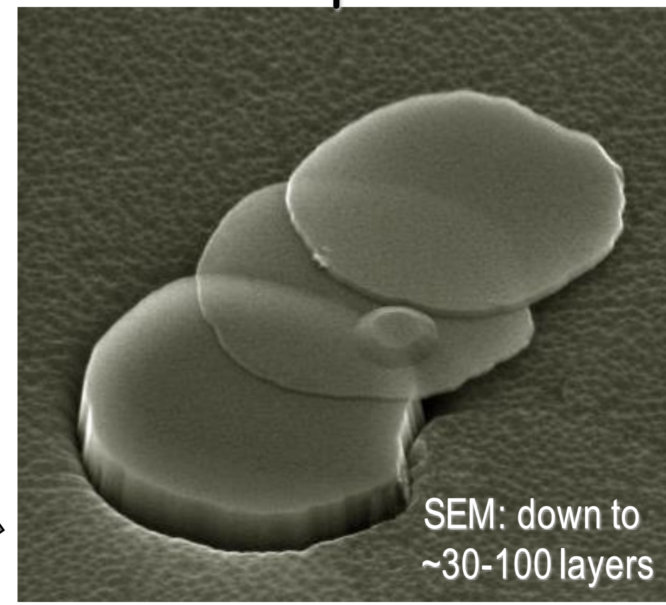


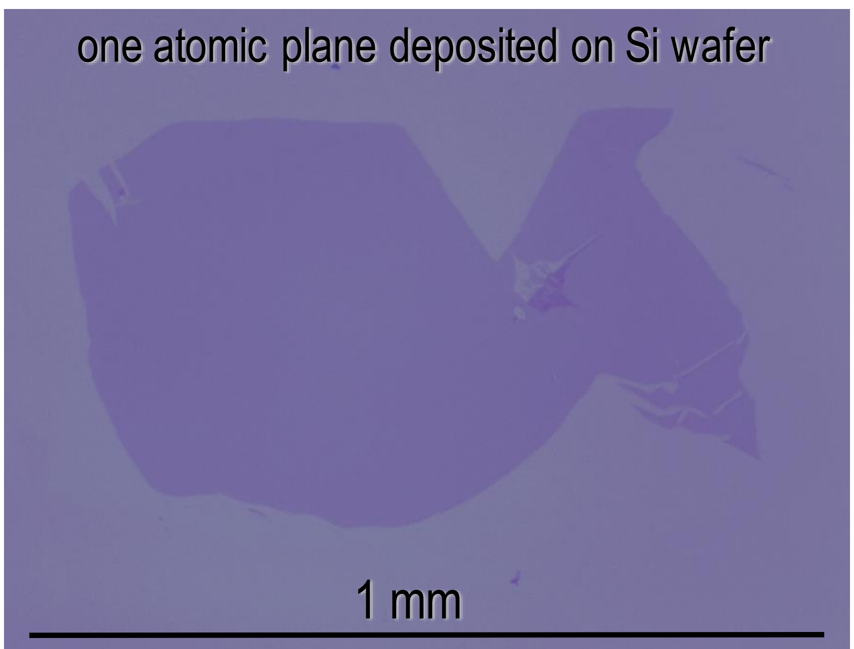
start with graphite

need strong in-plane bonds

Also: Kurtz 1991; Ebbesen 1995; Ohashi 1997
Ruoff 1999; Philip Kim 2005; McEuen 2005

split into increasingly thinner "pancakes"





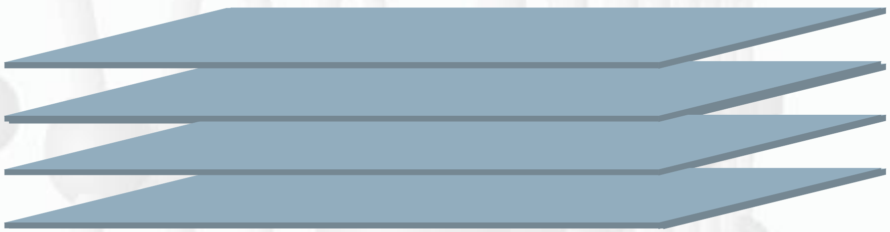
until we found a single layer called GRAPHENE

Manchester, *Science* 2004; *PNAS* 2005

extracting atomic planes en masse

SPLIT INTO
ATOMIC PLANES

ANY LAYERED MATERIAL



WHEN YOU KNOW THAT
ISOLATED ATOMIC PLANES CAN EXIST

Splitting Graphite into Graphene

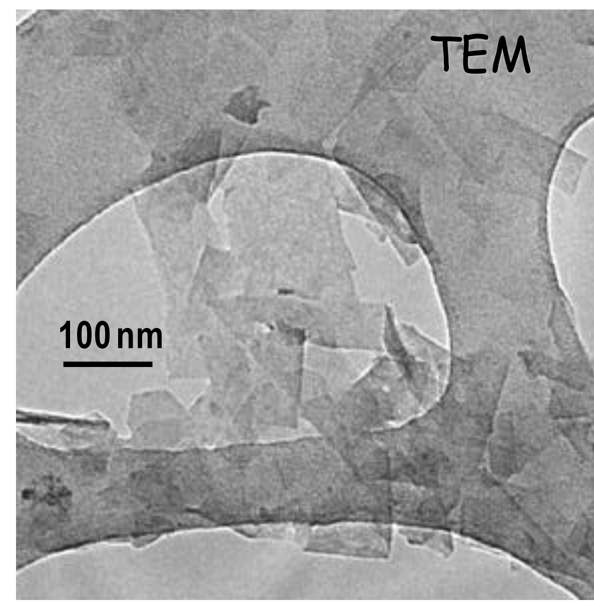
Manchester, *Nanolett '08*
Coleman et al, *Nature Nano '08*

15 min centrifugation

few hours sonication in organic solvent
(chloroform, DMF, etc)

relevant literature:
INTERCALATED GRAPHITE
TEM observations
of ultra-thin graphite/graphene
from Boehm 1962
to Horiuchi 2004
see Dresselhaus' review 1981

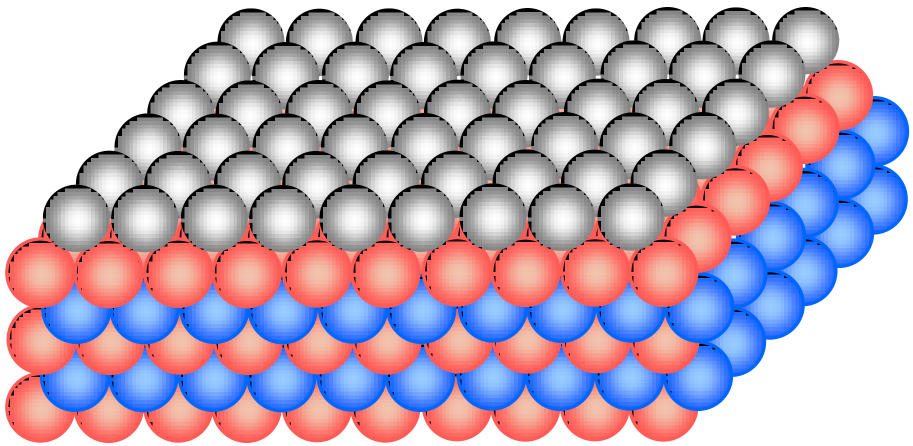
RENAISSANCE
starting with **graphene oxide**:
Ruoff, *Nature* 2006
also, Kern's, Kaner's groups



Chemically Removing Bulk

starting point
in <<2004
suggested in
Nature Mater 2007

epitaxial growth
⇓
removal substrate
⇓
transfer

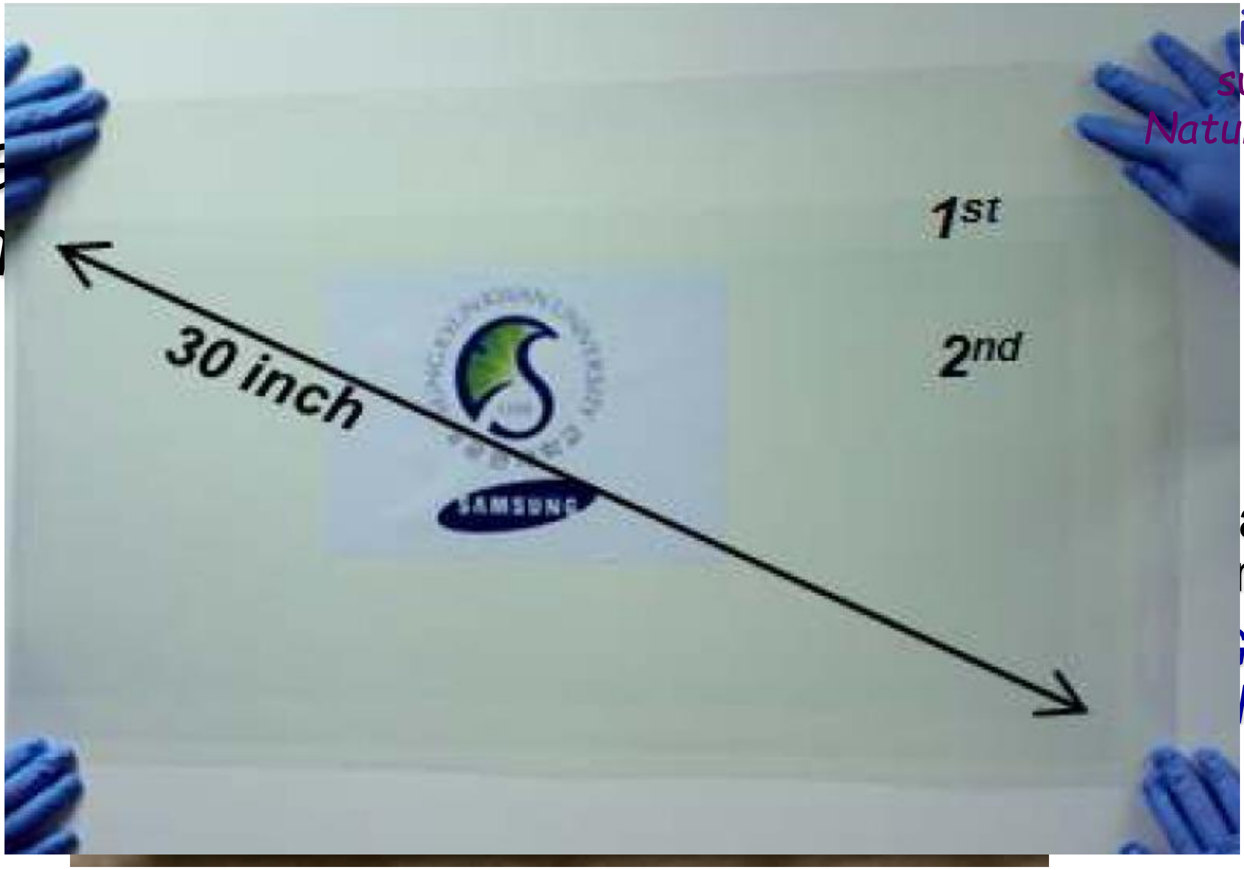


making 2D crystals out of epitaxial layers

Chemically Removing Bulk

starting point
in <<2004
suggested in
Nature Mater 2007

epitaxia
growth



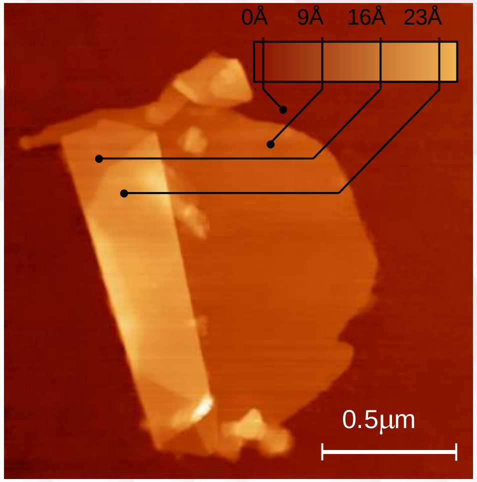
arbon poisoning
nd **Cu** surfaces

GH QUALITY
RAPHENE

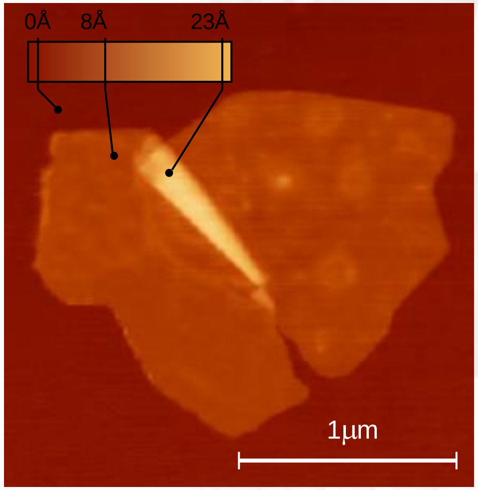
FIRST DEMONSTRATED
Kong et al, *Nano lett* 2009; Hong et al, *Nature* 2009
SKKU+Samsung: 30 inch graphene 'wafers'
Ruoff et al, *Science* 2009

Many Other 2D Materials Possible

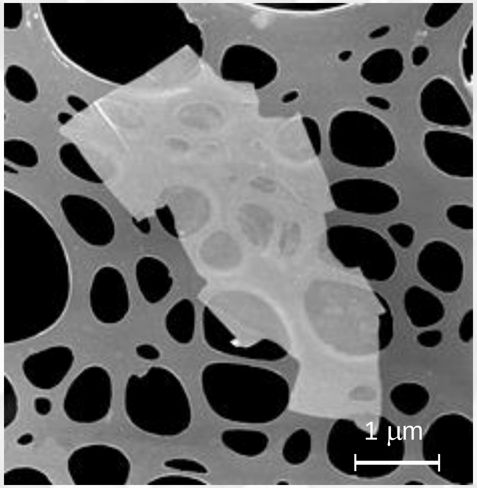
2D boron nitride in AFM



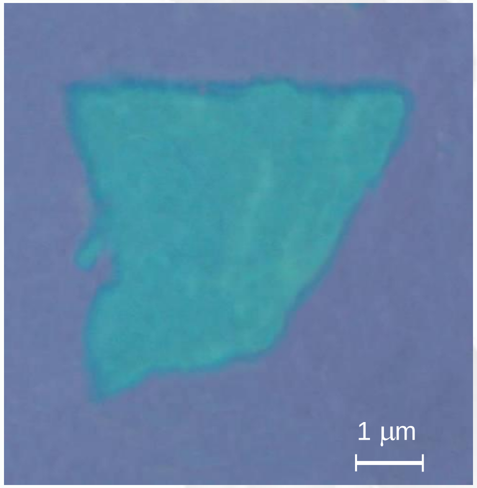
2D $NbSe_2$ in AFM



also,
2,3,4… layers



2D $Bi_2Sr_2CaCu_2O_x$ in SEM



2D MoS_2 in optics

Manchester, *PNAS* '05

MESSAGE TO TAKE AWAY

MATERIALS OF A NEW KIND:

ONE ATOM THICK

(atomic planes of graphite and other materials
were known before as constituents of 3D systems
but not as *ISOLATED* 2D crystals)

2D MATERIALS: not only from naturally layered materials;
any epitaxially grown monolayer with strong bonds

bits of graphene present in every pencil trace
- important to isolate, study, prove they are worth of studying
and eventually make use of them -

what is so special about graphene?

GRAPHENE'S SUPERLATIVES

thinnest imaginable material

strongest material 'ever measured' (theoretical limit)

stiffest known material (stiffer than diamond)

most stretchable crystal (up to 20% elastically)

record thermal conductivity (outperforming diamond)

highest current density at room T
(million times of those in copper)

highest intrinsic mobility (100 times more than in Si)

conducts electricity in the limit of no electrons

lightest charge carriers (zero rest mass)

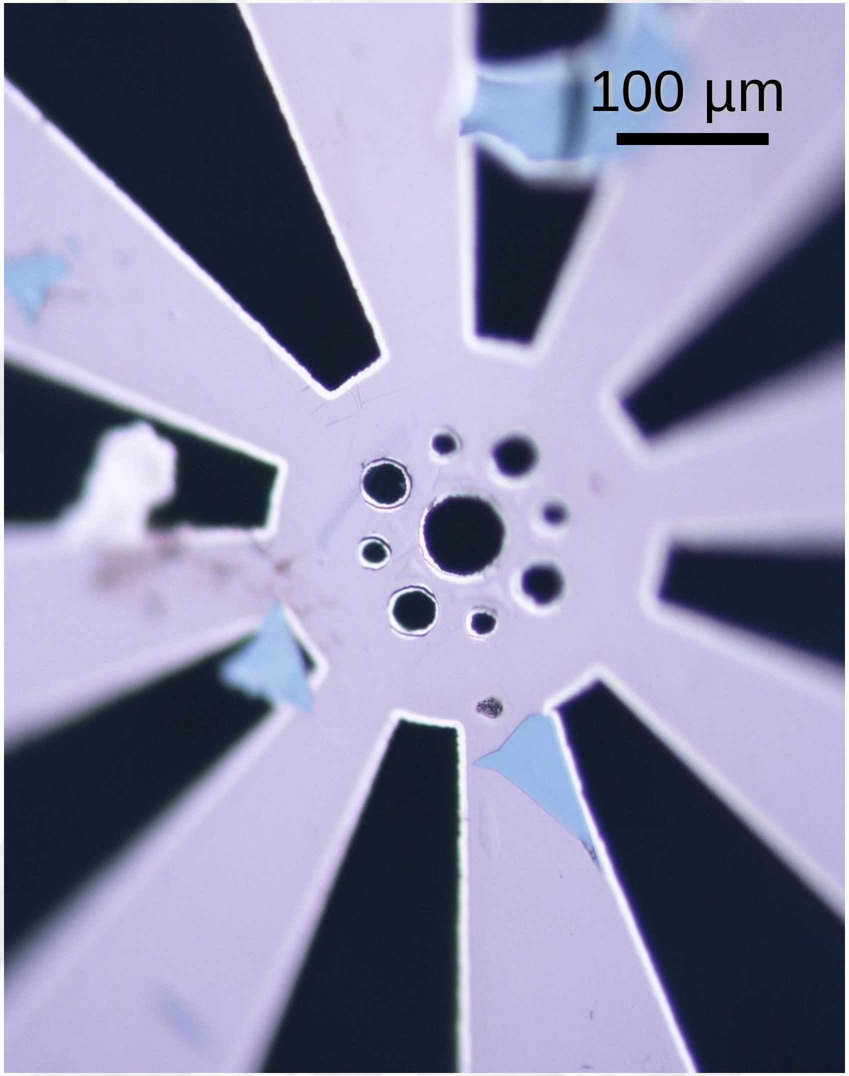
longest mean free path at room T (micron range)

most impermeable (even He atoms cannot squeeze through)

... ...

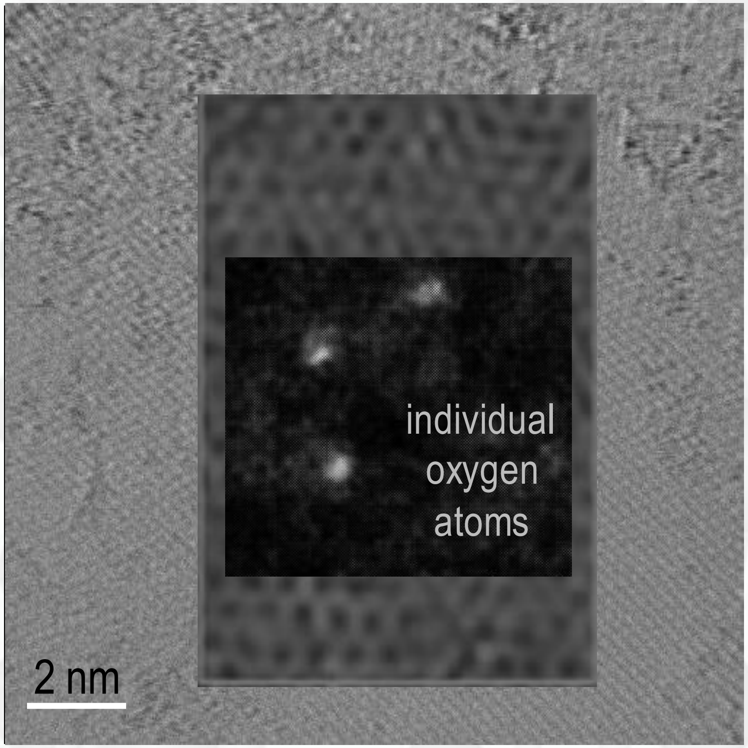
EXCEPTIONAL MECHANICAL PROPERTIES

Graphene Membranes



one-atom-thick
single-crystal membranes

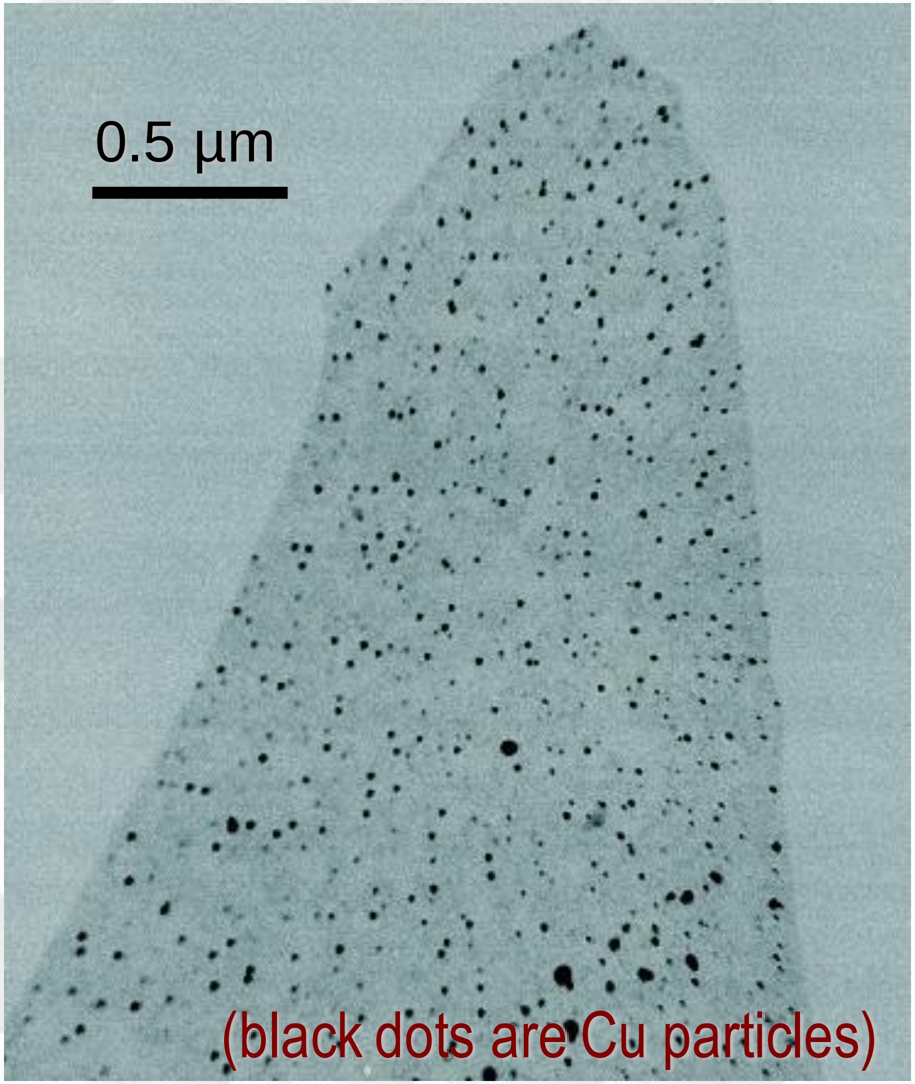
graphene lattice
in SuperSTEM



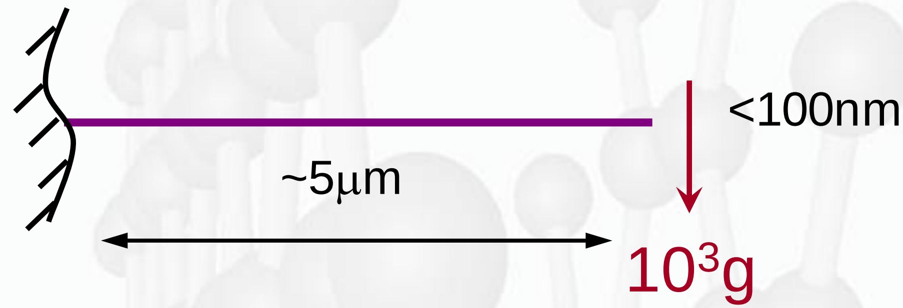
Manchester, *Nanolett* '08; *Nature Nano* '08

see J. Meyer *2007-2009*

Unsupported Graphene



Manchester, *Nanolett* '08



graphene crystallites
DO NOT ROLL UP OR BEND !

careful studies by AFM

Young's modulus ~1 TPa

intrinsic strength 40 N/m

Hone, *Science* 2008

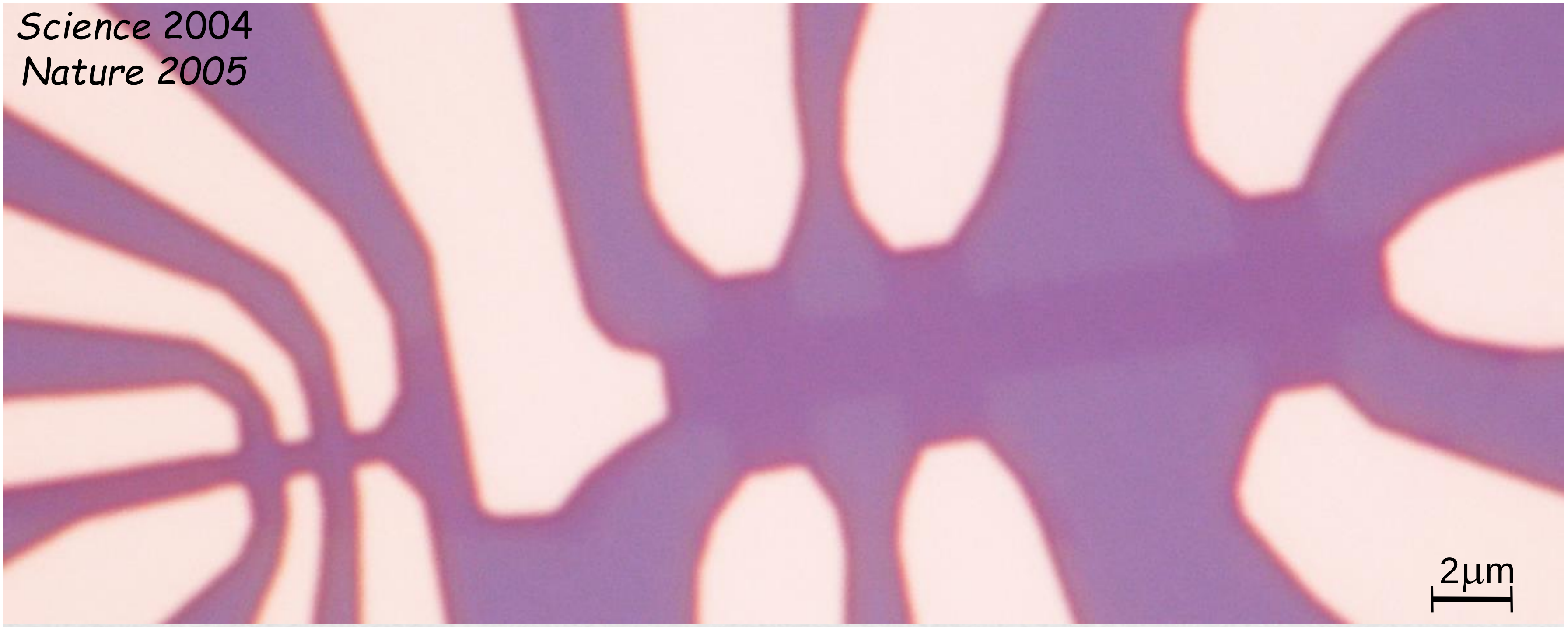
Van der Zant, *APL* 2007

graphene slivers are extremely stiff

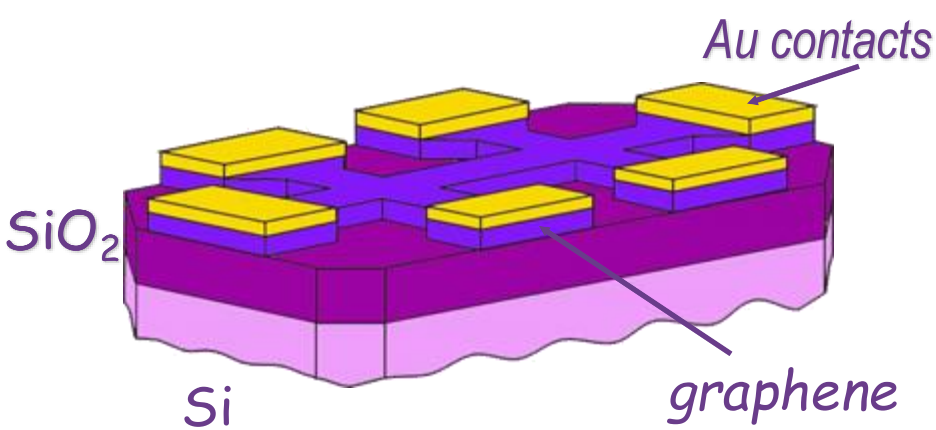
high Young's modulus as of carbon nanotubes

EXCEPTIONAL ELECTRONIC QUALITY

Our Graphene Devices

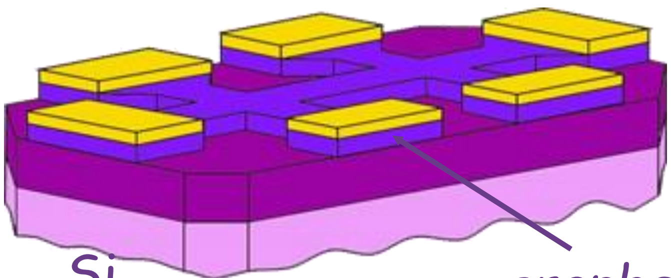


- optical imaging
- SEM imaging
- design
- fabrication

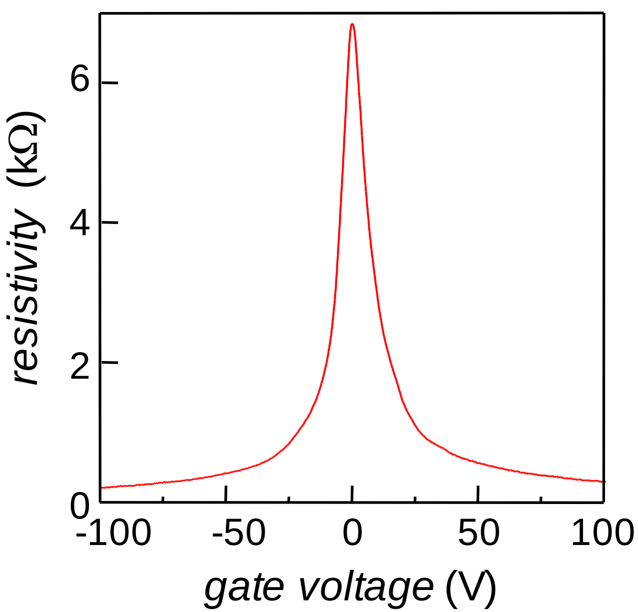


AMBIPOLAR ELECTRIC FIELD EFFECT

Manchester, *Science* 2004



the field effect proved
to be a very powerful tool



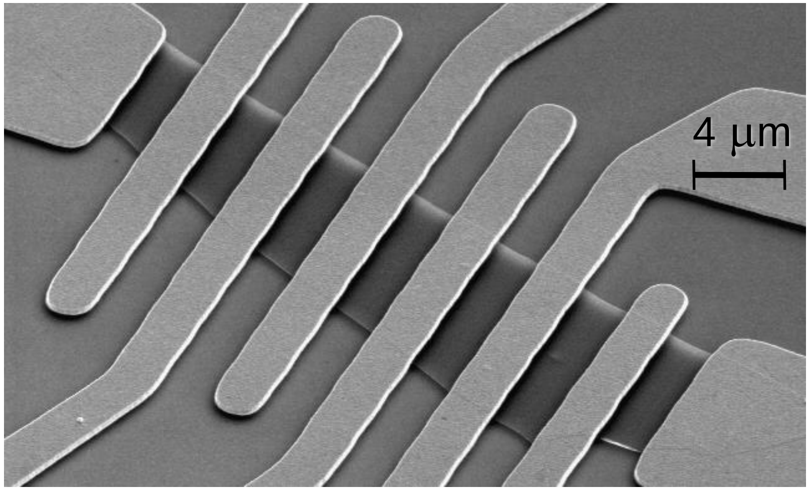
ELECTRONIC QUALITY

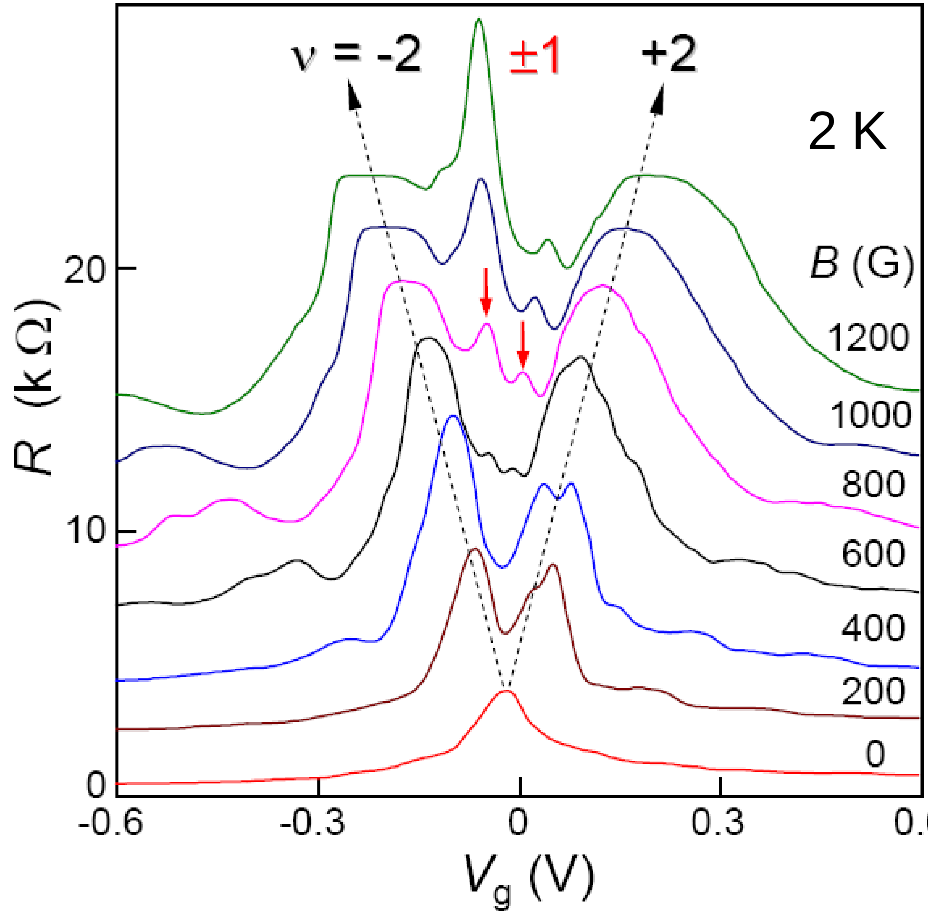
carrier mobility routinely:
up to ~15,000 $cm^2/V\cdot s$ at 300K

intrinsic (phonon-limited):
>200,000 $cm^2/V\cdot s$ at 300K
(higher than in any other material)
Manchester, *PRL* 2008

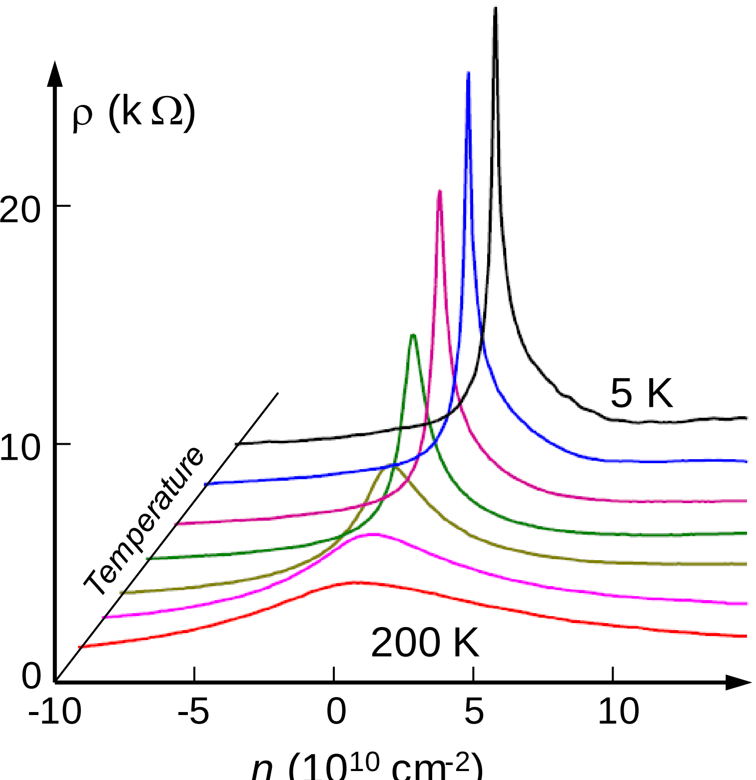
**ballistic transport
on submicron scale
under ambient conditions**

suspended devices



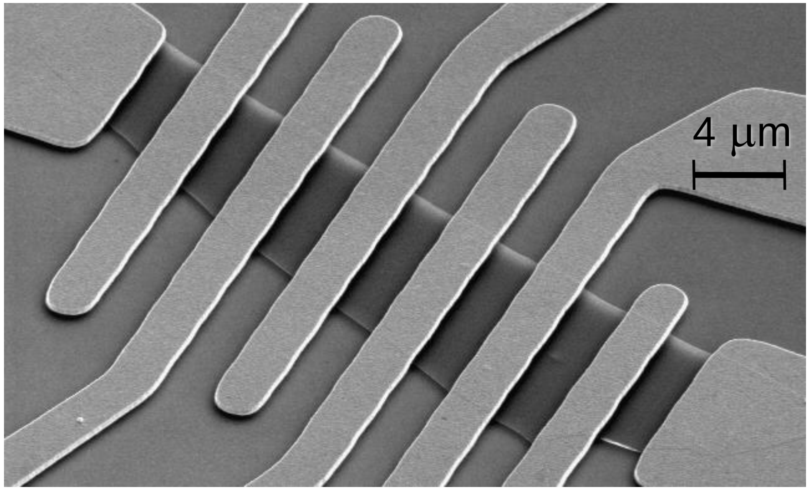


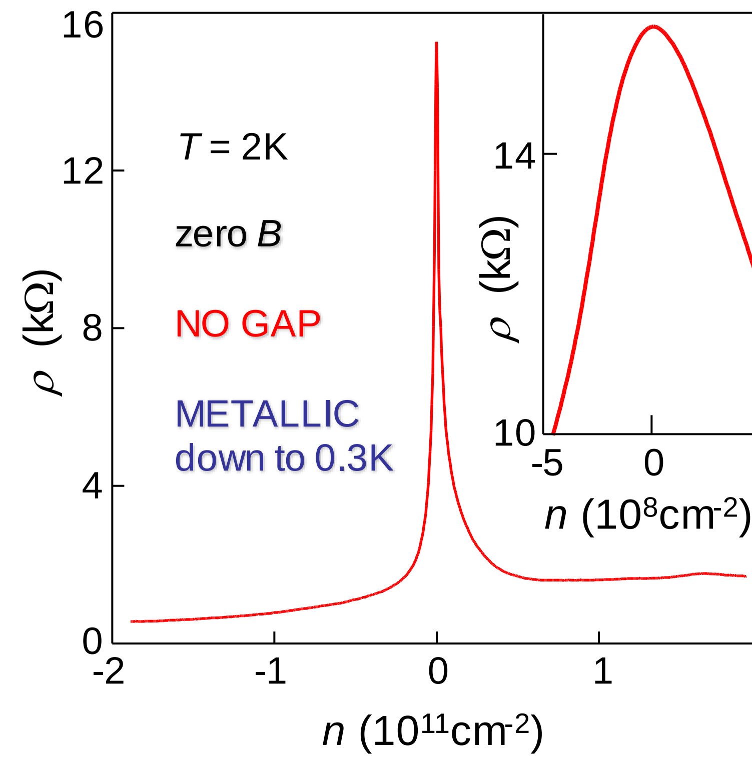
SdH oscillations start < 100G
level degeneracy lifted < 600G

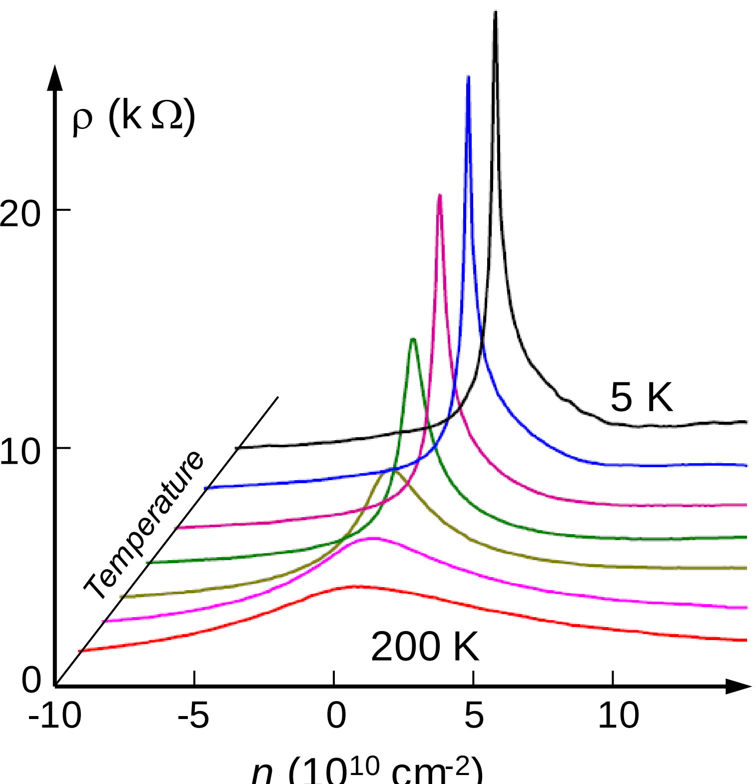


mobilities > 1,000,000 $cm^2/V \cdot s$
remnant doping < 10^9 cm^{-2}
charge inhomogeneity < 10^8 cm^{-2}

suspended devices



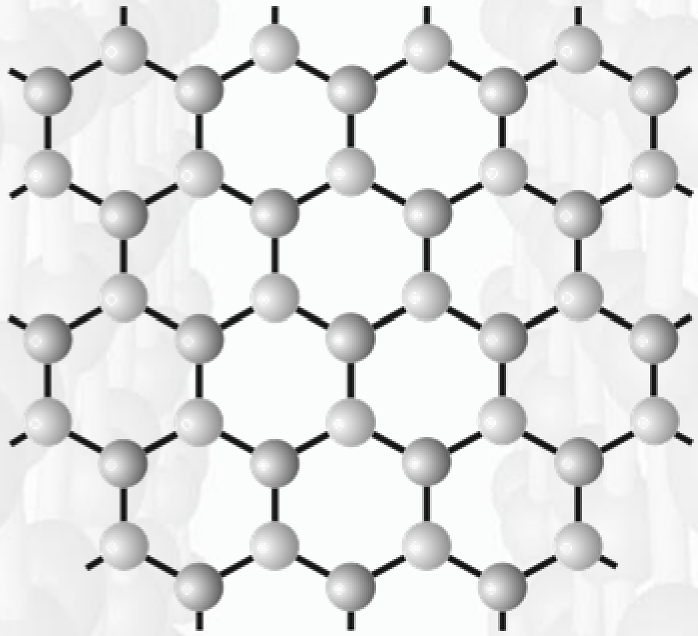




charge inhomogeneity < 10^8 cm^{-2}
less than ONE DIRAC FERMION
per micron-sized device
(no electron-hole puddles)

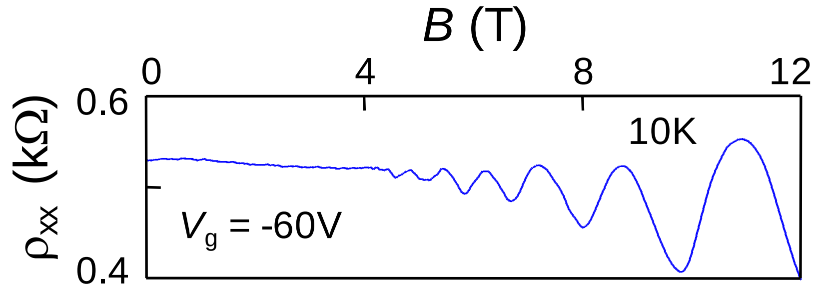
can probe the Dirac point
within <0.1 meV or ONE particle

EXCEPTIONAL ELECTRONIC STRUCTURE

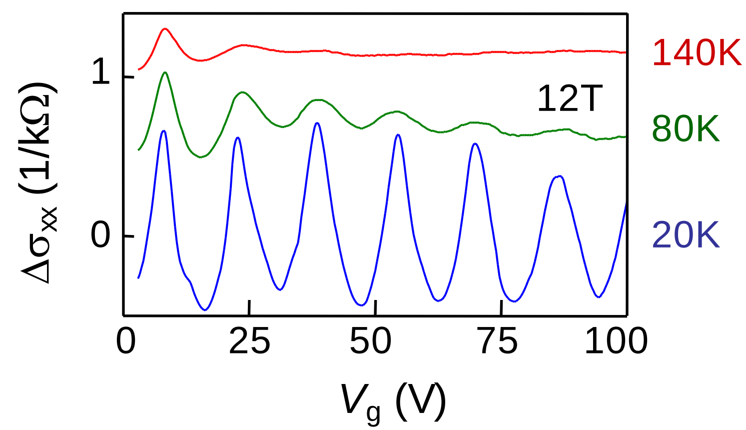


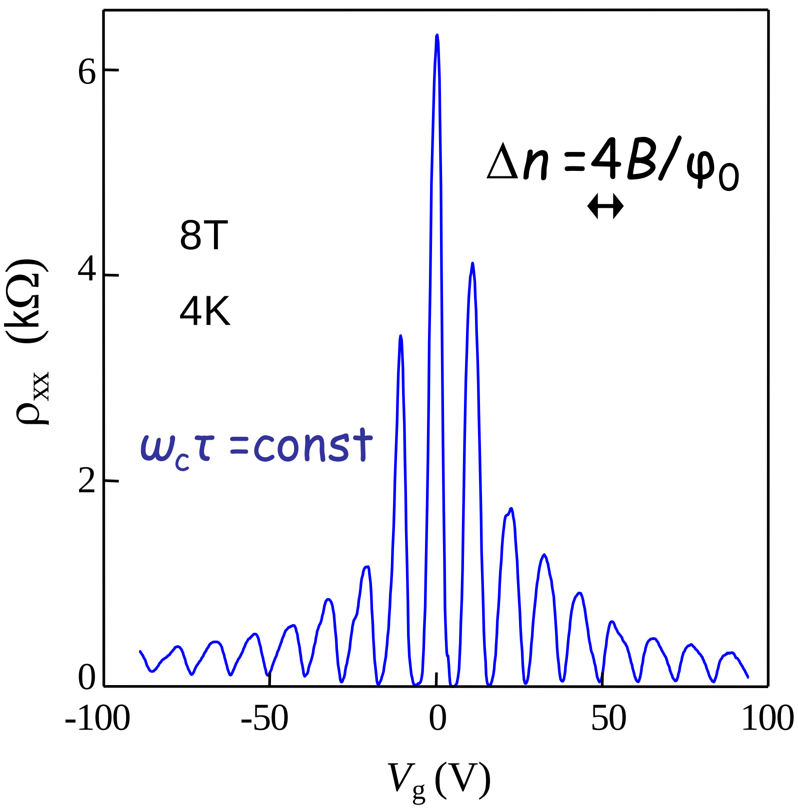
Finding Electronic Structure

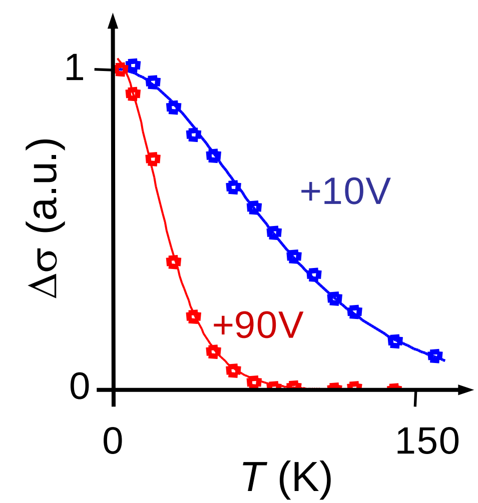
Manchester, *Science* '04 & *Nature* '05



degeneracy f =4
two spins & two valleys



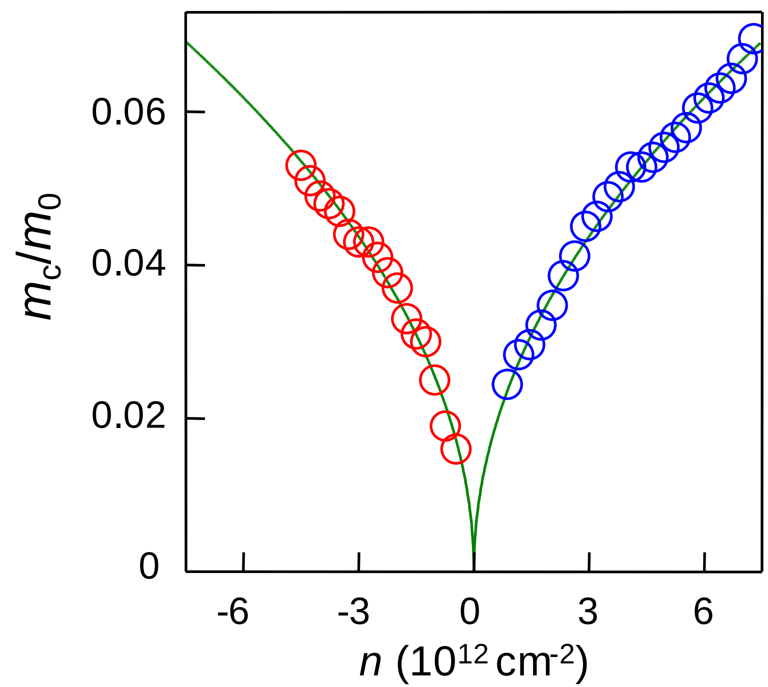




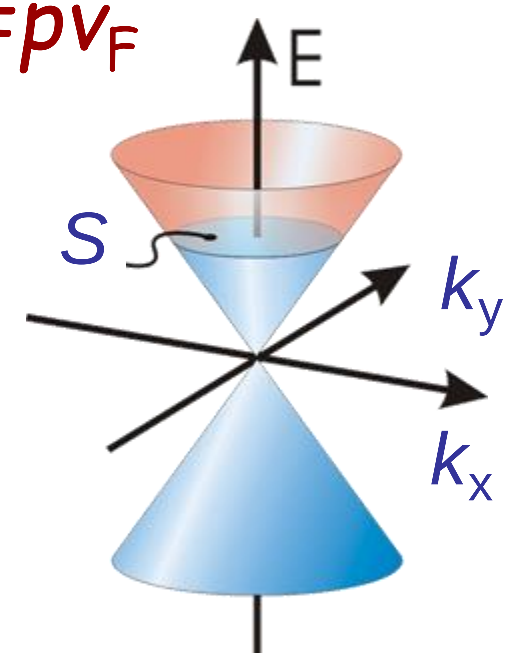
$$\Delta\sigma_{xx} \propto T/\sinh\left(\frac{2\pi^2 k_B T m_c}{\hbar e B}\right)$$

Finding Electronic Structure

mass of charge carriers strongly depends on concentration



$E = pv_F$



$B_F = (\hbar/2\pi e)S$ and $m_c = (\hbar^2/2\pi)\partial S/\partial E$

experimental dependences

$B_F \sim n$ and $m_c \sim n^{1/2}$

necessitates $S \sim E(k)^2$ or $E \sim k$

ZERO REST MASS:

effective mass

$E = m_c v_F^2$

$v_F = 10^6$ m/s ±5%

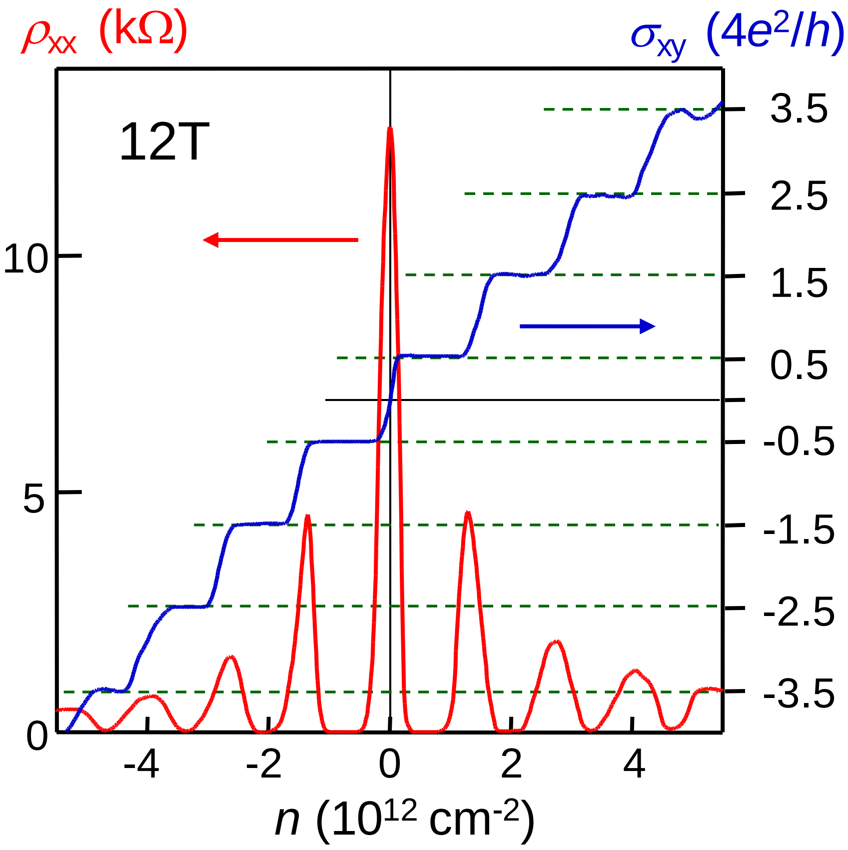
in agreement with theory:

Wallace 1947, McClure 1956, Semenoff 1984

massive & massless Dirac fermions

half-integer QHE

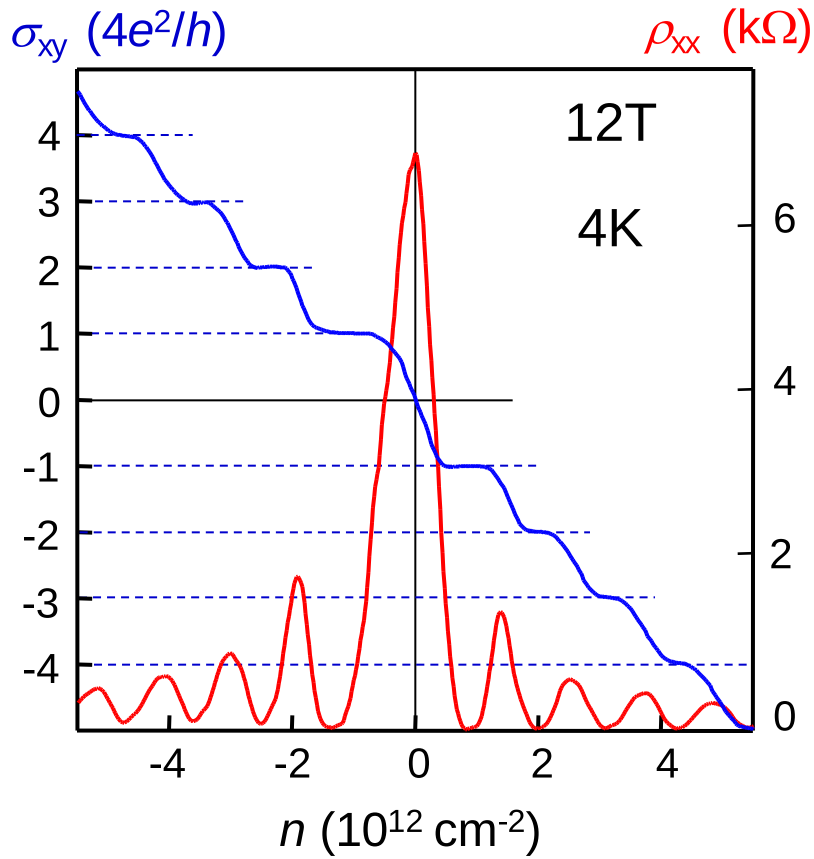
relativistic analogue of integer QHE



$$E \propto \pm\sqrt{B \cdot N}$$

Manchester, *Nature* '05; Columbia, *Nature* '05

"anomalous" QHE



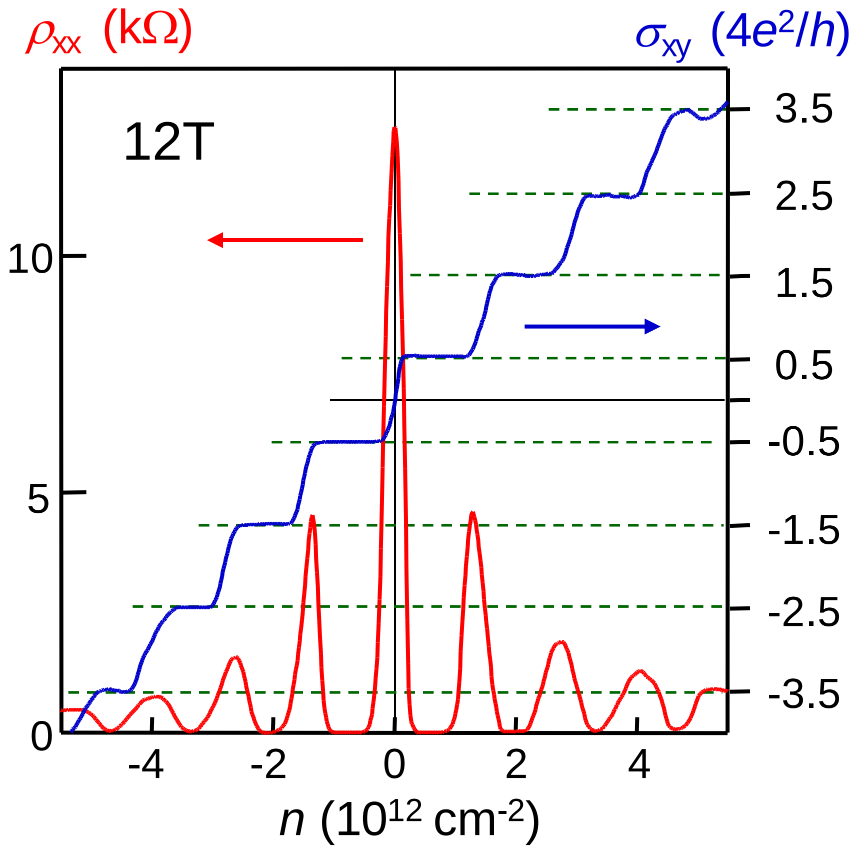
$$E \propto \pm B\sqrt{N(N-1)}$$

Manchester+Lancaster, *Nature Phys* '06

massive & massless Dirac fermions

half-integer QHE

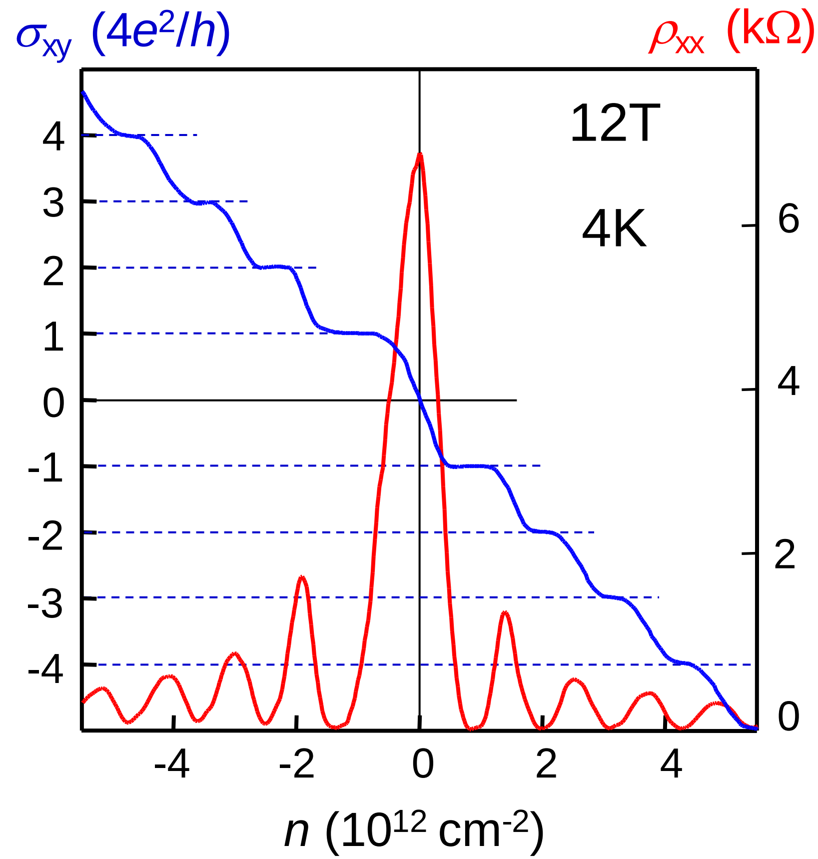
relativistic analogue of integer QHE



$$\hat{H} = v_F \begin{pmatrix} 0 & \hat{p}_x + i\hat{p}_y \\ \hat{p}_x - i\hat{p}_y & 0 \end{pmatrix}$$

Manchester, *Nature* '05; Columbia, *Nature* '05

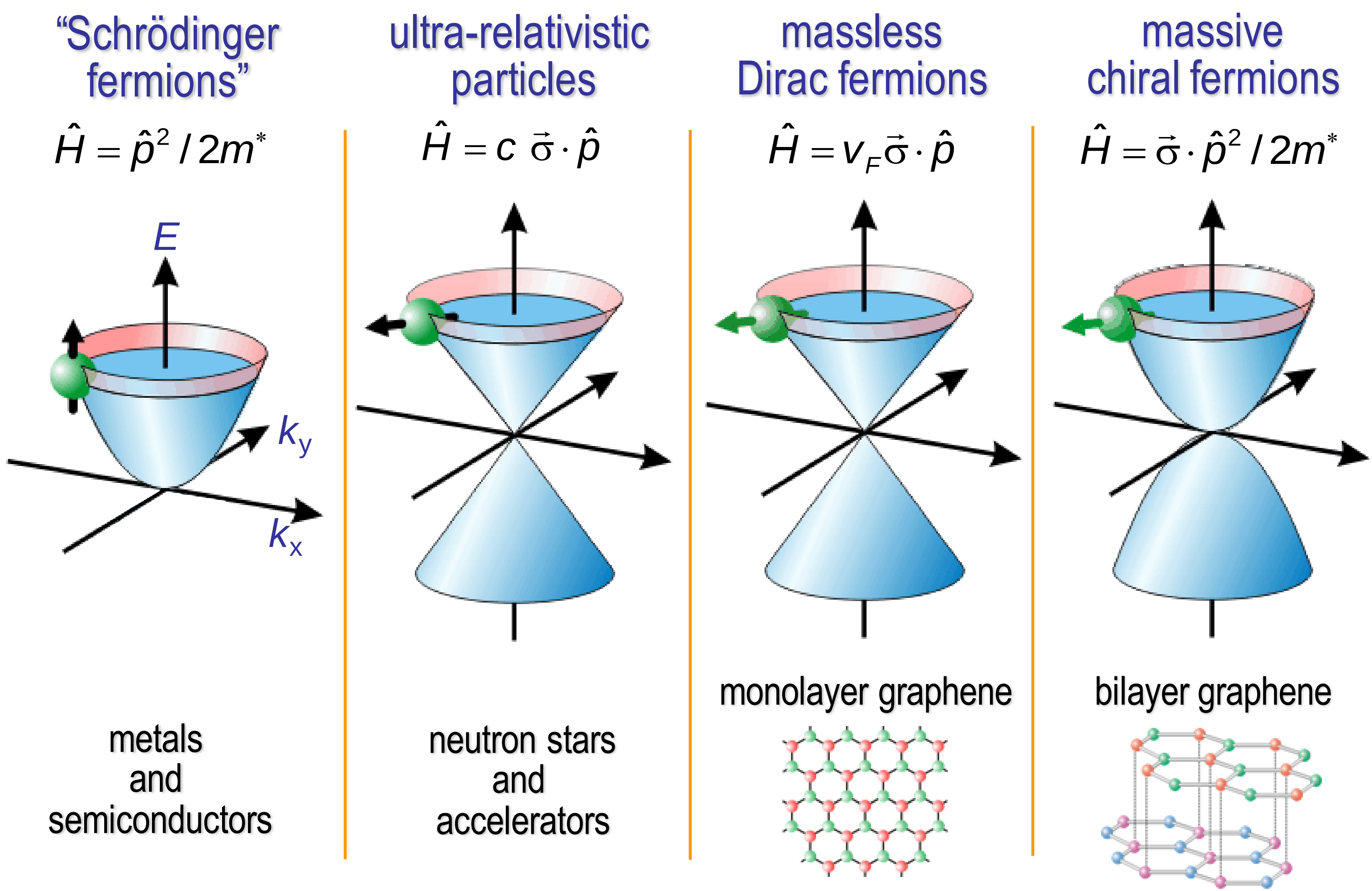
"anomalous" QHE



$$\hat{H} = -\frac{1}{2m} \begin{pmatrix} 0 & (\hat{p}_x + i\hat{p}_y)^2 \\ (\hat{p}_x - i\hat{p}_y)^2 & 0 \end{pmatrix}$$

Manchester+Lancaster, *Nature Phys* '06

EQUATION UNIVERSE BEFORE AND AFTER



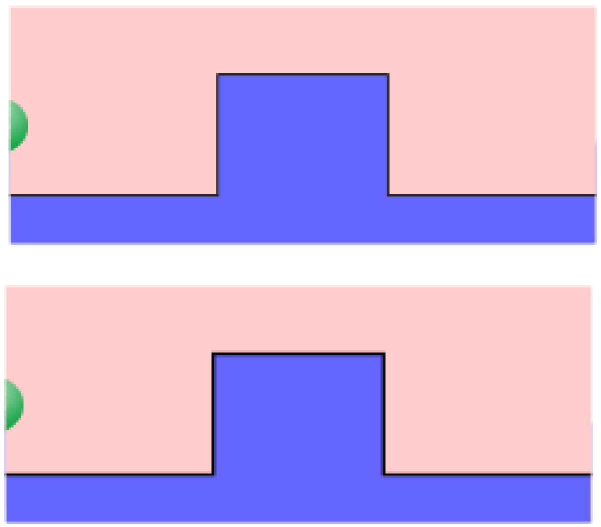
NEW PHYSICS

ACCESS TO RELATIVISTIC-LIKE PHYSICS
IN CONDENSED MATTER EXPERIMENT

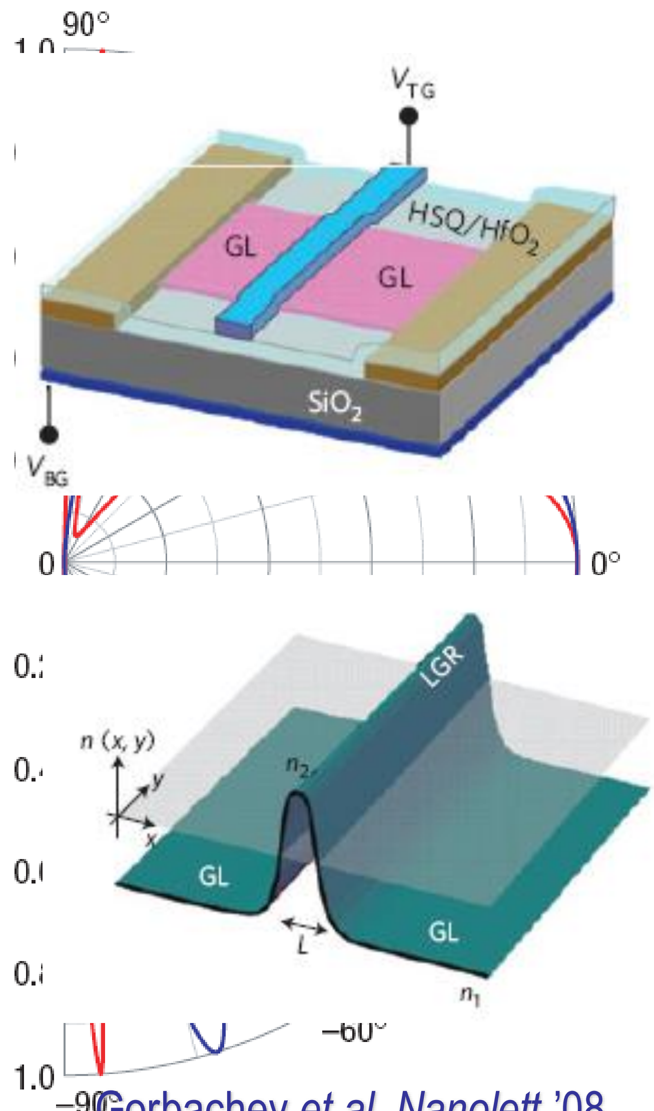
EXAMPLE #1:

Klein Tunnelling

Klein Tunnelling



Klein 1929
Katsnelson + Manchester 2006



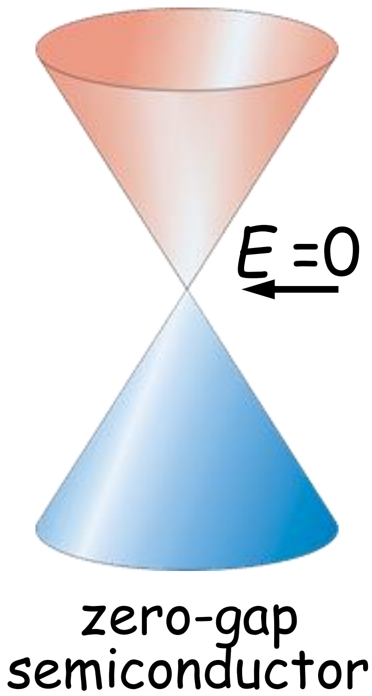
Gorbachev *et al*, *Nanolett* '08
Stander *et al*, *PRL* '09
Young *et al*, *Nature Phys* '09

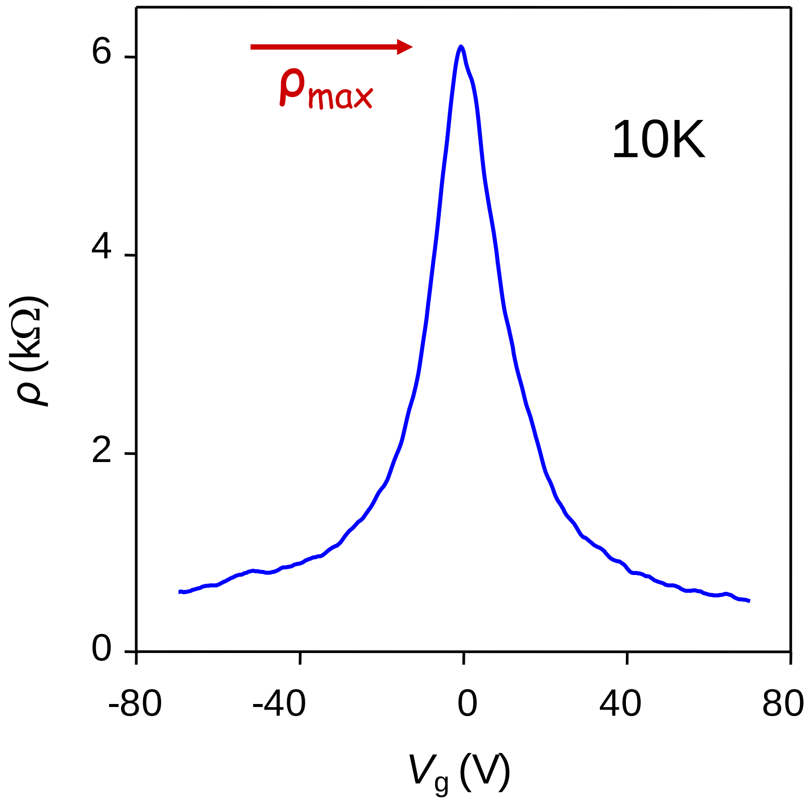
EXAMPLE #2:

conductivity "without" charge carriers

Manchester, *Nature* '05

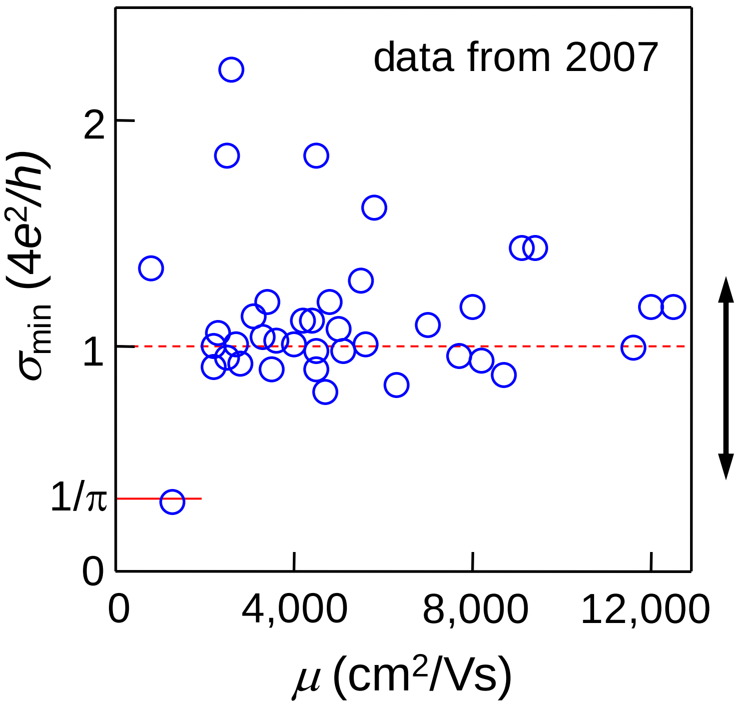
Minimum Quantum Conductivity





no localization
in the peak
down to 30mK
and
for million-range
mobilities

Minimum Quantum Conductivity



'quantized' conductivity
NOT conductance
(~e^2/h per spin and valley)

samples
with million mobility
when 1e left in μm^2

ROBUST METALLIC STATE
with high resistivity ~h/e^2

Fradkin 1986; Lee 1993; Ludwig 1994; Morita 1997; Ziegler 1998 …
Peres 2005; Gusynin 2005; Katsnelson 2006; Tworzydlo 2006; Cserti 2006; Ostrovsky 2006 …

EXAMPLE #3:

relativistic fall on superheavy nuclei

Shytov *et al PRL* 2007
Castro Neto *et al PRL* 2007
…..

Periodic table of the elements

- alkali metals
- alkaline earth metals
- transition metals
- other metals
- other nonmetals
- halogens
- noble gases
- rare earth elements (21, 39, 57–71) lanthanide elements (57–71 only)
- actinide elements

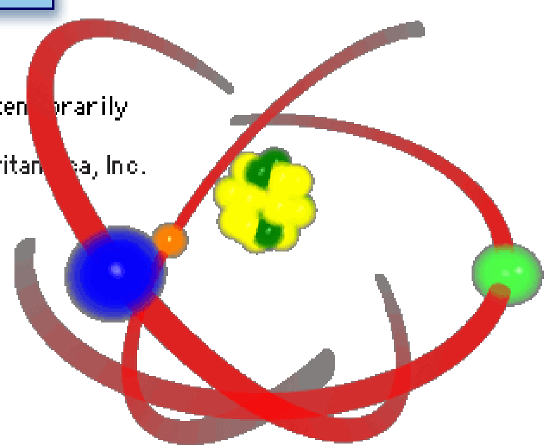
period \ group	1* Ia**	2 IIa	3 IIIb	4 IVb	5 Vb	6 VIb	7 VIIb	8 VIIIb	9 VIIIb	10 VIIIb	11 Ib	12 IIb	13 IIIa	14 IVa	15 Va	16 VIa	17 VIIa	18 0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 *** (Uub)	113 *** (Uut)	114 *** (Uuq)	115 *** (Uup)	116 *** (Uuh)		

lanthanide series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
actinide series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

* Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

** Numbering system widely used, especially in the U.S., from the mid-20th century.

*** Discoveries of elements 112–116 are claimed but not confirmed. Element names and symbols in parentheses are temporarily assigned by IUPAC.



Atomic Physics

$$Z < \frac{1}{\alpha} \approx 137$$

supercritical regime

$$Z > \frac{1}{\alpha} \approx 137$$

Positron emission

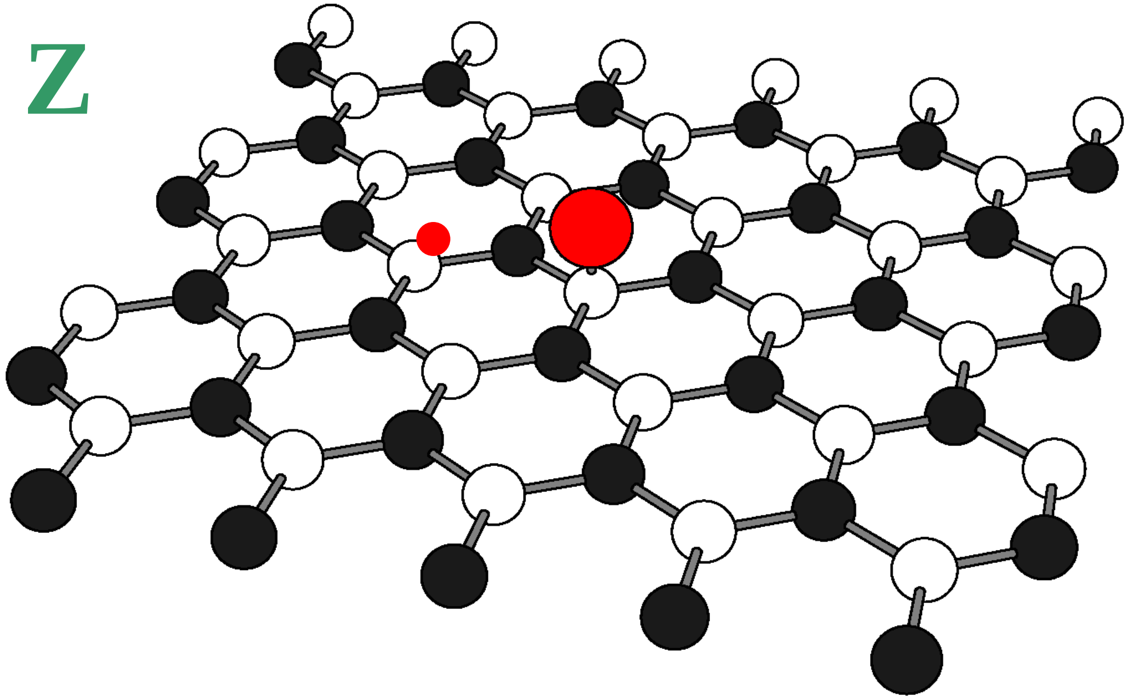
slides courtesy
of Antonio Castro Neto

Graphene Physics

"artificial atoms" easily become overcritical

$$\alpha_G = \frac{e^2}{\varepsilon_0 \hbar v_F} \approx \mathbf{1}$$

$$Z > \frac{1}{\alpha_G} \approx 1$$



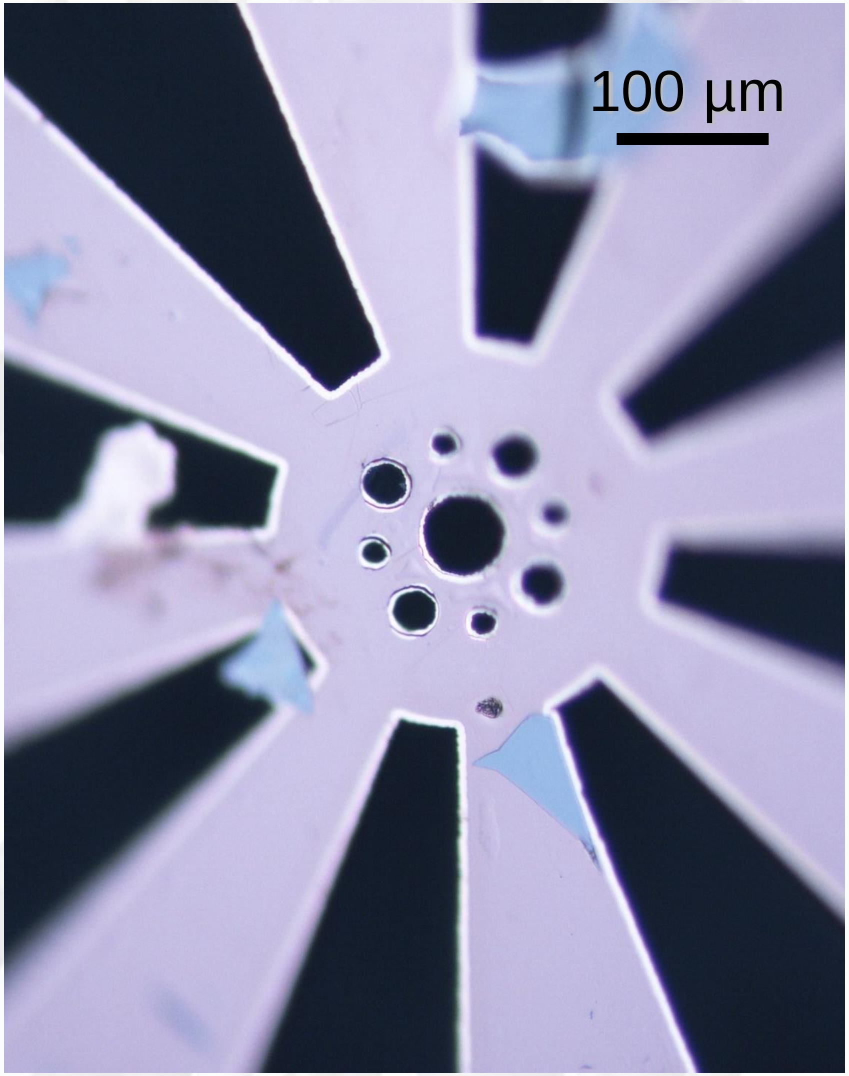
EXAMPLE #4:

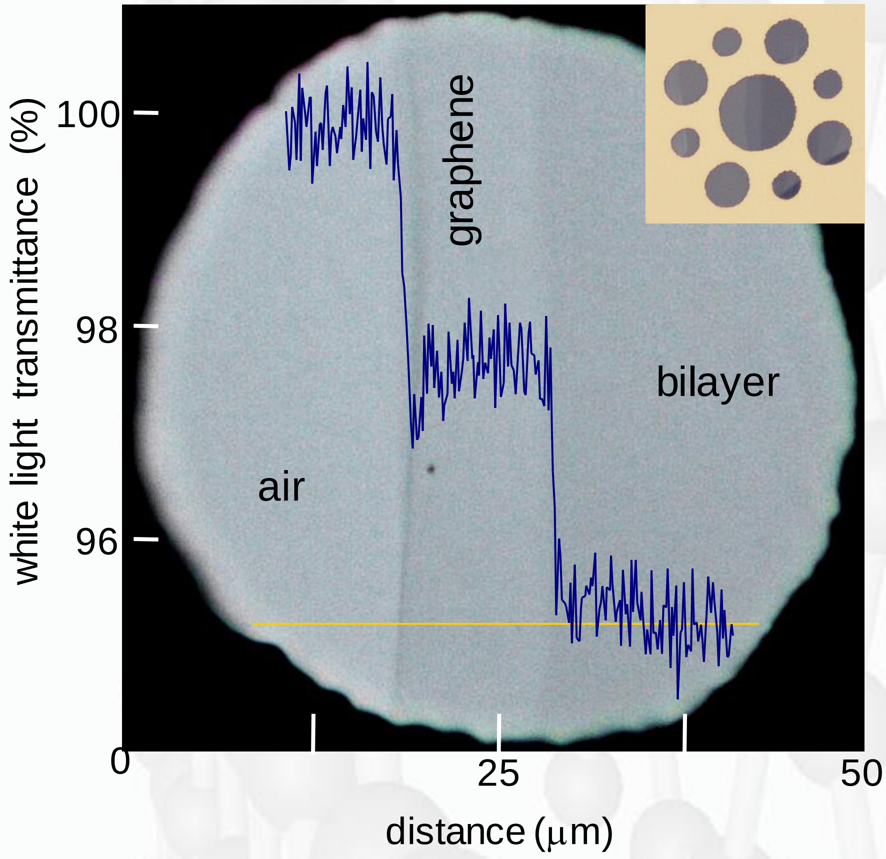
visualization of fine structure constant

Manchester, *Science* 2008

GRAPHENE OPTICS

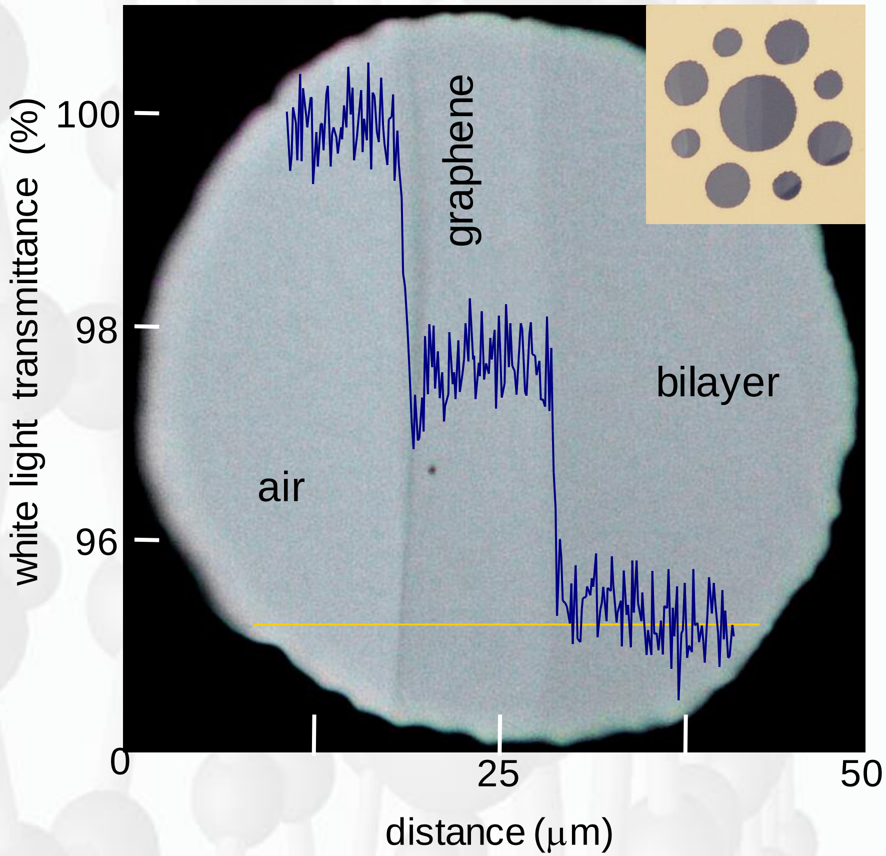
Manchester, *Science* '08



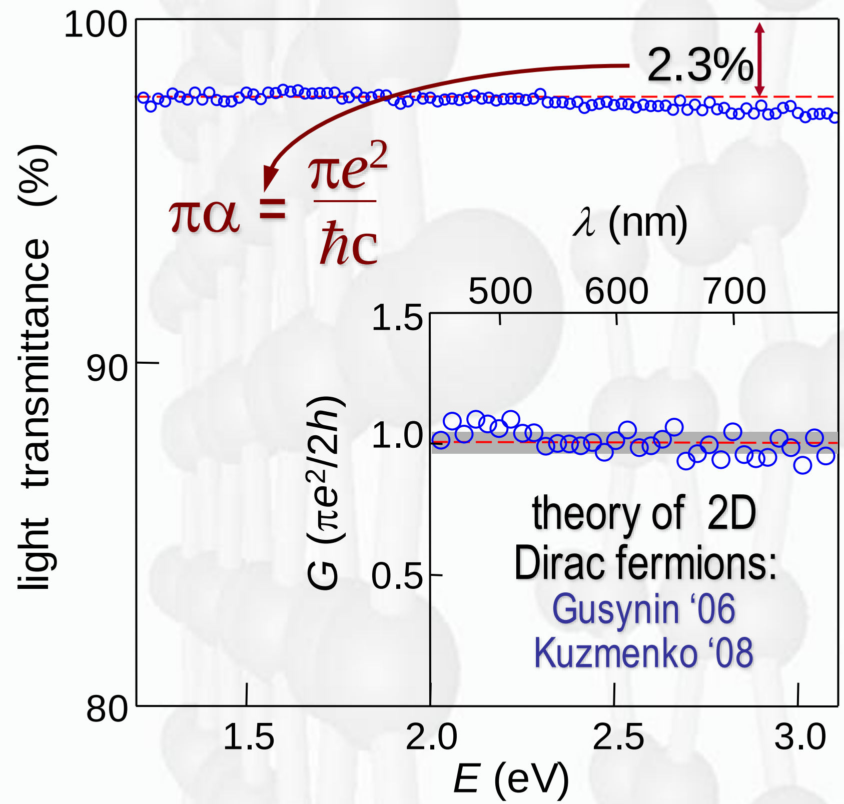


one-atom-thick single crystal
visible by naked eye

GRAPHENE OPTICS



one-atom-thick
single crystal
visible by naked eye



coupling of light with relativistic-like charges should be described by coupling constant α a.k.a. fine structure constant

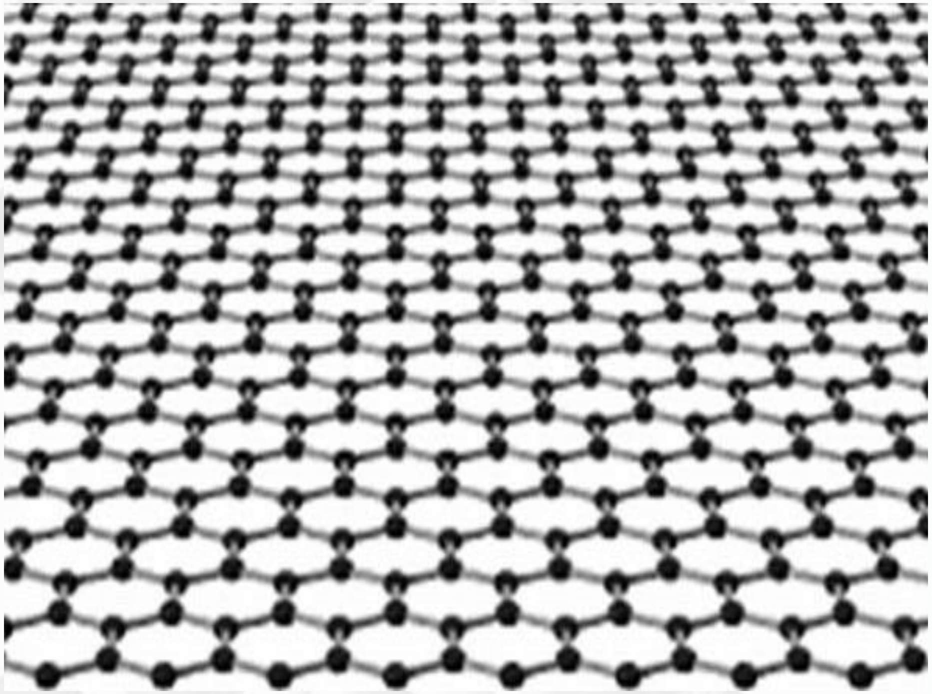
EXAMPLE #5:

New Graphene-Based Materials

Manchester, *Science* '09

Graphene as Giant Molecule

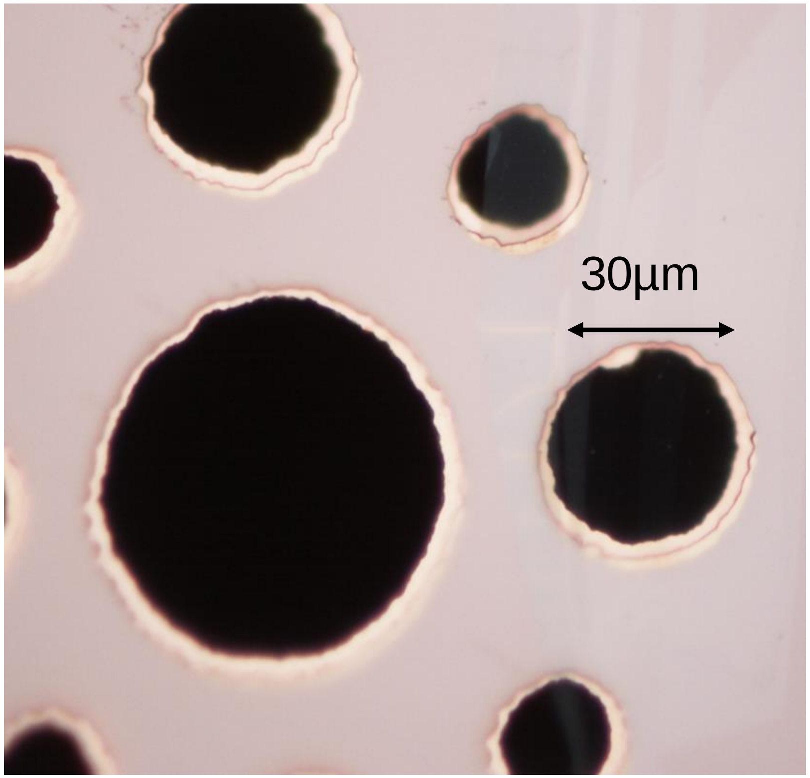
GRAPHENE

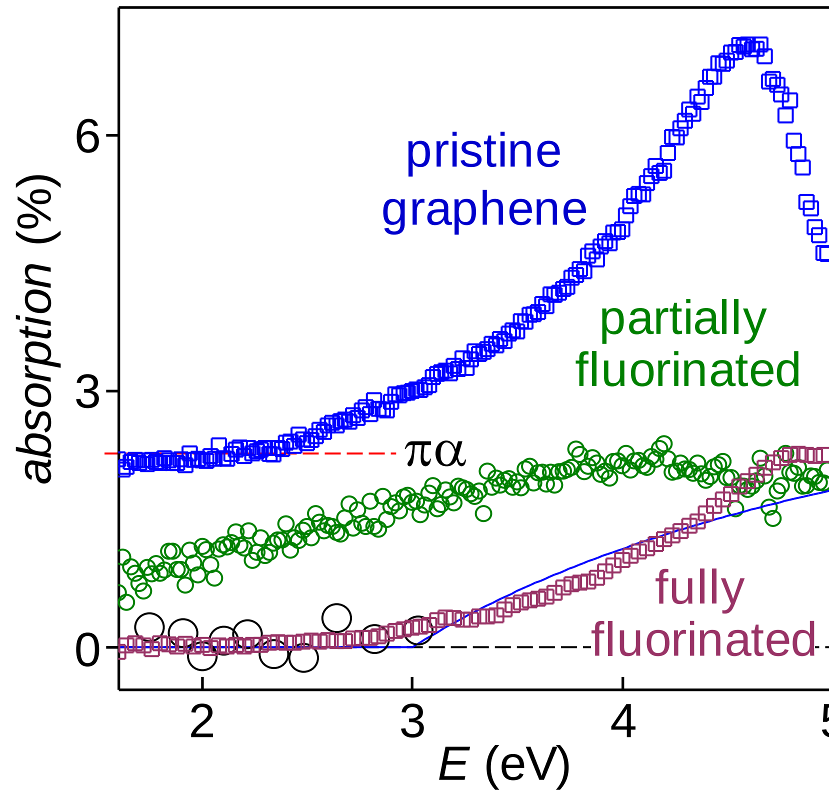


chemical reactions:
$C^{\infty} + \infty X \Rightarrow CX^{\infty}$

both surfaces available
(bi-surface chemistry; chemistry of individual macromolecules)

Stoichiometric Derivative





chemical reactions:

$C_\infty + \infty F \Rightarrow (CF)_\infty$

exposure to
atomic fluorine, using XeF_2

wide-gap semiconductor

Raman, optical, mechanical,
TEM and transport studies

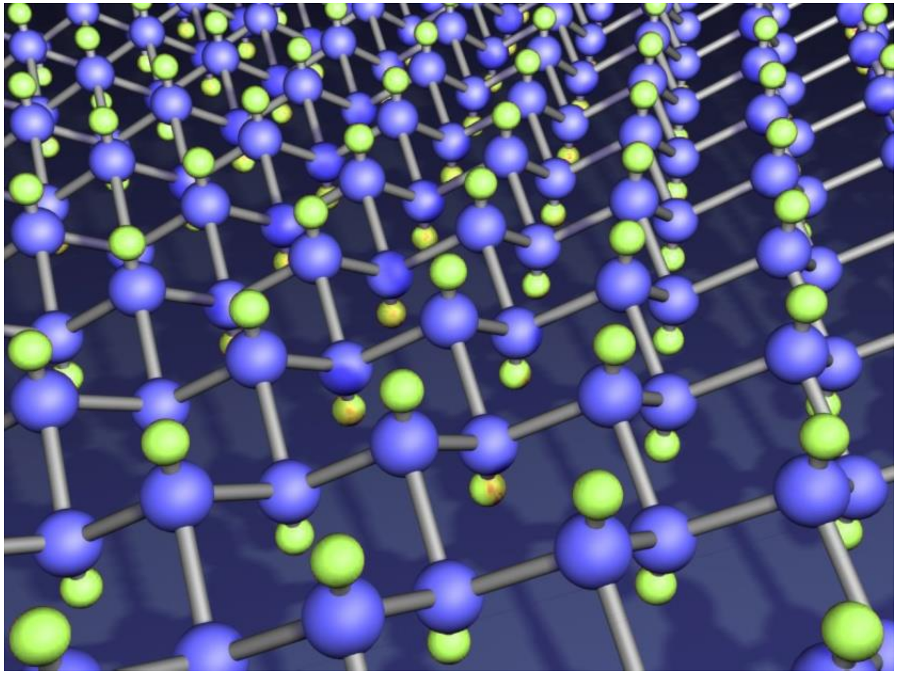
high-quality insulator

chemically & thermally stable

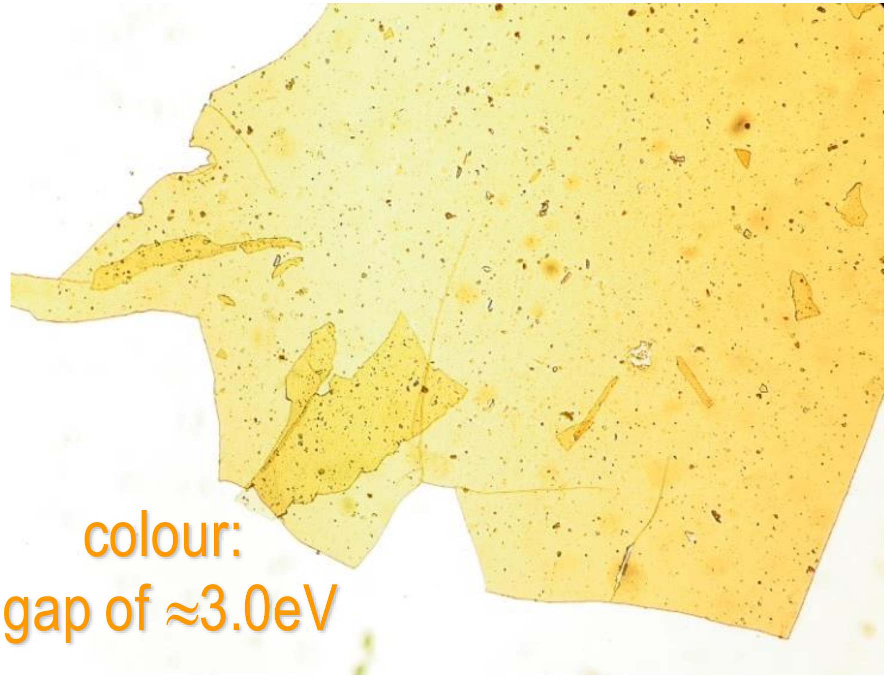
mechanically strong

Stoichiometric Derivative

fluorographene
("2D Teflon")



"fluorographene paper"



chemical reactions:

$C_\infty + \infty F \Rightarrow (CF)_\infty$

exposure to
atomic fluorine, using XeF_2

wide-gap semiconductor

high-quality insulator

chemically & thermally stable

mechanically strong

MESSAGE TO TAKE AWAY

CORNUCOPIA OF NEW SCIENCE

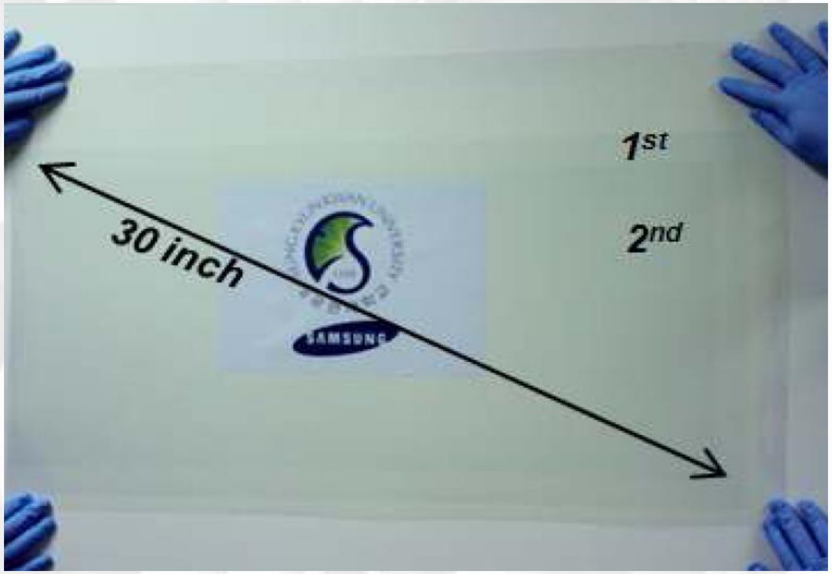
not only electronic properties

but optical, mechanical, chemical, etc.

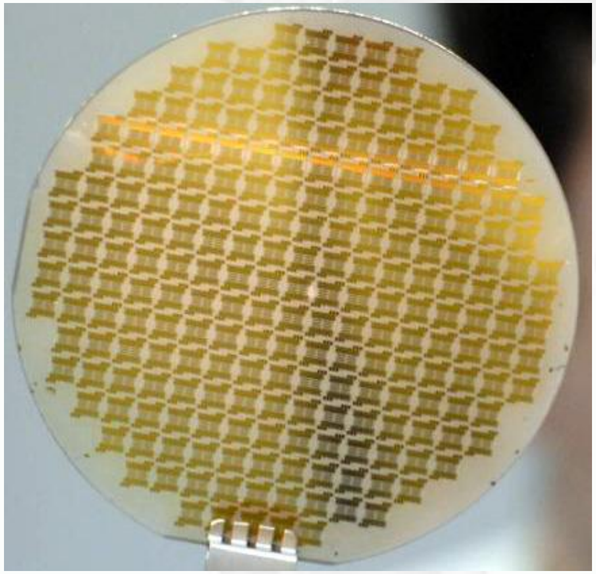
WHAT ABOUT APPLICATIONS?

INDUSTRIAL SCALE PRODUCTION IS A DONE DEAL

similar electronic quality



transfer
from Cu, Ni, etc.



growth on SiC

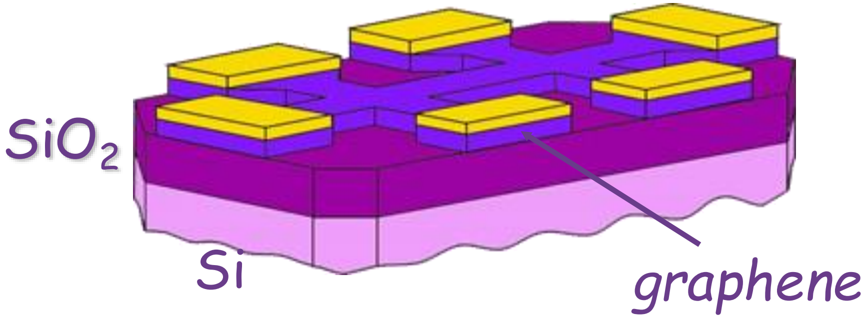
suspension

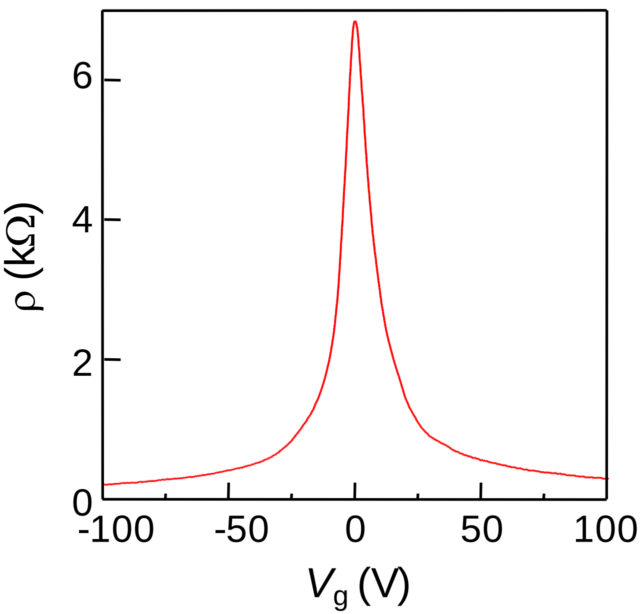
“graphene dreams”:

substitute for Si

Manchester, *Science* 2004
de Heer *et al*, *J.Phys.Chem.* 2004
see also Dresselhaus 1996

GRAPHENE ELECTRONICS





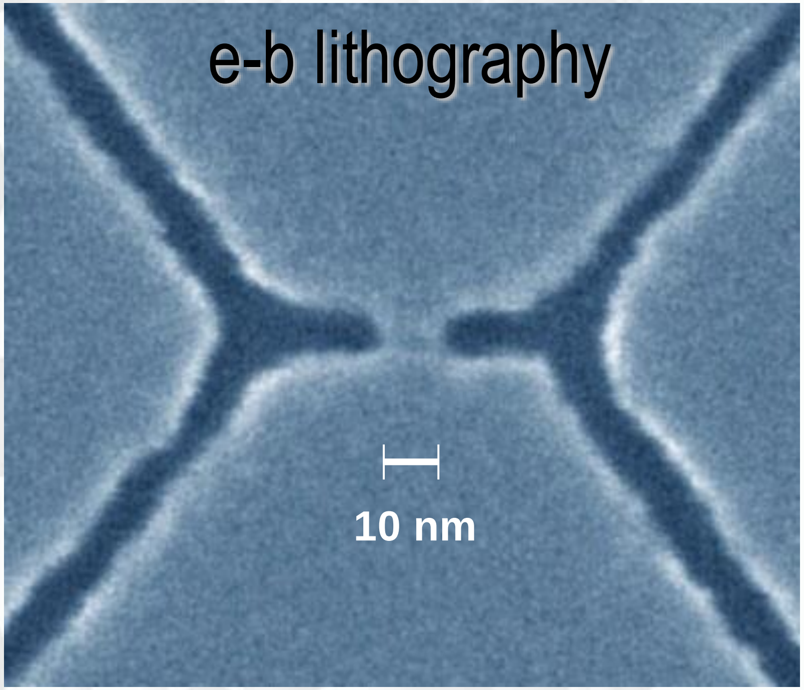
ballistic transport on submicron scale, high velocity, great electrostatics, scales to nm sizes

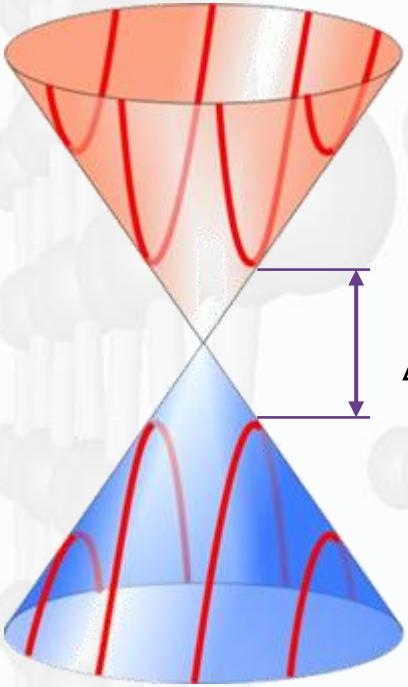
BUT

no pinch off

GRAPHENE NANO-CIRCUITS

$\Delta E = v_F h/2D$





$$\Delta E \approx \frac{1\ eV}{D(nm)}$$

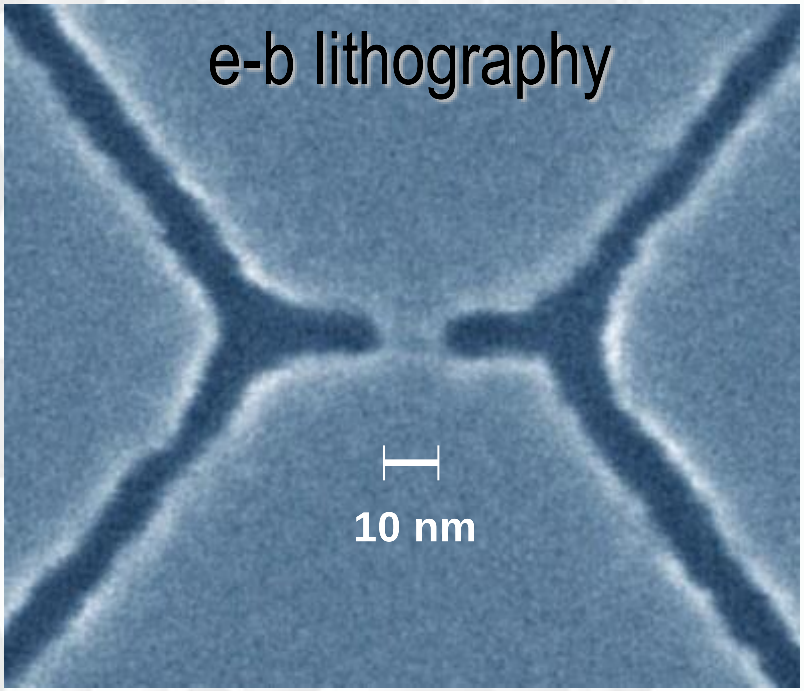
not $1/D^2$
as for electrons
but much larger $1/D$
as for slow photons

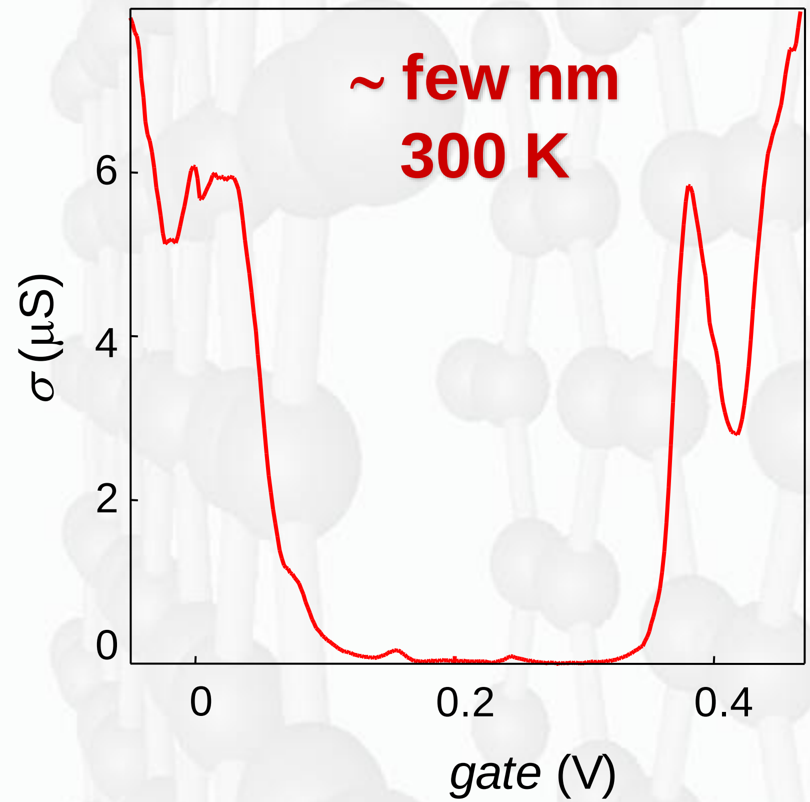
GRAPHENE NANO-CIRCUITS

stable and robust down to a few nm in size

$\Delta E = v_F\, h/2D$

sustains large (~1 μA per atom) currents



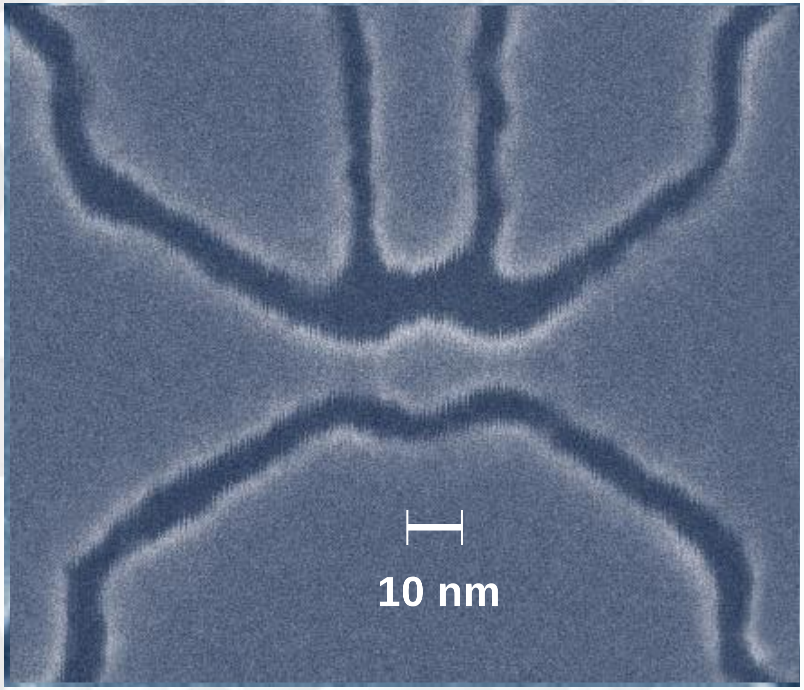


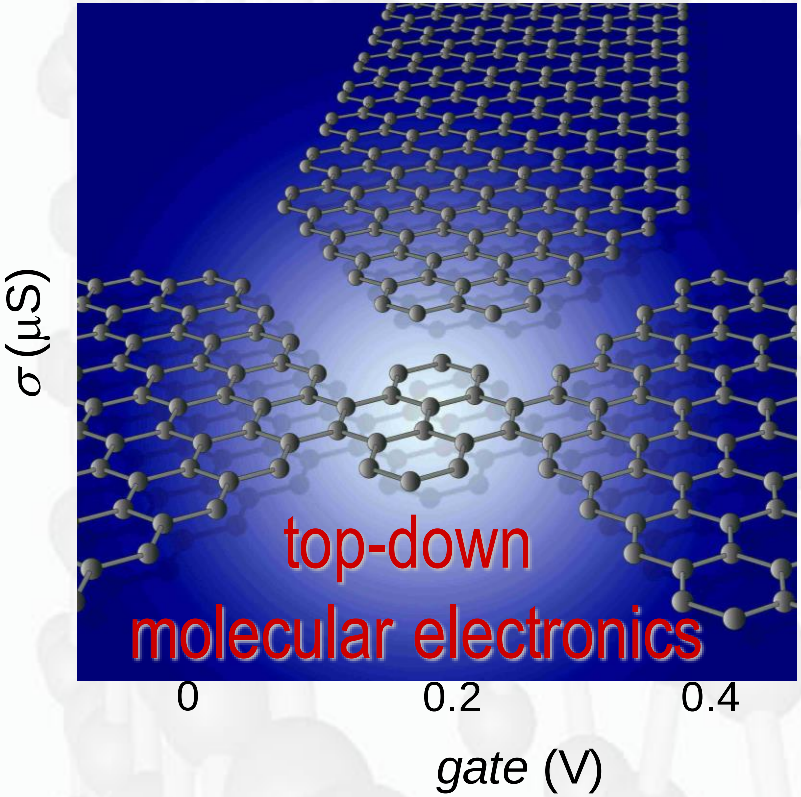
Manchester, *Science* '08

also, *Dai et al*, *Science* '08

GRAPHENE NANO-CIRCUITS

stable and robust down to a few nm in size
sustains large (~1 μA per atom) currents

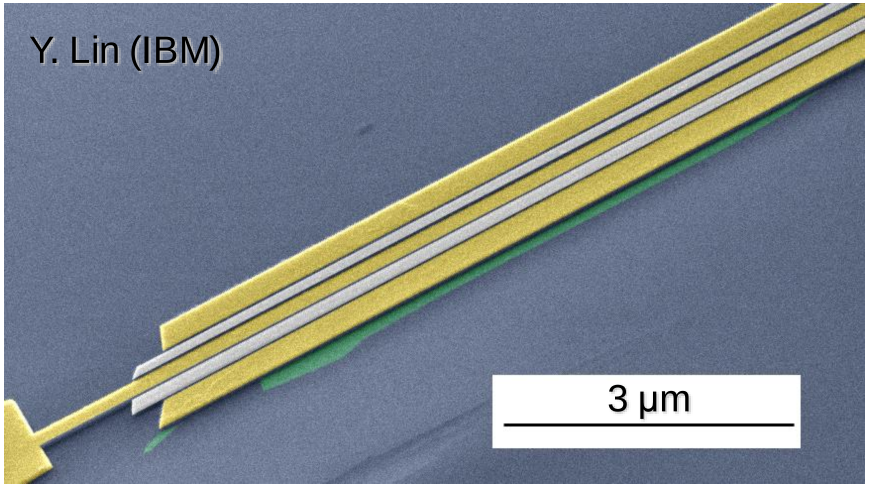


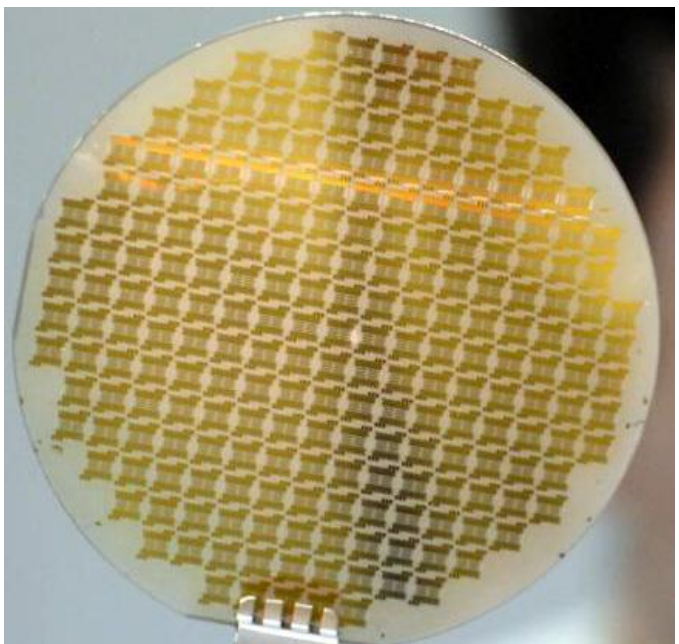


PROBLEM: no tools to sculpture at true nm scale
(same for any other nanoelectronics approach)

"in progress"

THz Transistors





ballistic transport between source & drain: *THz range*

ultra high-*f* analogue transistors: HEMT design; "standard" mobilities; on-off ratio: ~100

Manchester, *Science '04*

DARPA + MURI programs:
0.1 THz individual transistors on sale in 4 years

demonstrated (IBM & HRL 2009):
~100 GHz even for low μ & long channels

ONLY STEPSTONES:
scaling allows transistors up to 1THz

“non-grandeur” applications

FILLER FOR PLASTICS

production: > 100 tons per year

WHY GRAPHENE?

strength, lipophilicity, conductivity

both sides work

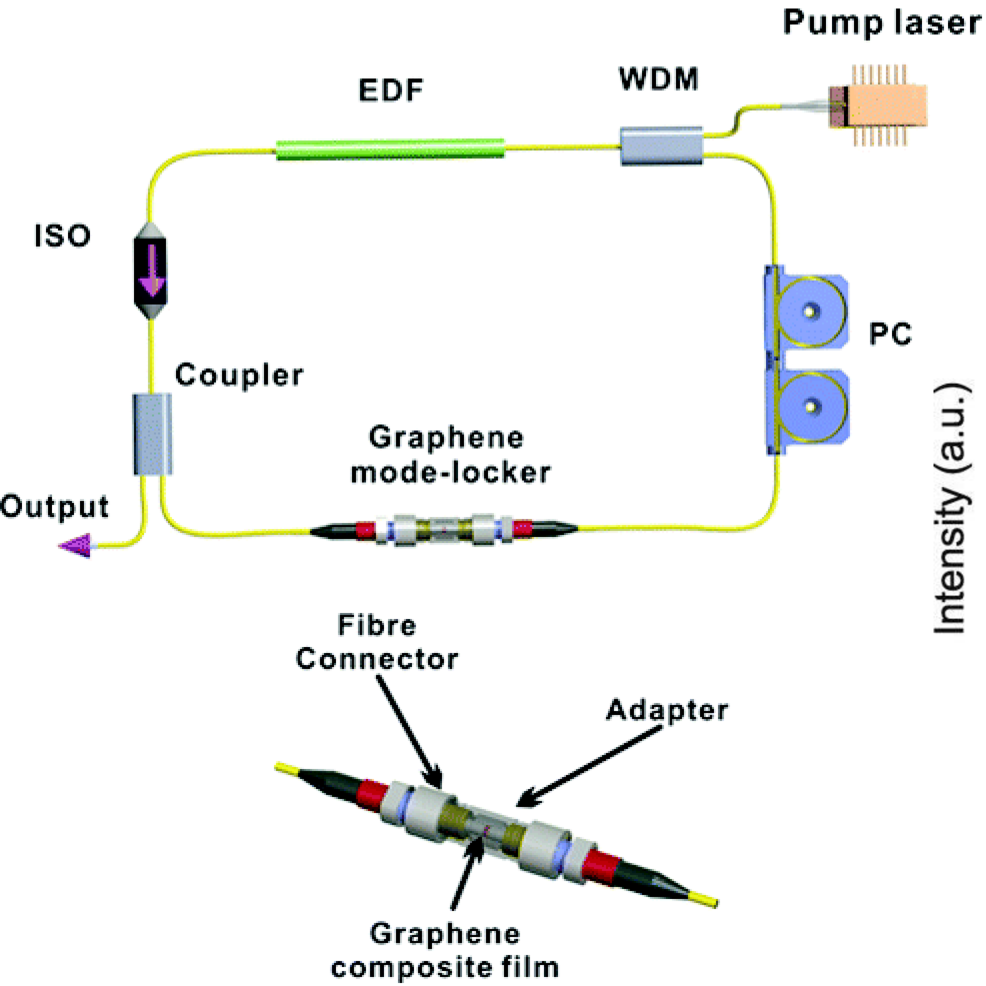
monolayers cannot cleave

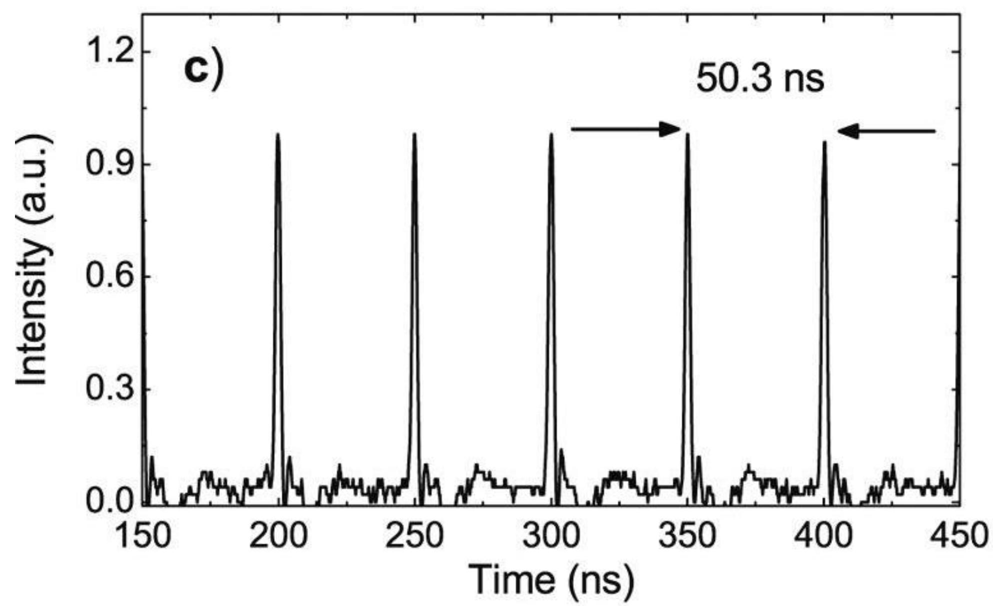
NICHE APPLICATIONS

broadband saturable absorbers

(from far-infrared to deep UV; ~10 fs response)

several papers
from Singapore & Cambridge, 2009-2010





FLEXIBLE OPTOELECTRONICS

substitute for ITO, etc

ρ <100Ω/□ transparency ~97%

Manchester, *Nanolet* '08;

also, Müllen, *Nanolet '08*

WORKING 10 μm
GRAPHENE PIXEL

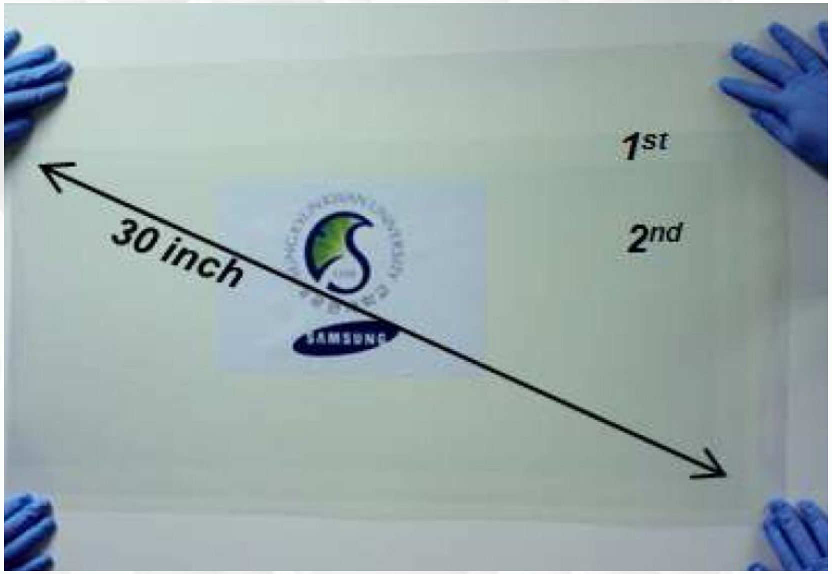
FLEXIBLE OPTOELECTRONICS

substitute for ITO, etc

ρ <100Ω/□ transparency ~97%

Manchester, *Nanolet* '08;

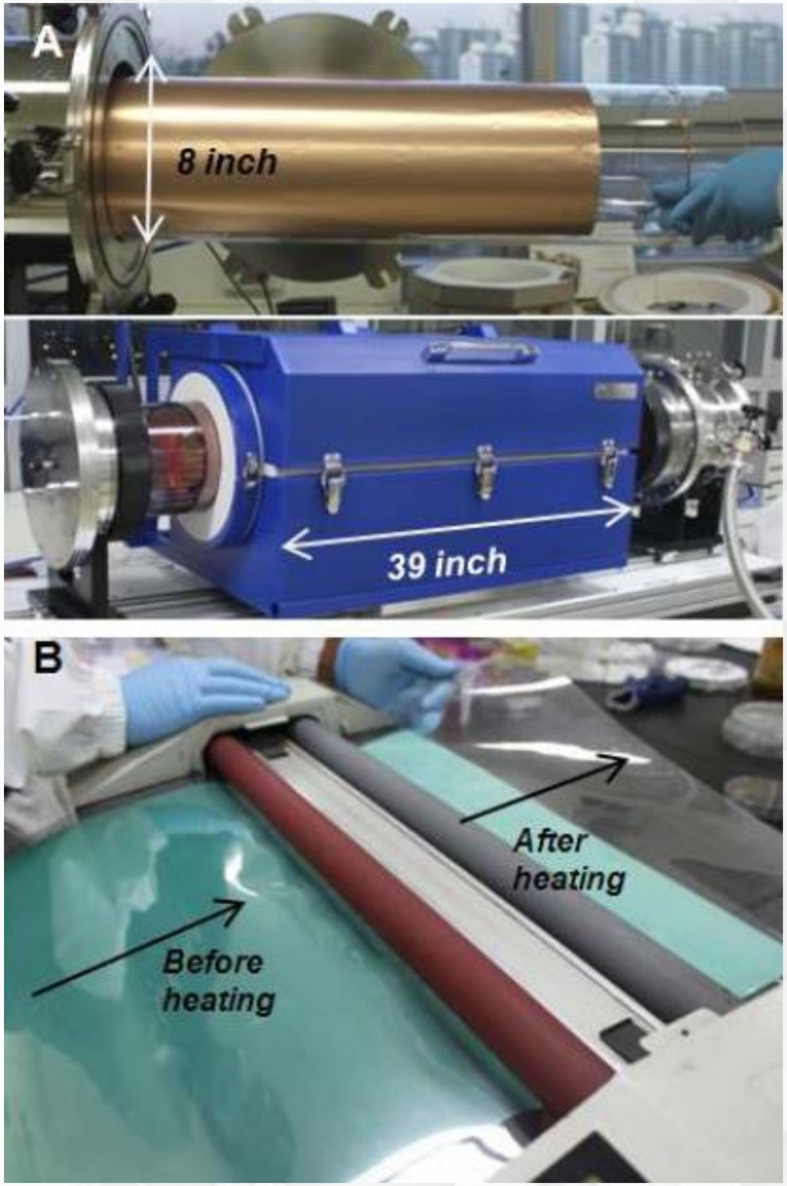
also, Müllen, *Nanolet* '08



ρ ~40Ω/□ transparency ~90%

μ ~5,000 cm^2/Vs

Hong, Nature 2009; arxiv 2010



FLEXIBLE OPTOELECTRONICS

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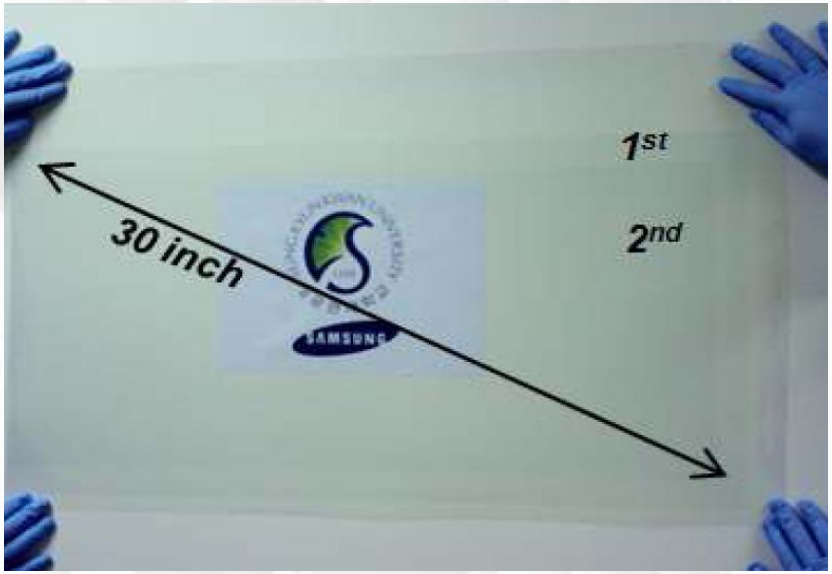


ρ ~40Ω/□ transparency ~90%

μ ~5,000 cm^2/Vs

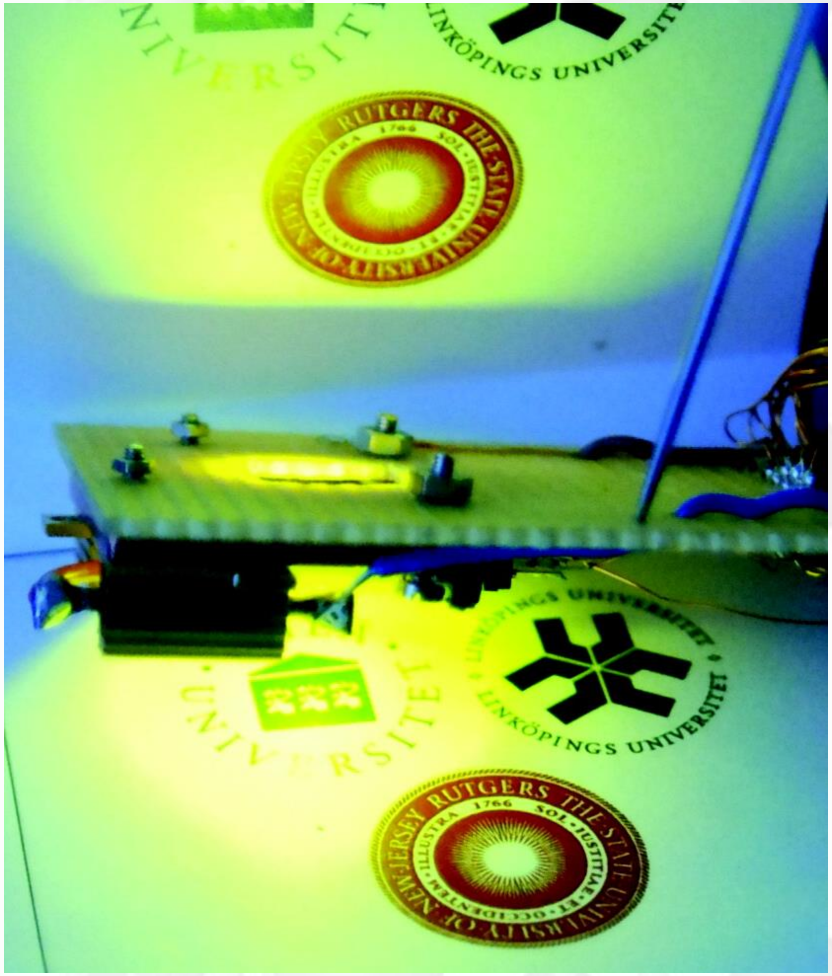
Hong, Nature 2009; arxiv 2010

flexibility comes on top

perfect match for OLED

both graphene anode & cathode

FOR LIGHTING



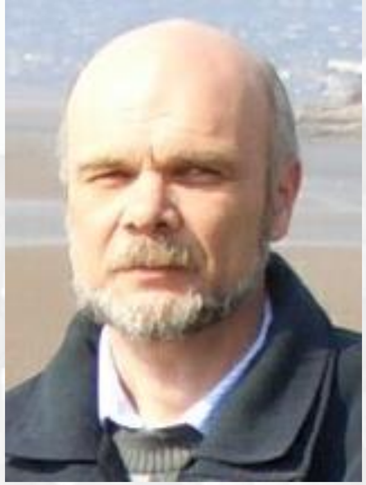
Robinson et al, ACS Nano 2010

FINAL MESSAGE TO TAKE AWAY

only after 5 years
Applications Are No Longer
a Wishful Thinking

maybe, OTHER 2D MATERIALS (?)

Kostya Novoselov

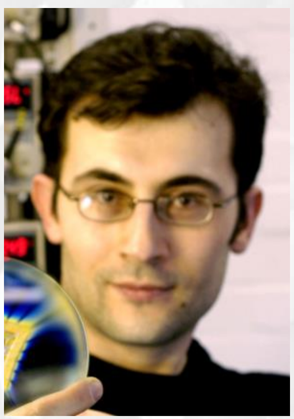


Sergey Morozov (Chernogolovka)

Rahul Nair

Misha Katsnelson (Nijmegen)

Irina Grigorieva



L.Ponomarenko

F. Schedin

P. Blake

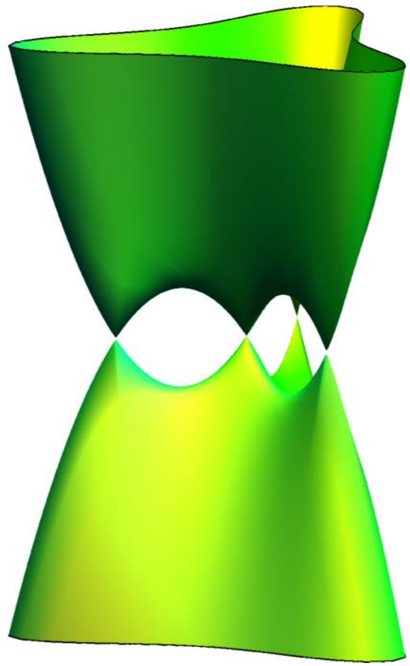
A. Castro Neto (Boston)

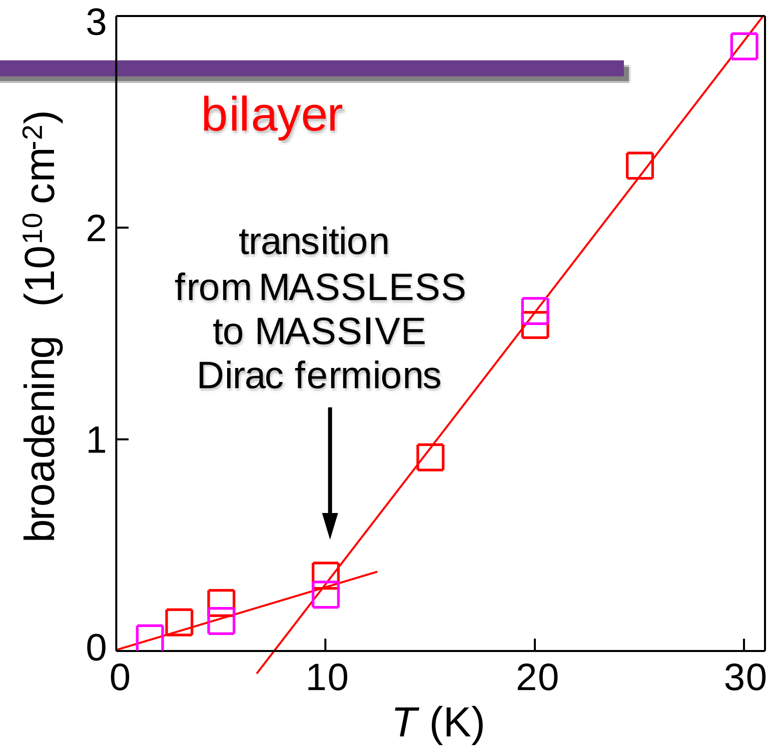
D. Elias

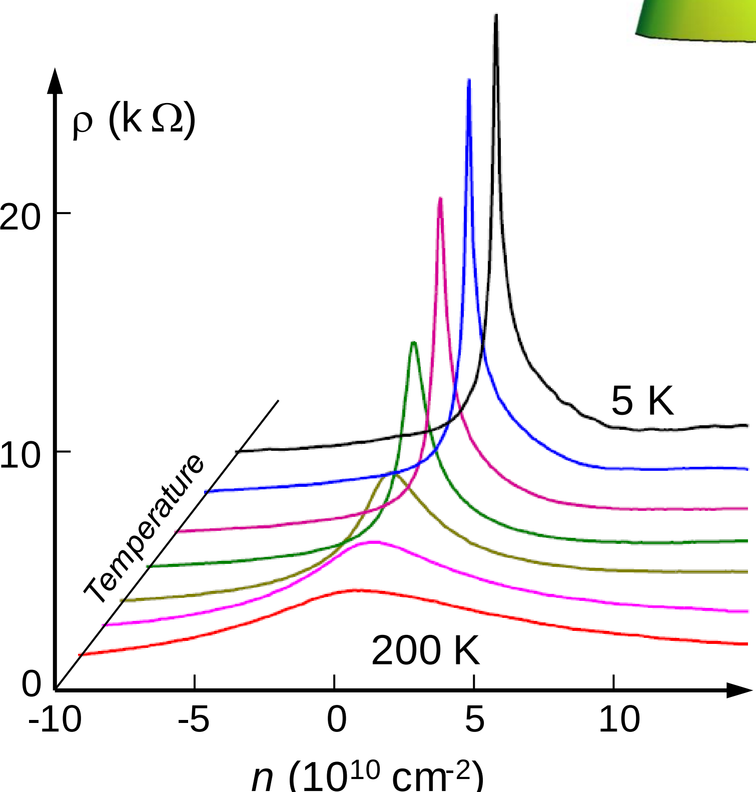
A. Ferrari (Cambridge)

Nuno Peres (Porto), Paco Guinea (Madrid), Leonid Levitov (Boston), Rui Yang, Soeren Neubeck, Ernie Hill, Sasha Zhukov, Sasha Grigorenko

graphene reviews: Nature Mat ‘07; *RMP* ’09; *Science* ‘09







NO GAP:
METALLIC STATE
at ~1meV

probing
the Dirac point