Chun Ning Lau
(Jeanie)

UNIVERSITY of CALIFORNIA
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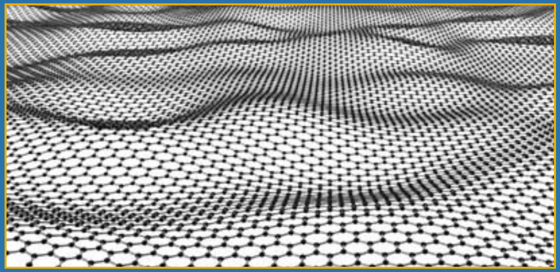
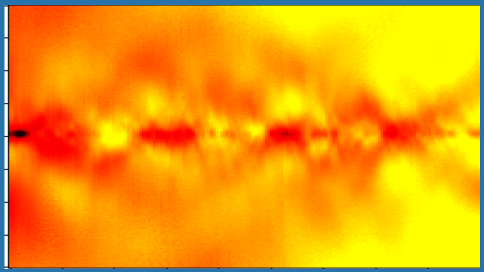
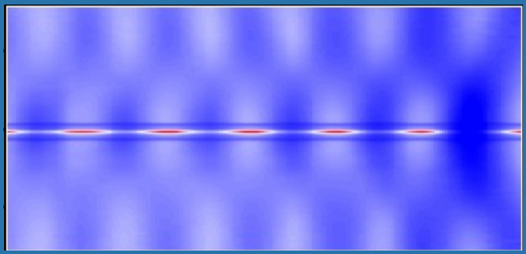
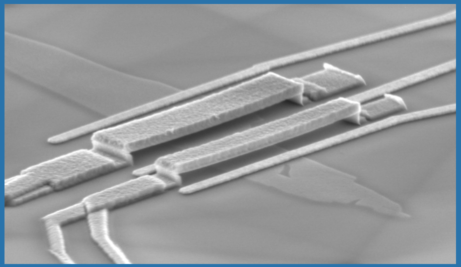




Size Matters: Nanotechnology and Other Wonders in graphene





Nanotechnology 101

What is Nanotechnology?

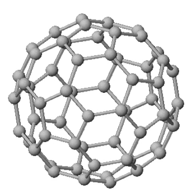
the creation, control and manipulation of matters on the scale of 1 - 100 nanometers.

How big is a nanometer?

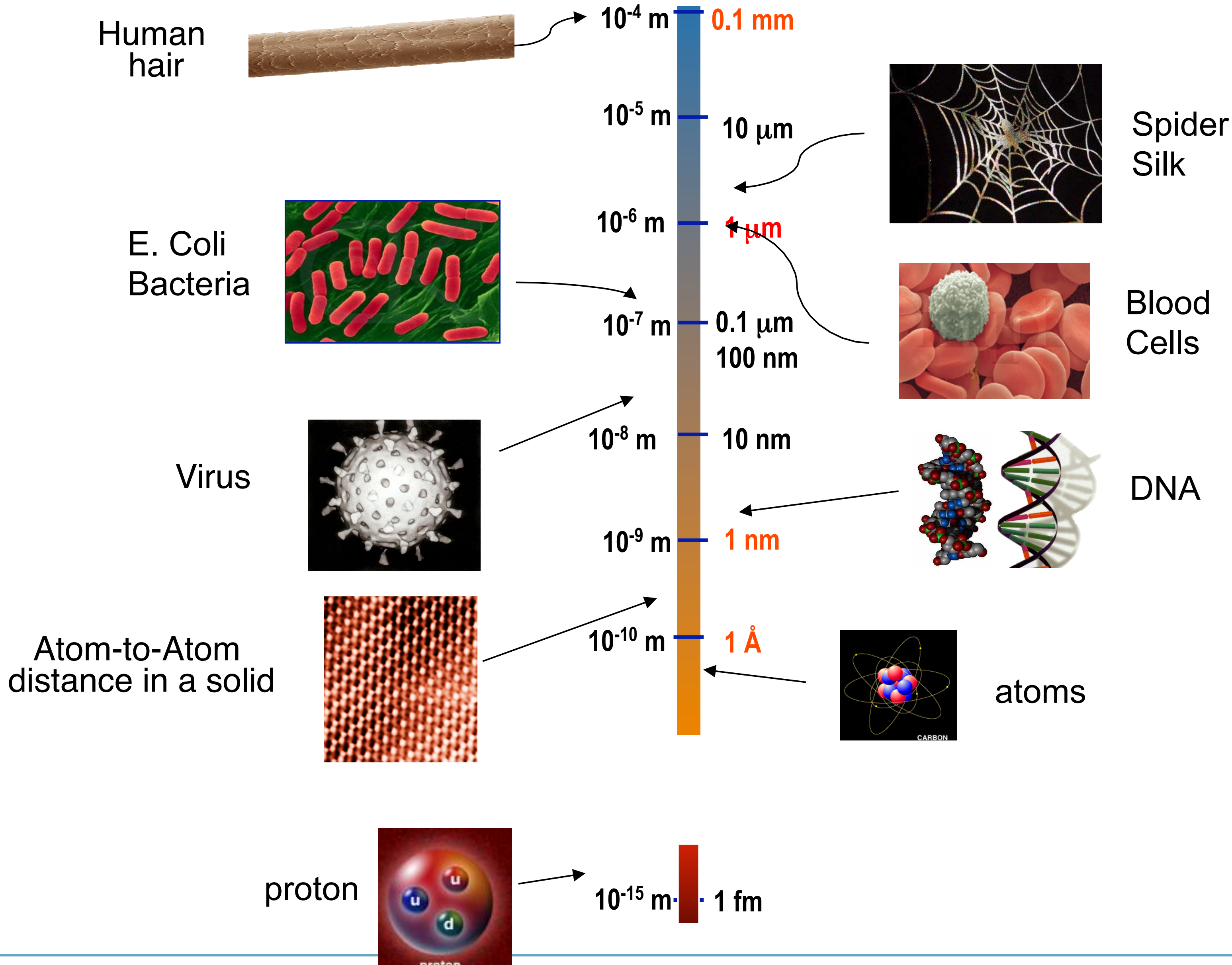
1 nanometer is 0.000000001 of a meter, or 0.00001 of the width of a human hair

I still don't know how small it is.

Buckyball,
1.1 nm diameter



Scale of Things



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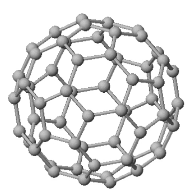


Why should I care?

Because it's there

J.J. Thomson

Parliament member:
Is there any use of these electrons?

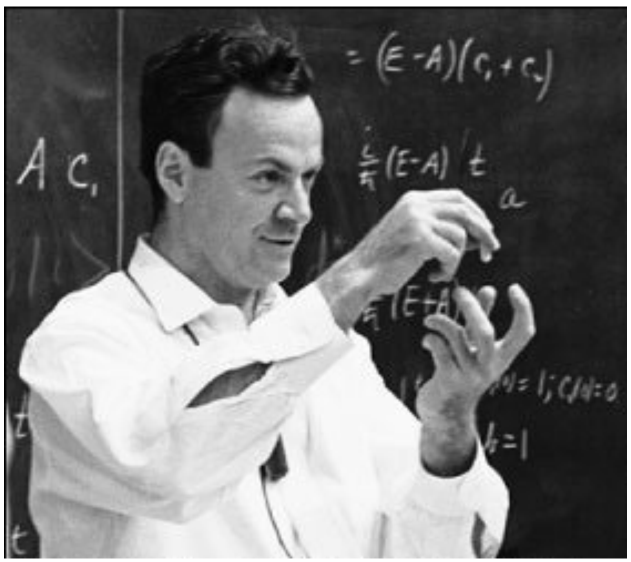
I don't know but I'm sure you'll find a way to tax it.

Discovered electrons in 1897

Nanotechnology Past -- The Beginning

There's Plenty of Room at the Bottom

An invitation to enter a new field of physics



Richard Feynman, Nobel Laureate.

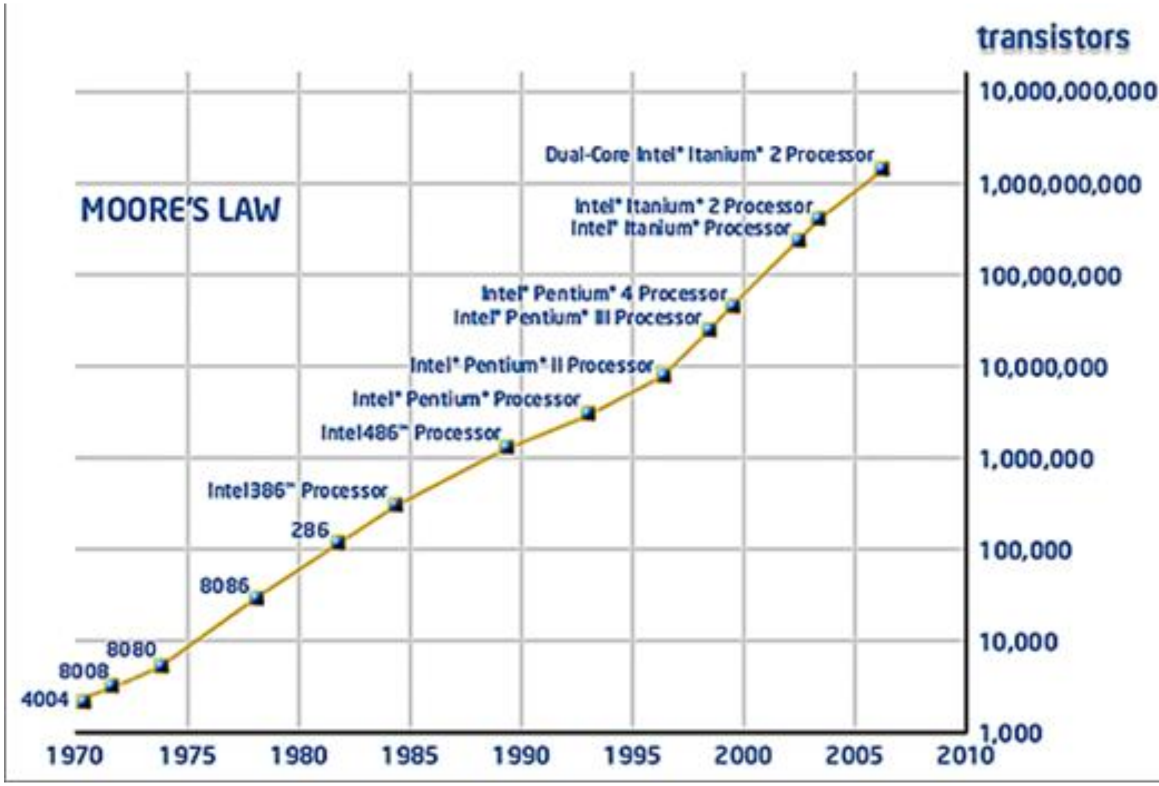
American Physical Society Meeting, Dec. 29th, 1959

I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle. …. What I want to talk about is the problem of manipulating and controlling things on a small scale… miniaturization.

All of the information that man has carefully accumulated in all the books in the world can be written… in a cube of material one two-hundredth of an inch wide, which is the barest piece of dust that can be made out by the human eye. So there is *plenty* of room at the bottom! Don't tell me about microfilm!…

I do know that computing machines are very large; they fill rooms. Why can't we make them very small, make them of little wires, little elements -- and by little, I mean *little*. For instance, the wires should be 10 or 100 atoms in diameter, and the circuits should be a few thousand angstroms across. Everybody who has analyzed the logical theory of computers has come to the conclusion that the possibilities of computers are very interesting -- if they could be made to be more complicated by several orders of magnitude. If they had millions of times as many elements, they could make judgments. They would have time to calculate what is the best way to make the calculation that they are about to make.

Moore's Law

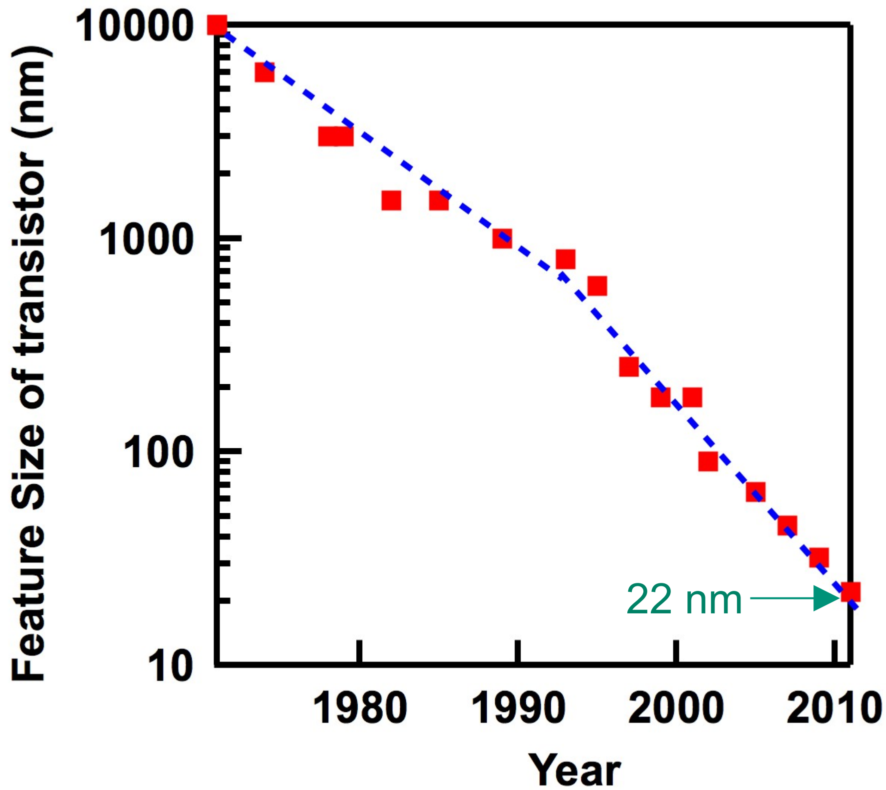


Gordon E. Moore
Intel Co-founder

The number of transistors on an integrated circuit doubles every 18-24 months

Not a Law of Nature

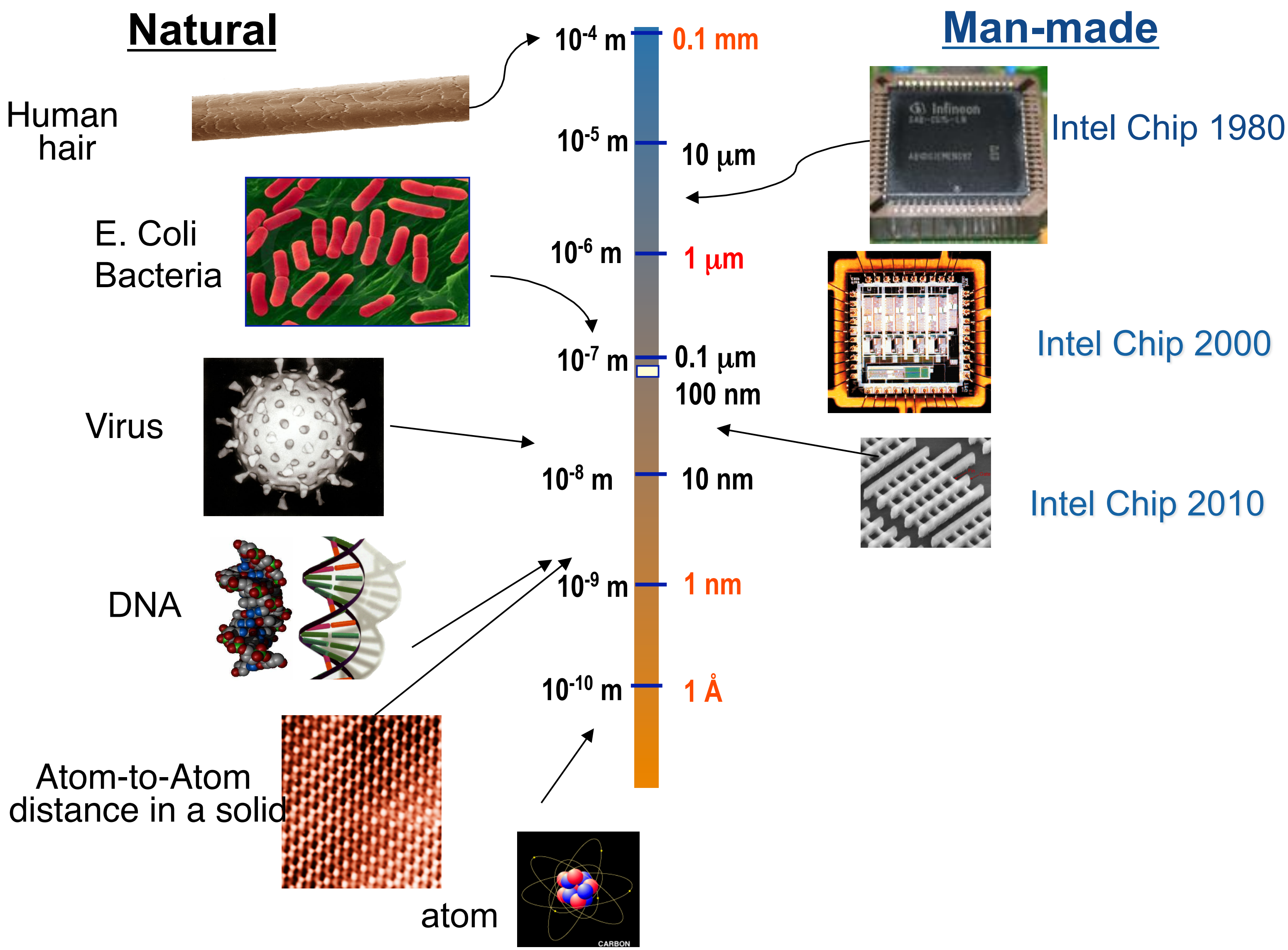
Moore's Law



Gordon Moore, Intel Co-founder

The size of a transistor is reduced by 30% every 18-24 months.

Nanotechnology -- Present



Moore's Law -- the past 50 years

1944: IBM-Harvard Automatic Sequence Controlled Calculator

- Size: 51 feet long, 8 feet wide
- Weight: 9400 pound
- Speed: 9 digit multiplication -- 6 seconds
- $30,000 ($500,000 in 2010 money)

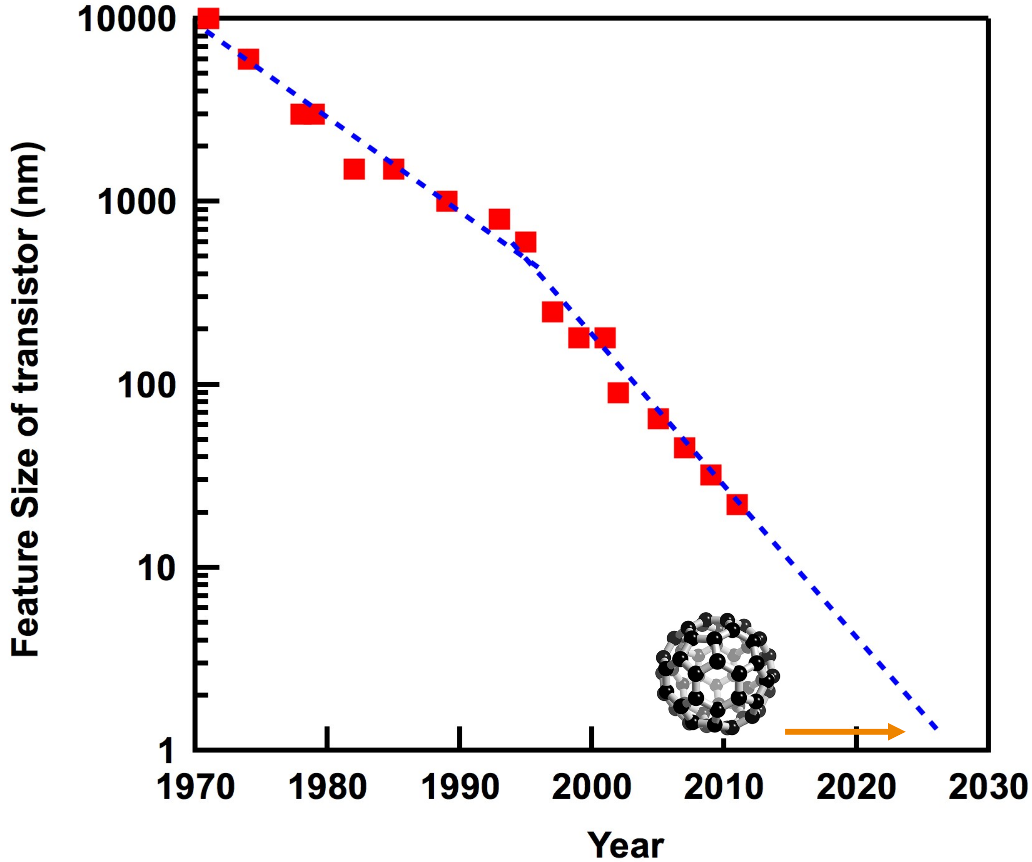
iPhone

- Size: 4.5 x 2.3 inches
- Weight: 5 oz
- Speed:2GHZ
- Camera+phone+iPod +GPS+calculator +games+…
- $300

“There is plenty of room at the bottom”

1960	**Feynman’s Prediction**	**Now**
Room-size	Computing machines can be much smaller	palm size
wires 0.1 mm	wires 10 - 100 atoms in diameter	22 nm (~60 atoms across)
simple calculation	computer judgment	

How much further can we take Moore's Law?

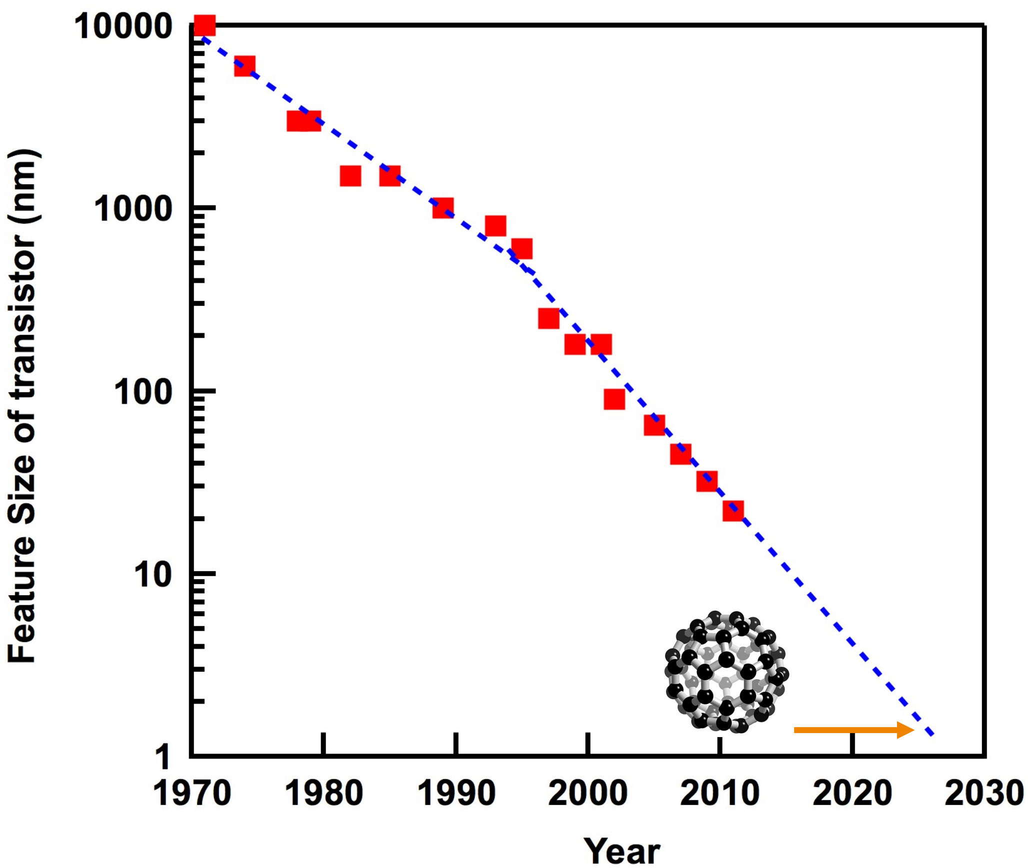


Gordon Moore, Intel Co-founder

Every 18-24 months the size of a transistor is reduced by 30%.

By 2025, a transistor size will be comparable to atoms or molecules.

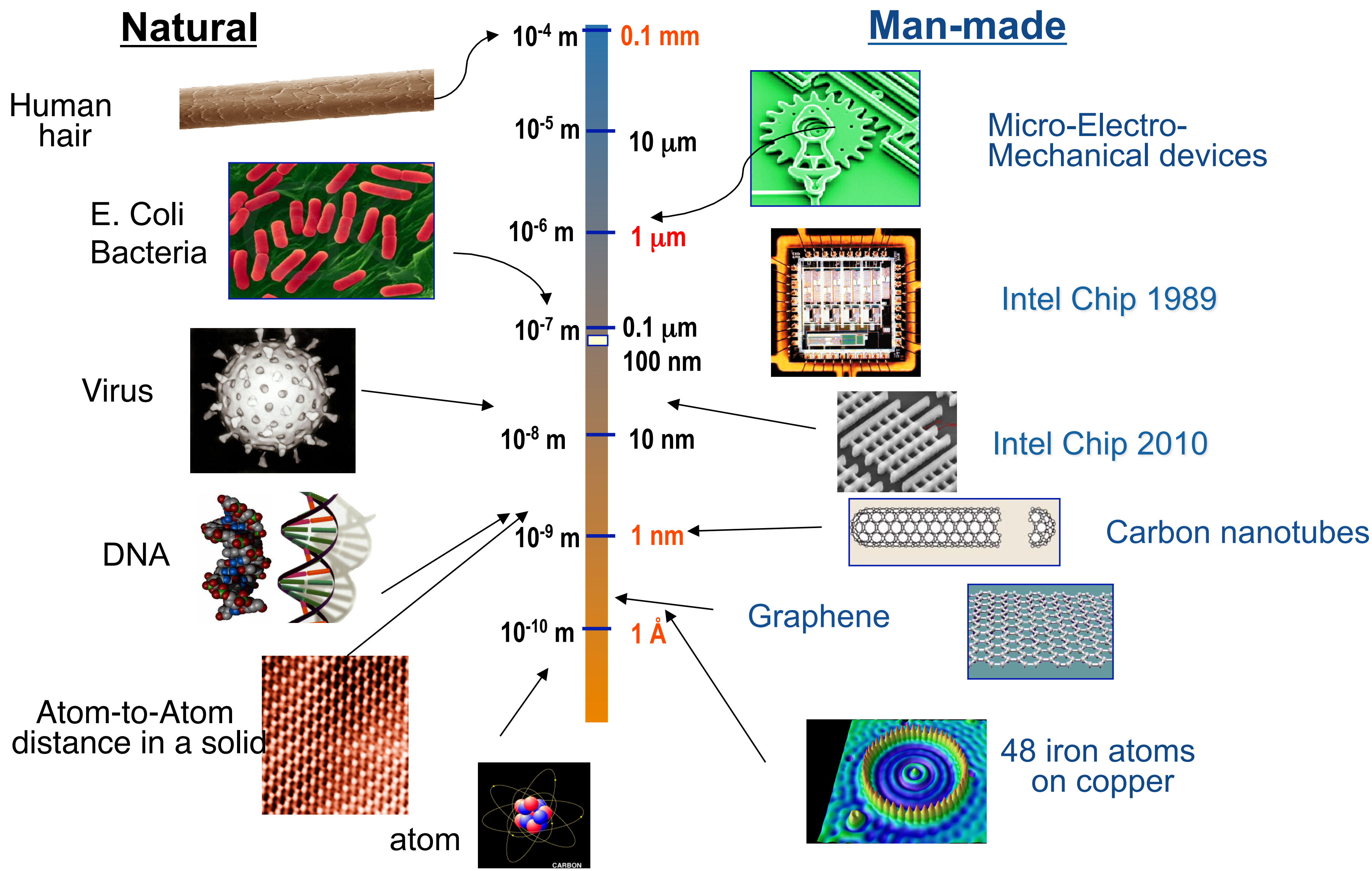
Moore's Law -- Past, Present and Future?



- Charge leakage
  (remember atoms in a metal are only 0.3 nm apart)
- Heat removal
  (laptop burns, anyone?)
- Current carrying limit
  (narrow metal wires = little fuses)
- Homogeneous fabrication
  (small imperfection on atomic scale fatal to devices)
- Unexpected phenomena arising from confining electrons and atoms to nanometer scale (both challenge and opportunity)

To continue miniaturization of electronics
⇨we need to understand how electrons and atoms behave in the nanometer range
⇨may need new material other than silicon

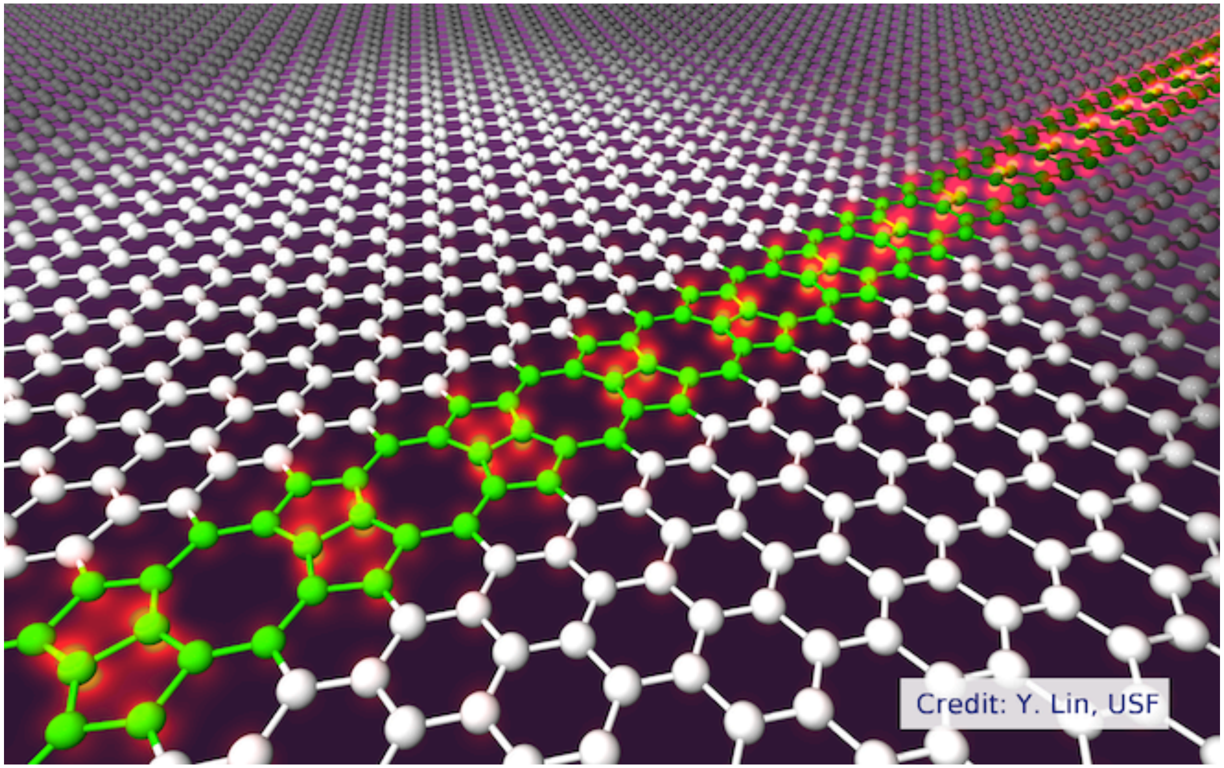
Nanotechnology -- Present and Future



Outline

- Introduction to Nanotechnology
- Nanotechnology Past
- Nanotechnology Present
- Carbon Flatland -- Graphene
    - What is graphene
    - Why is it interesting
    - What can it do for me
- Conclusion

Graphene

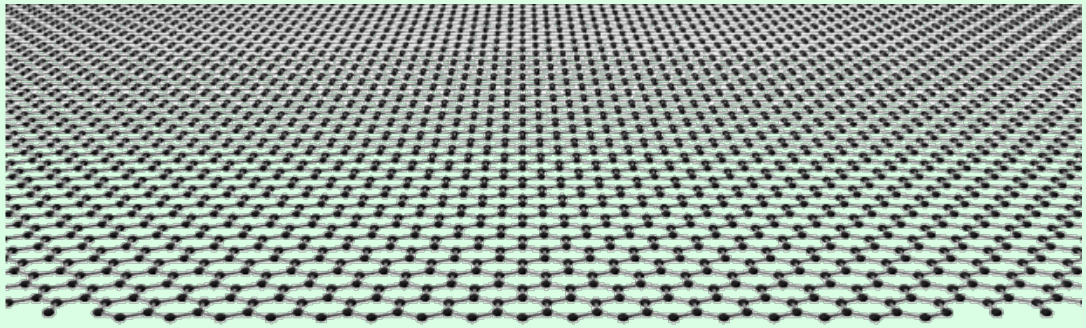


- A single layer of graphite
- Atoms arranged in honeycomb lattice (hexagons)
- Each carbon atom covalently bonded to 3 neighbours, "donates" 1 electron that roams freely on the sheet → good electrical conductor
- Graphite layers are held together by weak van der Waal's forces

Mother of Carbon Allotropes

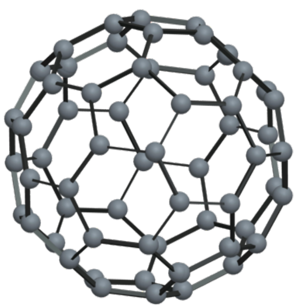
2d

GRAPHENE
2004



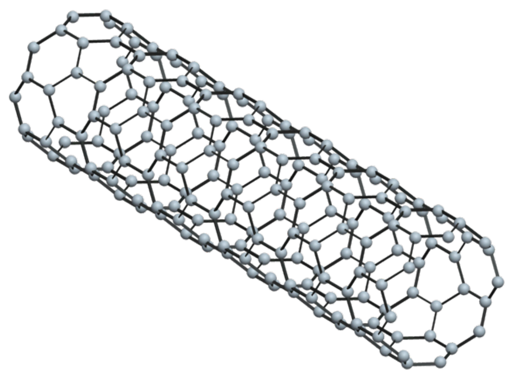
From Novoselov talk at IWNEPM, Kirchberg '07.

0d



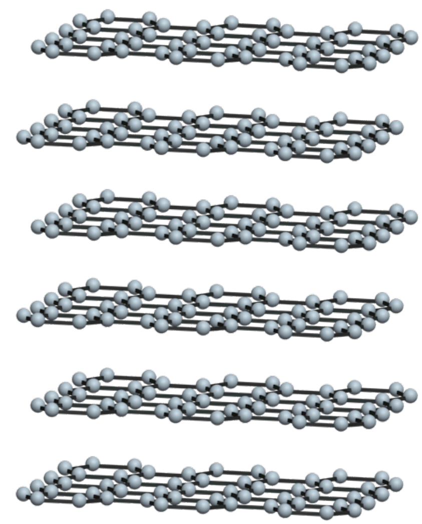
"Buckyball" C_{60}
1985

1d



Carbon Nanotube
1991

3d



Graphite

A Brief History of Graphene

1550 -- Graphite mine discovered, used to mark sheep

1800 -- Graphite + Clay + Wood casing = Pencil

1900 -- Graphite for industrial use: crucibles, steel-m king, electrodes, lubricants,…

1947 -- Theory of electron movement in si… …tiple layers of graphite

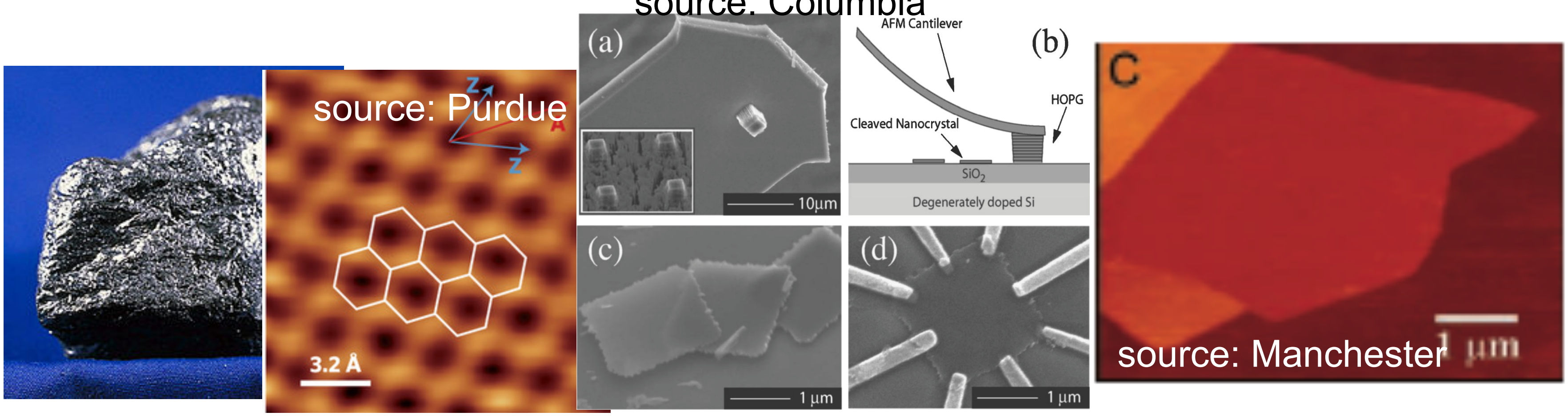
1960-90 -- nuisance of "monol… …found on metal surfaces at high vacuum

1995-2003 -- attempts t… …raphene with fancy techniques

the rest is history

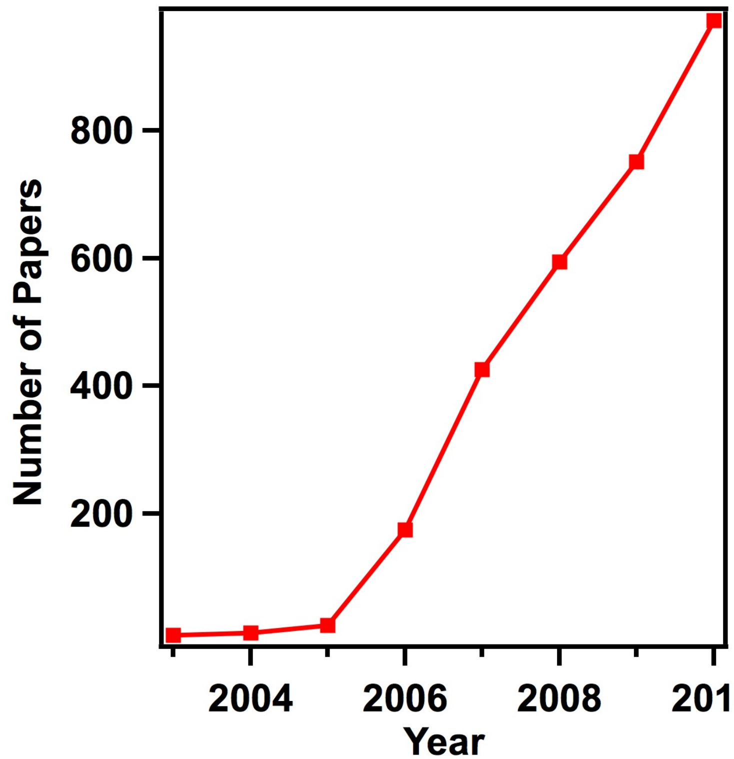
2004 -- Geim and Novoselov at Manchester isolated graphene using scotch tape

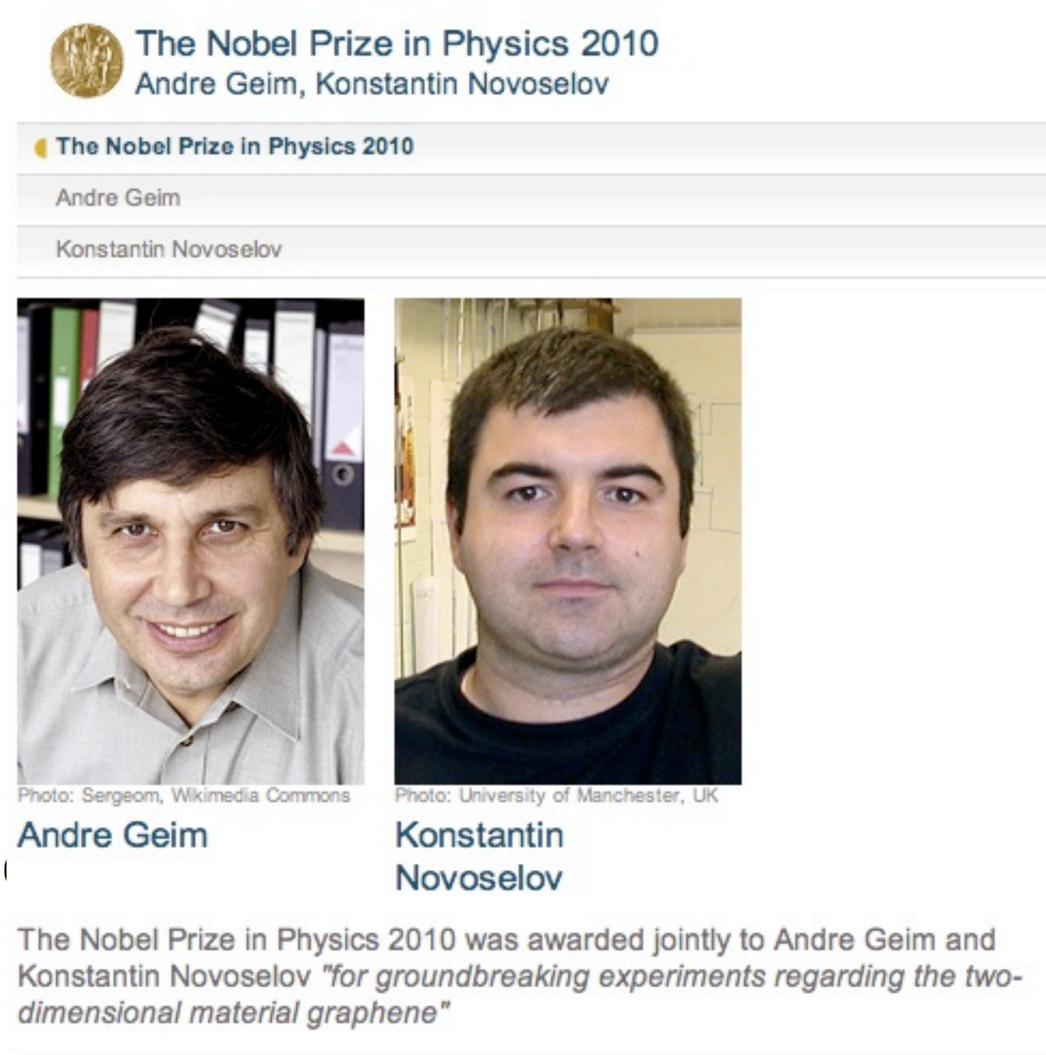
2005 -- Machester & Columbia groups showed that electrons in graphene are massless



The Bandwagon!

Number of papers on arXiv
with keyword graphene





The Nobel-winning Experiment

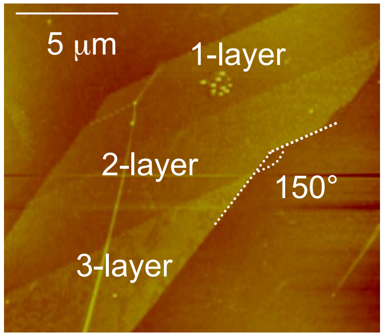
Making Graphene

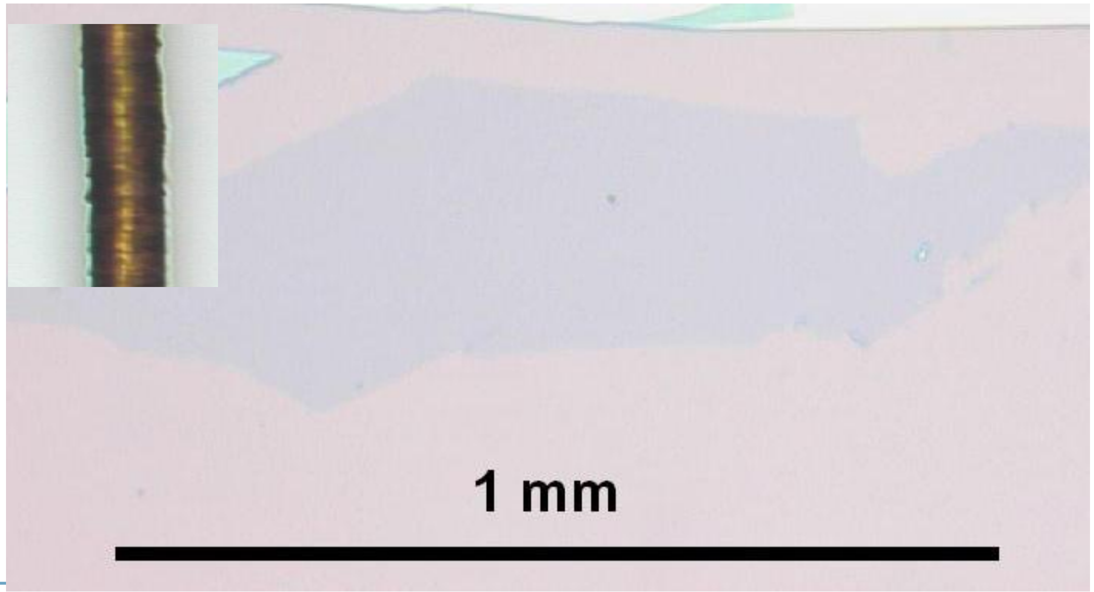
Mechanical Exfoliation

"rubbing"
"pencil writing"

Finding Graphene

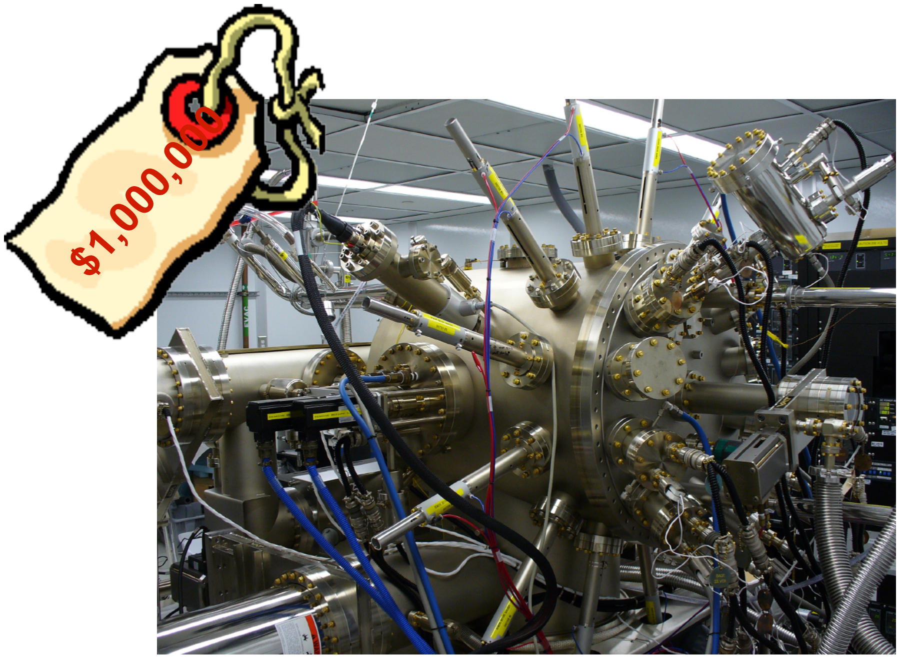
Eye (Optical Microscope)





Study of 2-Dimensional Electron Systems

- expensive equipment
- years of specialized training

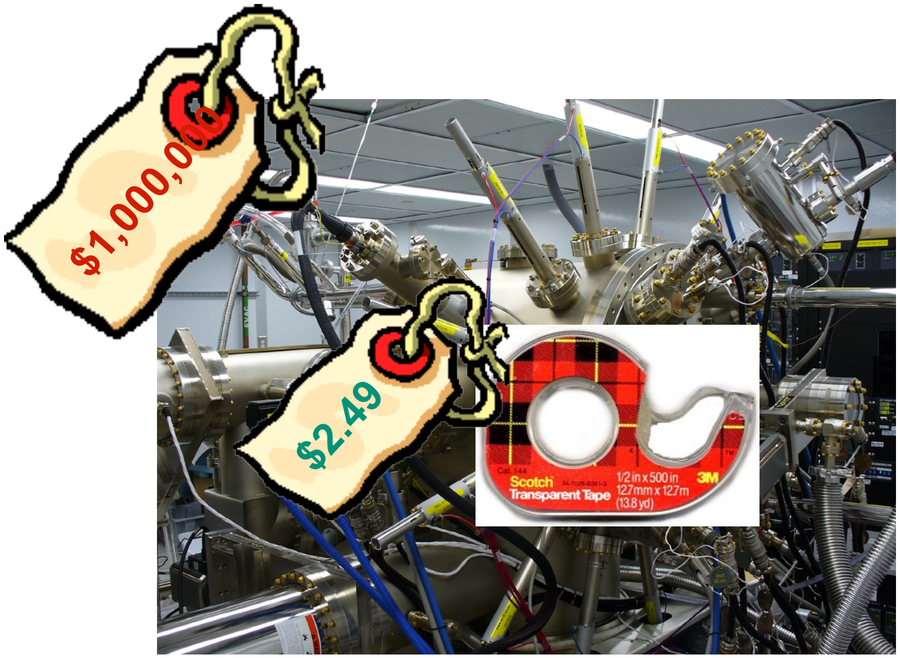


Molecular Beam Epitaxy

Scanning Electron Microscope

Graphene -- the "democratic material"

- only need scotch tape and optical microscope

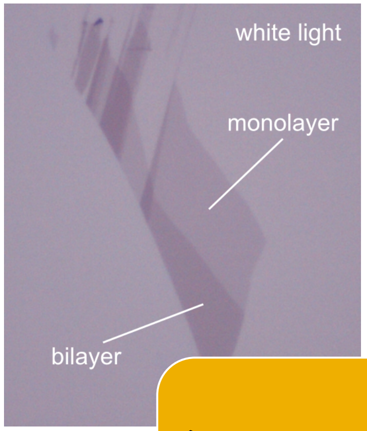


Molecular Beam Epitaxy

Scanning Electron Microscope

Most Expensive Material Ever (in 2008)

GRAPHENE INDUSTRIES



Pricing guide
≈ £ 0.50 -- 2 per μm^2 area

1 £ ~ 2 US $
1 μm^2 contains 3 x 10^7 atoms
1g contains 5 x 10^{22} atoms

Cost per gram: ~ US $ 10^{15}

Cost of Bailout ~ $7 x 10^{11}
US National Debt ~ $ 10^{13}

(former) Secretary of Treasury,
Henry Paulson

Bandwagon Evolving...

Science

Technology

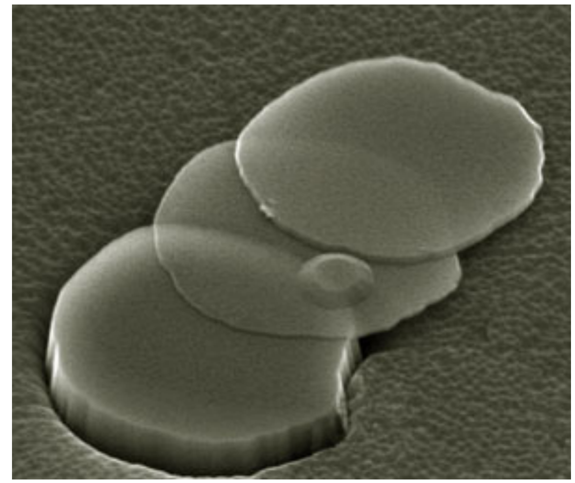
Why is Graphene Physicists' Favorite Toy?

- Truly two-dimensional, only single-atom thick

Electrons lose their mass in carbon sheets

Nov 9, 2005

Two teams of physicists have discovered previously unseen exotic behaviour in sheets of carbon atoms. The teams have shown that electrons move through the sheets as if they have no rest mass. They have also observed a minimum value of conductivity for the sheets and an unusual form of the quantum Hall effect (*Nature* **438** 197 and 201).



Source: Machester

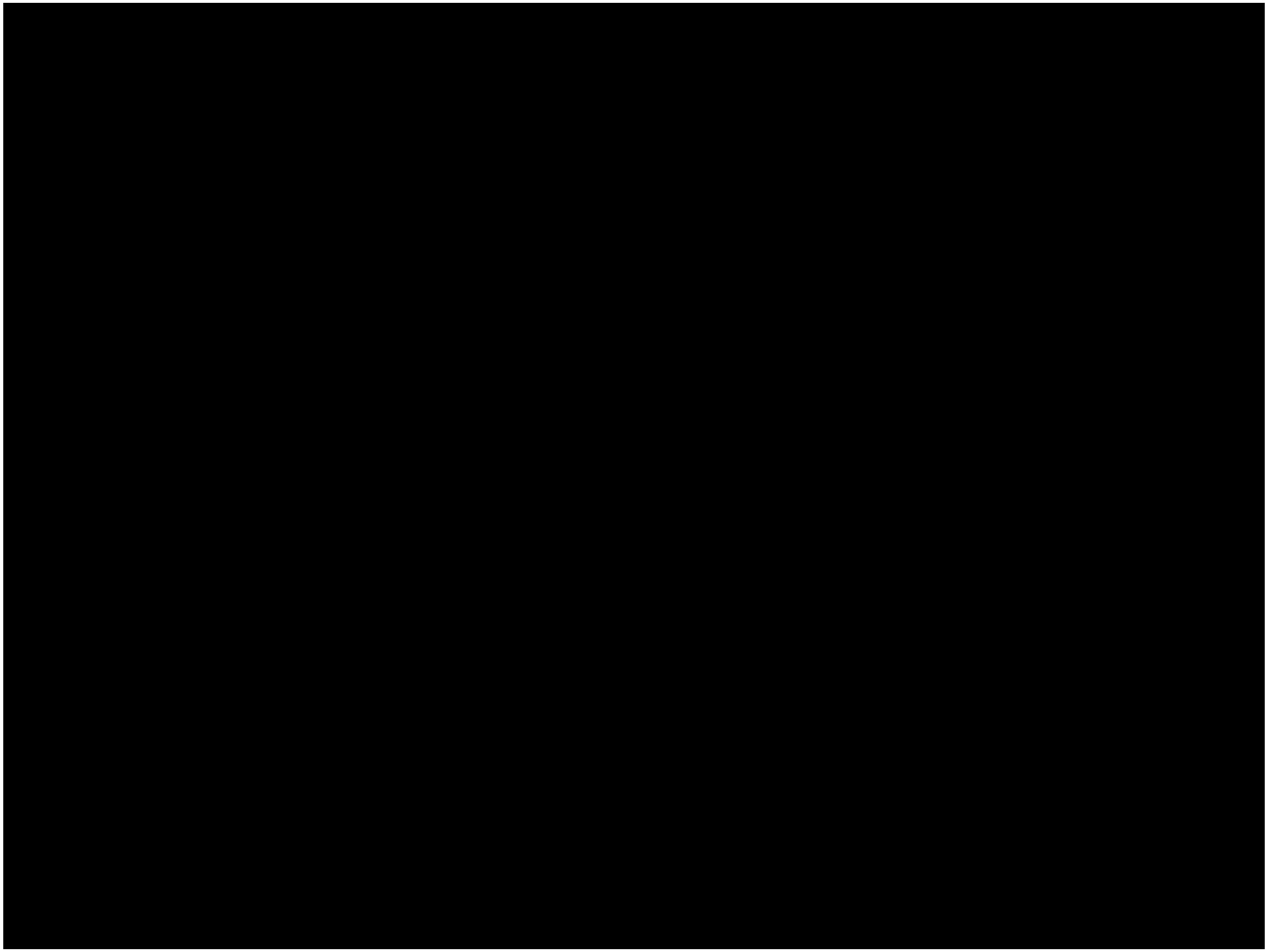
Graphene: Exploring carbon flatland

Andrey K. Geim and Allan H. MacDonald

Just one atom thick, this two-dimensional semiconductor does not resemble any known material.

Physics Today, 2007

A Puzzling Phenomenon….



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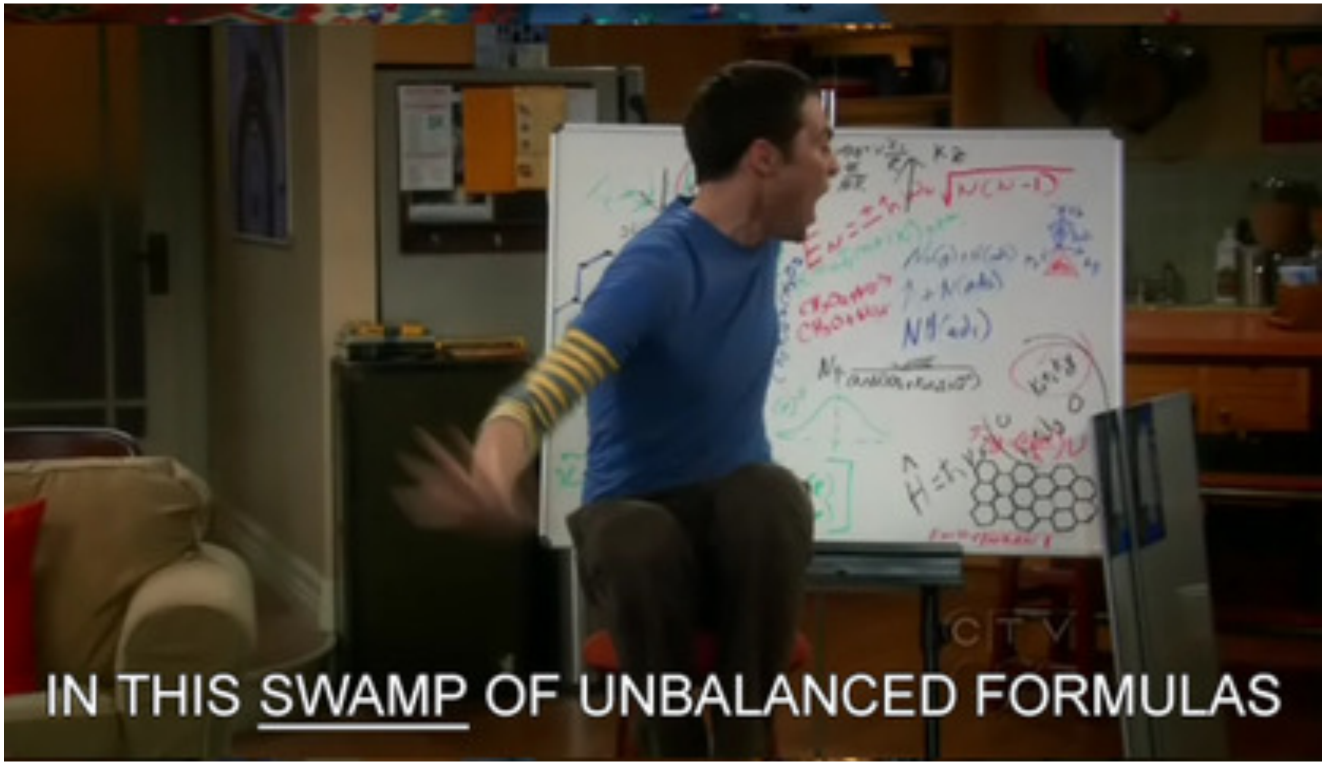
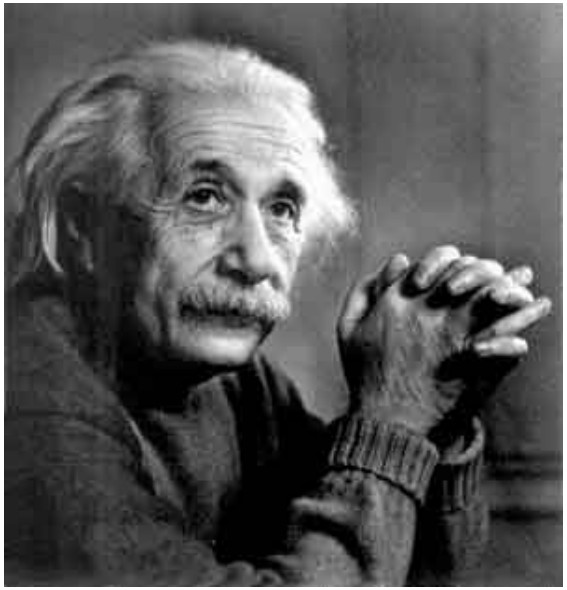
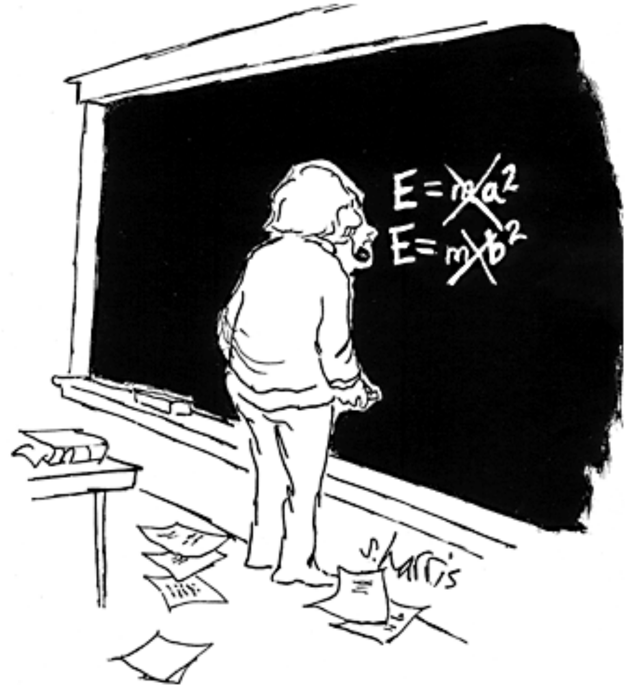


Einstein's Theory of Relativity





the Whole Formula

Special Theory of Relativity

$$E=mc^2$$

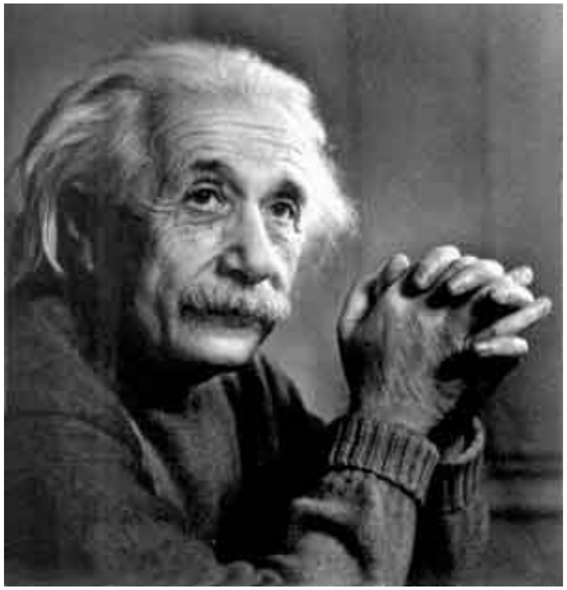
$$E^2 = (mc^2)^2 + (pc)^2$$

p = momentum
c=speed of light

For massless particles, m=0

$$E=pc$$

Massless objects and relativity



Special Theory of Relativity

$$E^2 = (mc^2)^2 + (pc)^2$$

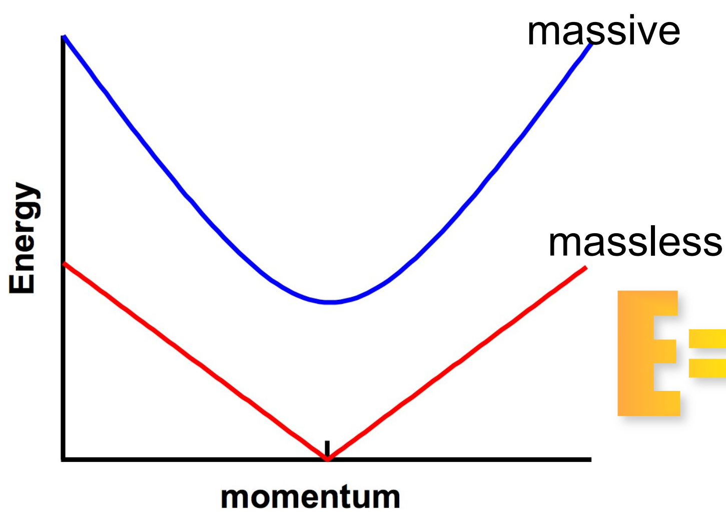
p = momentum, c=speed of light

When a particle's energy is strictly proportional to its momentum, it either

- has zero mass and moves at speed of light,

or

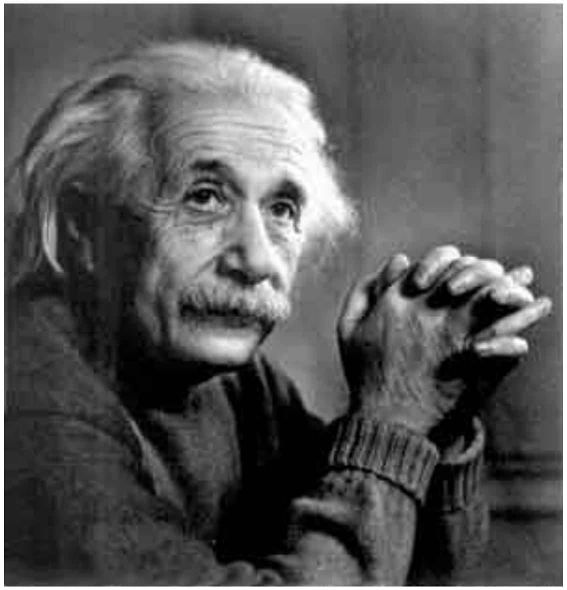
- has mass, but moves so fast that its speed is approaching speed of light

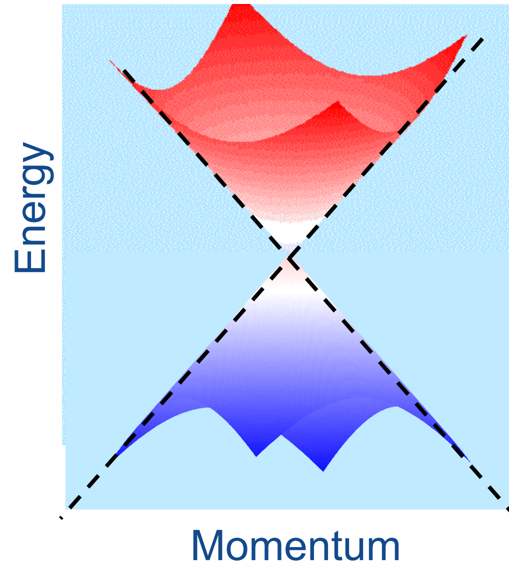


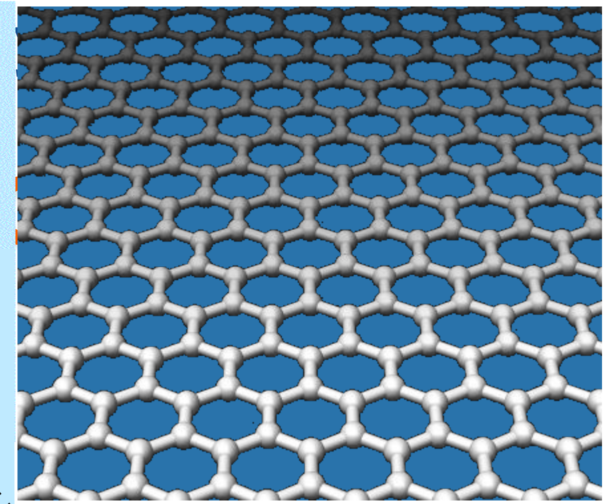
$E=pc$

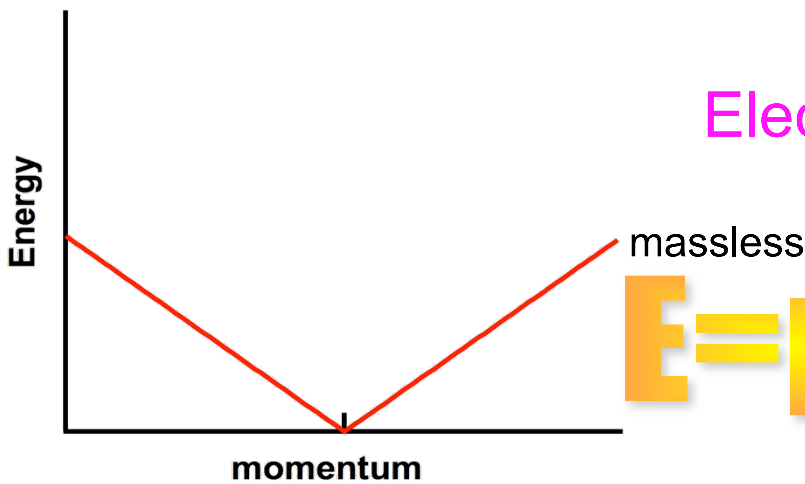
→ relativistic particles

Electrons lose their mass in graphene









Electrons in graphene are massless

relativistic particles

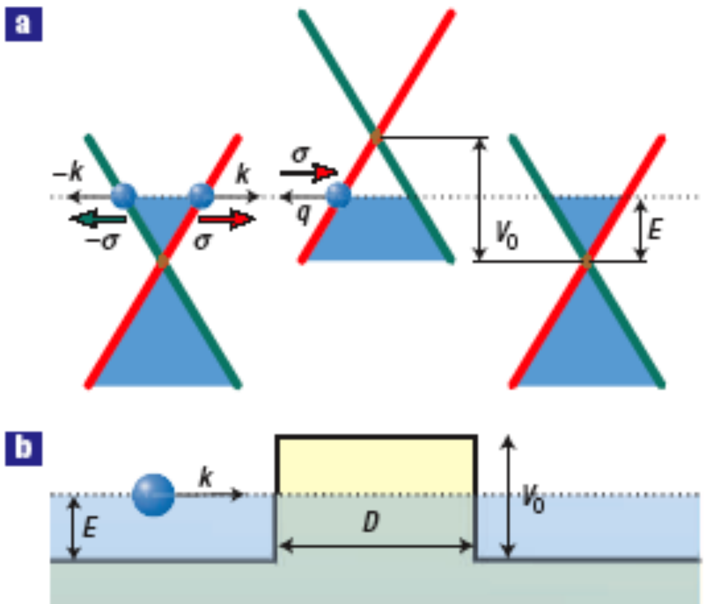
E=pc

speed of electrons in graphene = 1/300 speed of light

Klein Tunneling

Oskar Klein

Relativistic particles can pass through a barrier perfectly, if the barrier is big enough.



Cheianov and Falko, *PRB* (2006)
Katsnelson *et al*, *Nature Physics* (2006).

- Thought to be realizable at the edge of blackholes
- Graphene: electrons in conduction band → holes in valence band
- Transmission probability depends on incidence angle

Electrical Transport Spectroscopy

Measure graphene's resistance

- **A powerful tool to study**
  - Electronic states
  - Spin states
  - Electron-phonon interactions
  - Charge quantization or wave properties of charge carriers
  - Transport of energy…
- **An art to**
  - fabricate and locate the nanostructures
  - couple to the macroscopic world
  - perform low noise, low temperature measurements
  - learn the physics

How do we do it?

Our Goal: to measure the resistance of graphene

How do we do it?

- Produce Graphene (rubbing)
- Image and search for them (Look under microscope)
- Attach electrodes
- Measure

How do We Make and Identify Graphene?

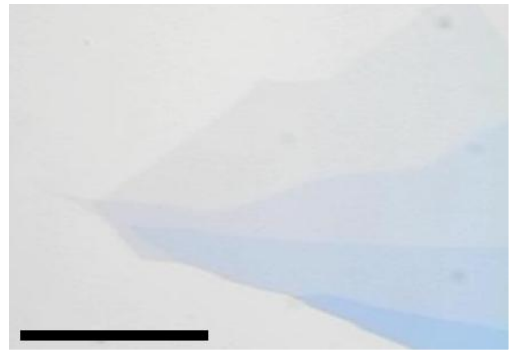
Fabrication

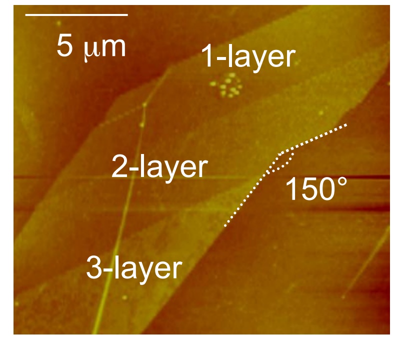
Mechanical Exfoliation

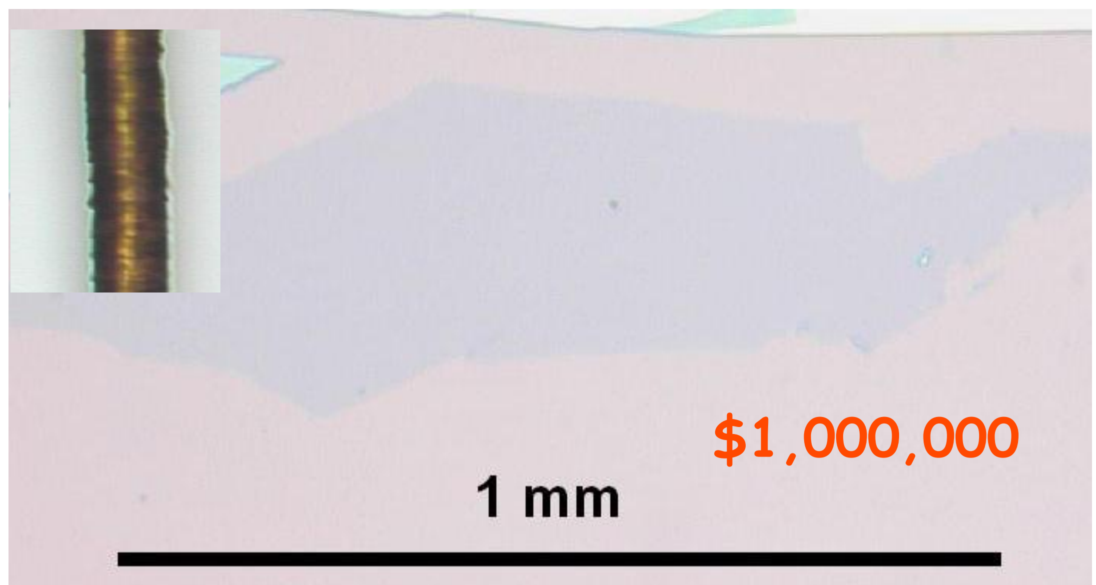
“rubbing”
“pencil writing”

Locating

Eye (Optical Microscope)

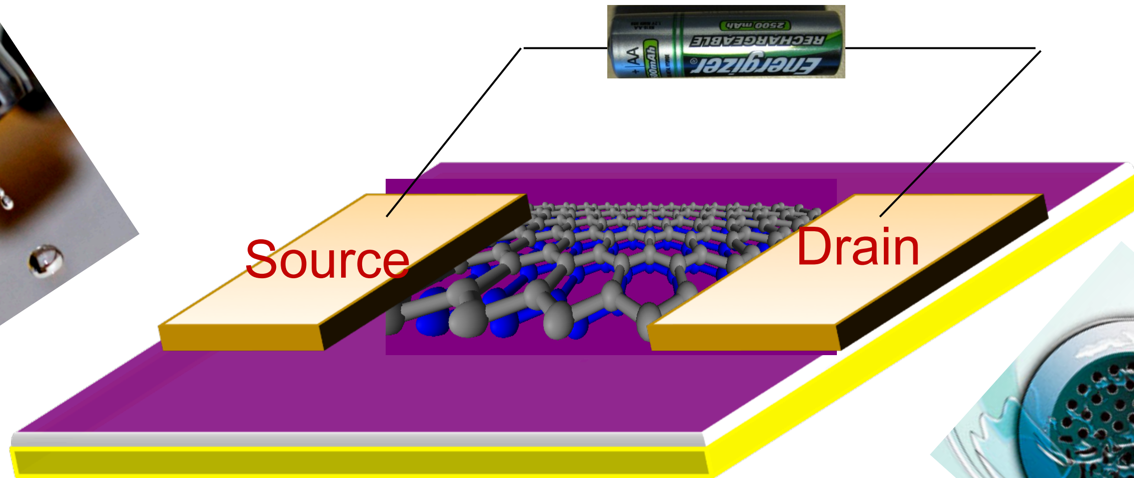






Graphene Transistor

injects electrons

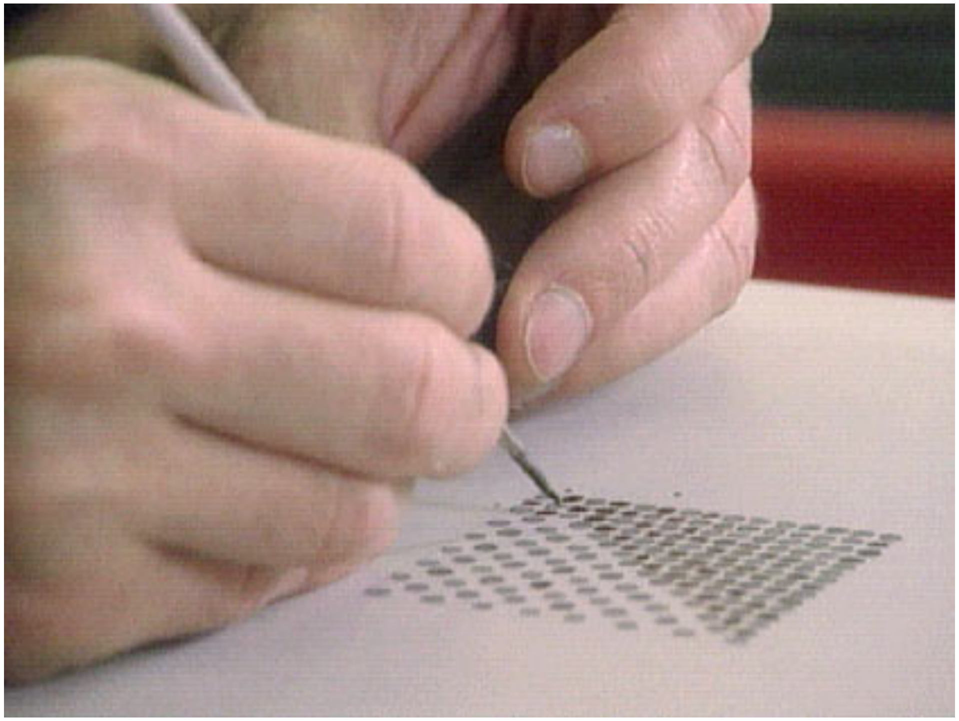


Gate

"drains" electrons

controls the total number of electrons on graphene

Attaching Electrodes



Lithography printing

• put wax layer on plate

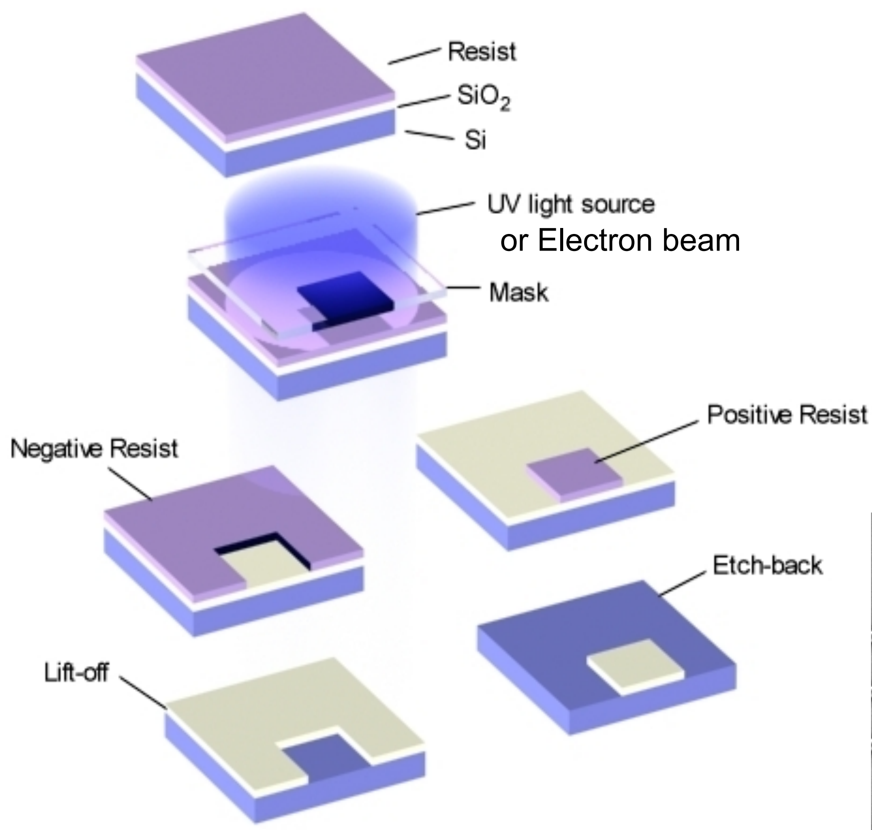
• use knife to carve patterns on wax

• pour ink

• remove wax

Attaching Electrodes

Lithography (same technique used by semiconductor industry to make integrated circuits and computer chips)



Lithography printing

polymer (resist)

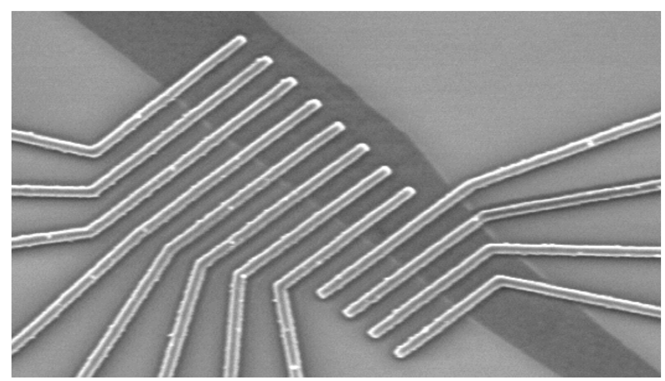
- put ~~wax layer~~ on plate

light or electrons

- use ~~knife~~ to carve patterns on wax

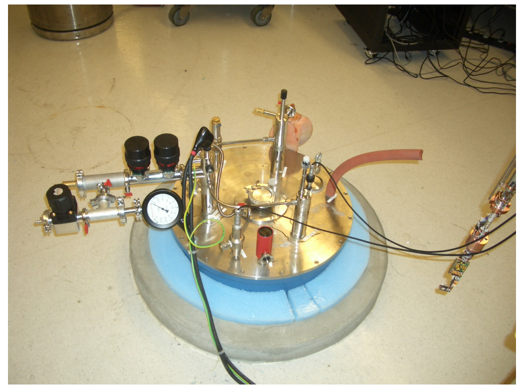
metal

- pour ~~ink~~



Measurement at low Temperature

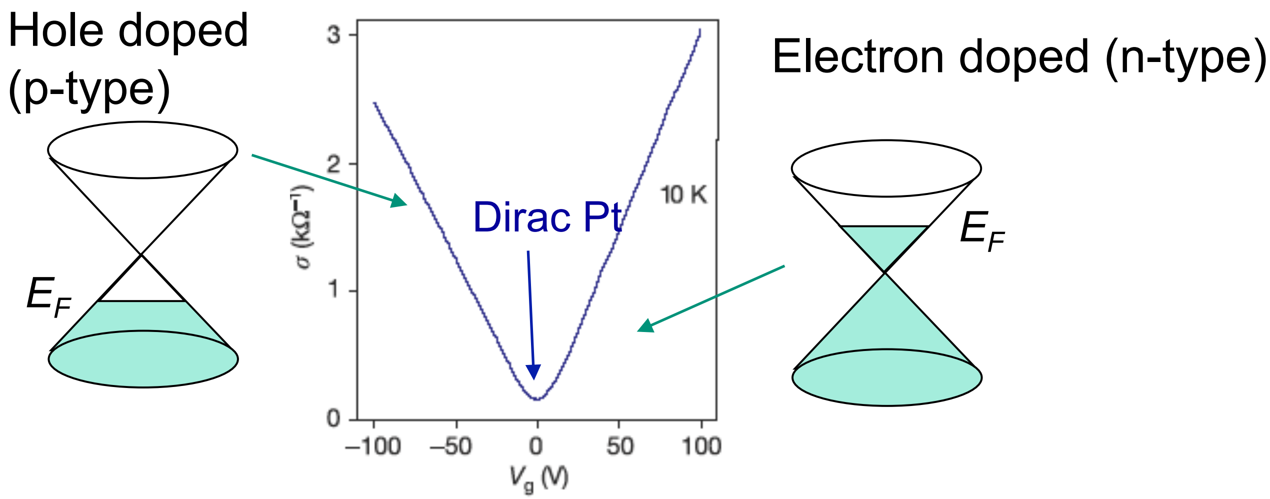
Helium-III Fridge with 8/10T Magnet



- Liquid He3 boils at 3.2 K
- manufactured from nuclear reaction (e.g. dismantling of nuclear weapons)
- Evaporating He3 --> 0.25 K

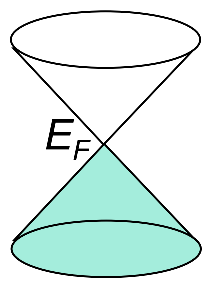
cooler than outer space

Graphene Bipolar FET



Novoselov et al, *Science*, 2004.

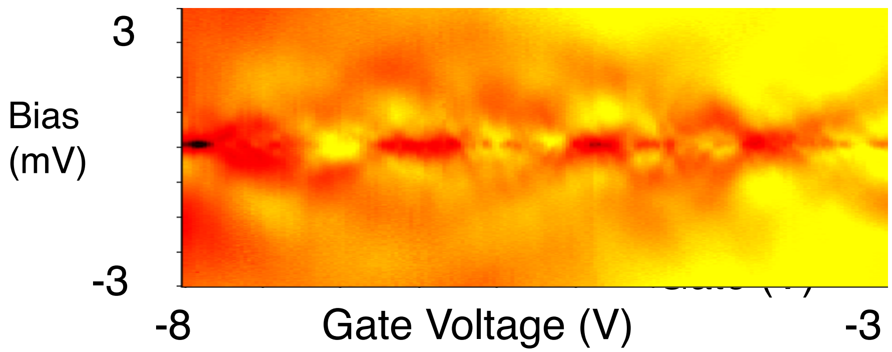
Miao et al, *Science*, 2007.



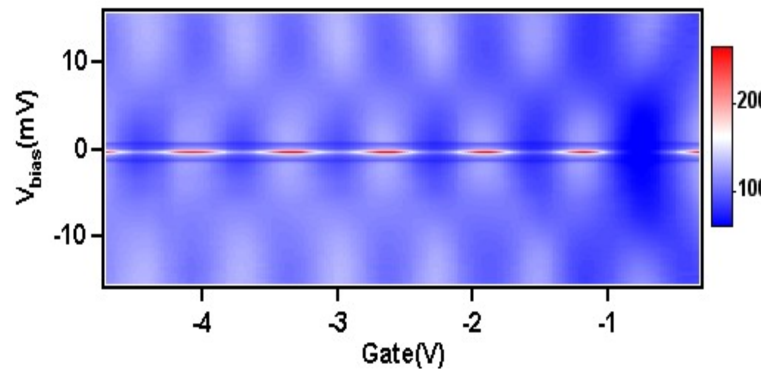
- Conductivity increases (more or less) linearly with number of electrons
- High current density (10^8 -10^9 mA/μm, or μA/atomic row)

Graphene is ~20 times more conductive than silicon.

Electronic Interference in graphene



Nanotube data



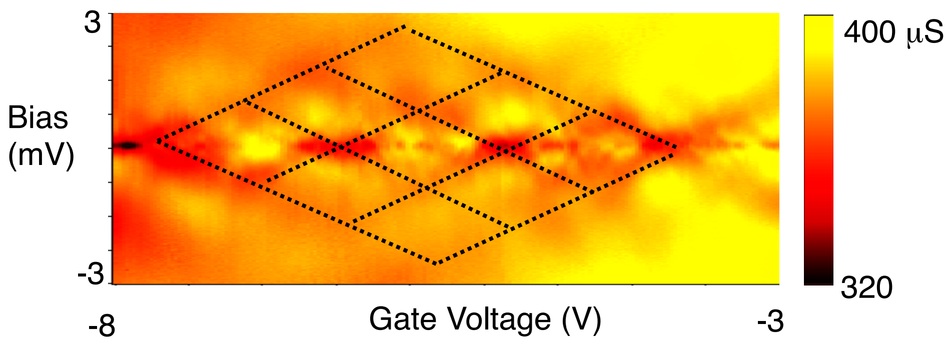
Color: conductance
Horizontal axis: Gate voltage (controls density of electrons)
Vertical axis: applied voltage (controls electron's energy)

<u>Fabry-Perot Interference</u>
Electrons act as waves: they are reflected back and forth between the electrodes, and interfere with each other
→ form standing waves

Electronic Interference in graphene

Promises: Electron Optics

- Exploit the wave-like nature of electrons in graphene
- Control electrons like optics



Fabry-Perot resonant cavity

- interference of multiply-reflected electron and hole waves between partially transmitting electrodes.

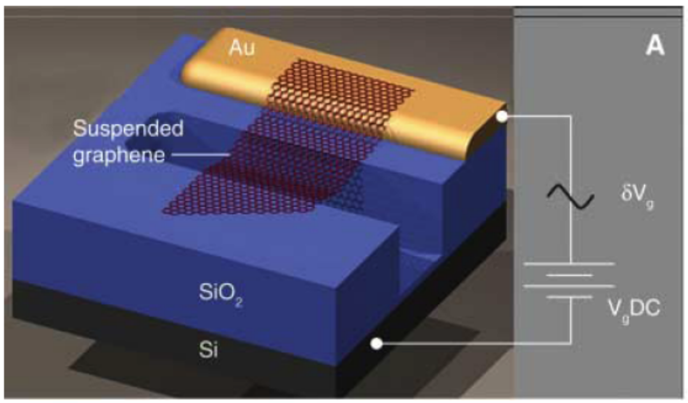
Lau group, Science, 2007.

pn junctions as basis for Veselago lenses

Kim group, Nature Physics, 2008

Mechanical Properties

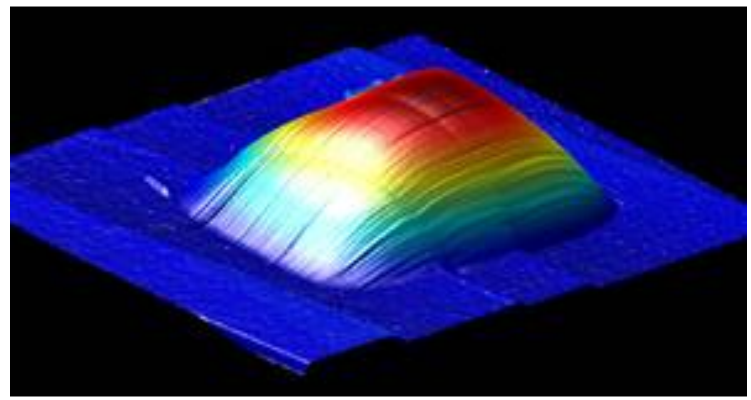
- Single Atomic Layer Mechanical Resonator



Bunch *et al*, Science (2007)

World's smallest drum

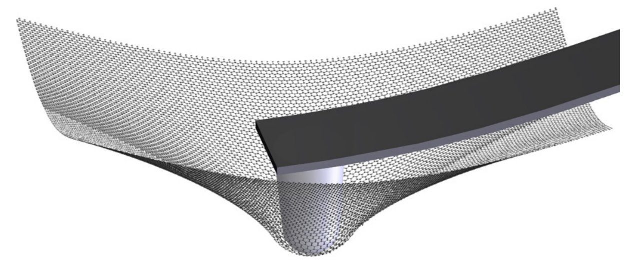
- Impermeable Membrane



Bunch *et al*, Nano Letters (2008)

World's smallest balloon

Strange Graphene Mechanics



Source: Columbia Univ.

Graphene is very strong and tough

Breaking strength is ~ 200 times of steel

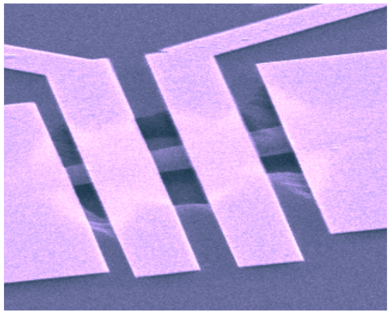
Graphene is very elastic

can be stretched by 25% and return to its original shape
(most materials can only be stretched by one-tenth of 1 percent)

Graphene is very soft

Single atomic layer, bends or
buckles very easily

(Attempts to) Fabricate Suspended Graphene Devices



Du et al, *Nature Physics* (2008)

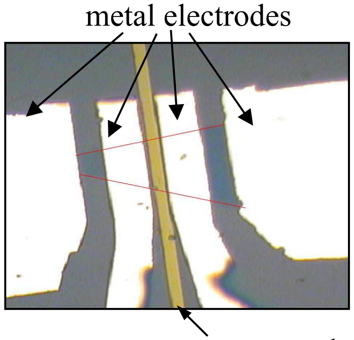
Successful Technique (Kim and Andrei groups, 2008)

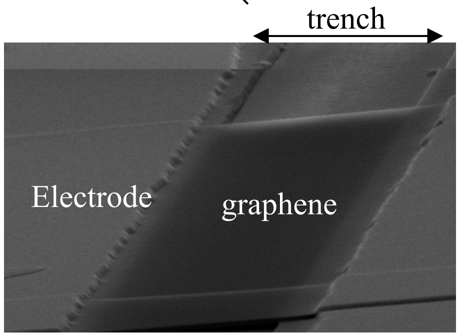
- Exfoliate graphene onto substrates
- Deposit electrodes
- Release completed devices from SiO_2 using HF etching
- Anneal
- Observed much higher mobility (up to 250,000)

Our technique

- Etch trenches on substrates
- Directly exfoliate graphene sheets across trenches
- Deposit electrodes
- Anneal
- Initial test: very low mobility (~100-500)

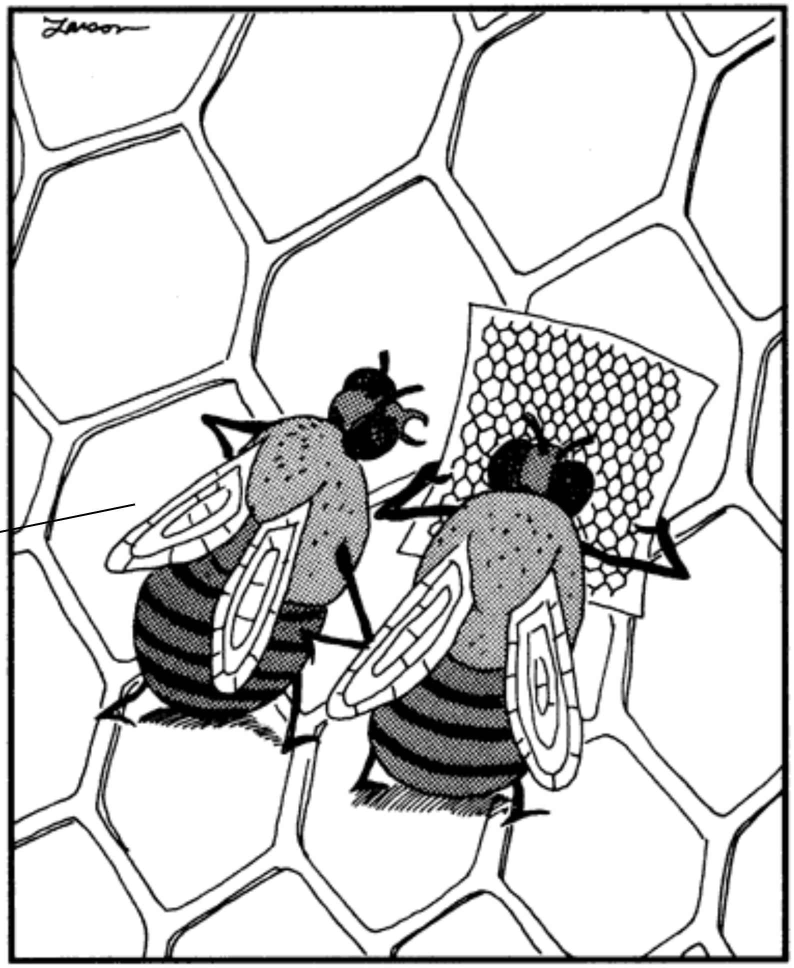
our typical substrate-supported devices: ~ 2,000-10,000





Graduate
Student

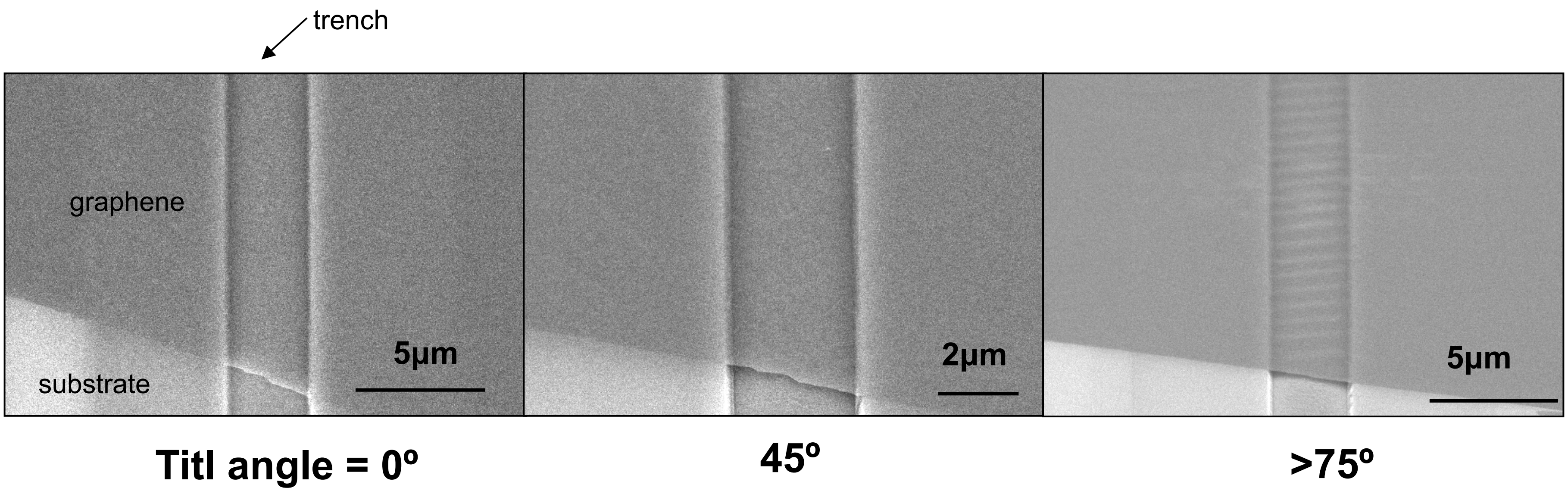
Face it, Jeanie,
you're lost!



Huh?

"You can see a lot by just looking"

- Directly exfoliate graphene sheets across pre-defined trenches
- Image under SEM

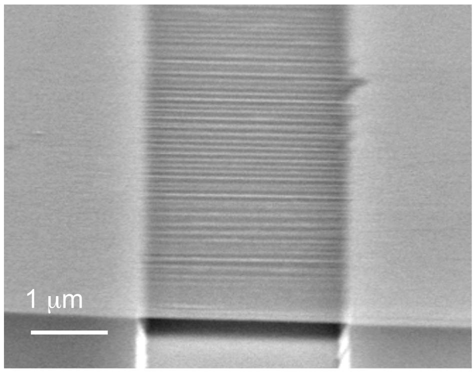


Spontaneous, Periodic Ripple Formation in Graphene

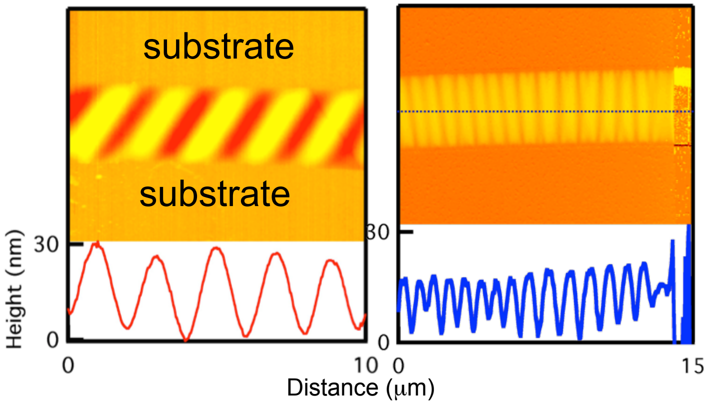
Directly exfoliate graphene sheets across pre-defined trenches

- Many graphene sheets are not flat, but spontaneously form ripples
- Almost perfectly sinusoidal profile
  - ♦ thickness: 0.3 nm (single layer) -- 16 nm
  - ♦ amplitude: 0.7 to 30 nm
  - ♦ wavelength: 370 nm -- 5 μm

SEM



AFM

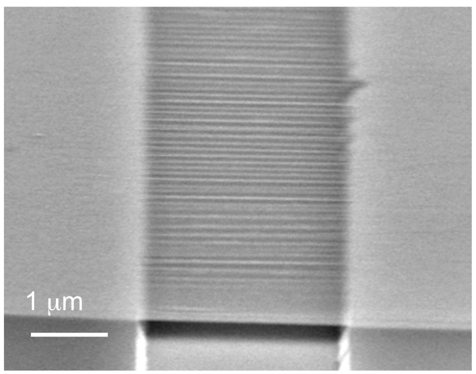


Graphene as an Elastic Membrane

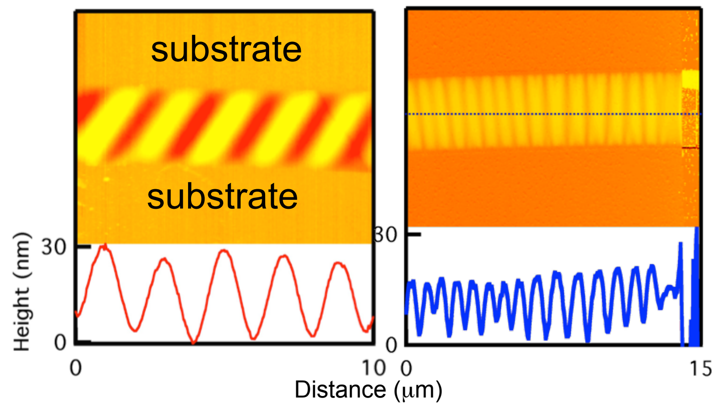
Directly "rub" graphene sheets across pre-defined trenches

- Many graphene sheets are not flat, but spontaneously form periodic ripples
- Almost perfectly sinusoidal profile

SEM



AFM



VOLUME 90, NUMBER 7 PHYSICAL REVIEW LETTERS 21 FE

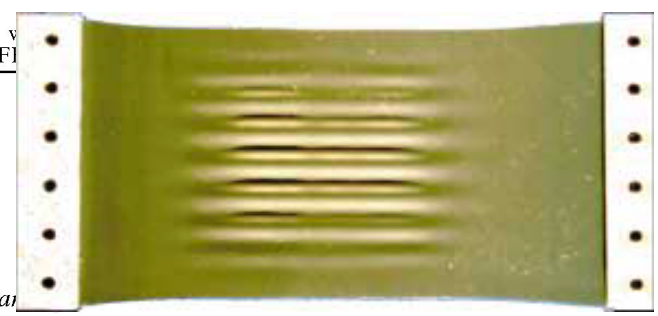
Geometry and Physics of Wrinkling

E. Cerda[1,2] and L. Mahadevan[1,*]

[1]*Department of Applied Mathematics and Theoretical Physics, University of Cambridge, Silver Street, Cambridge CB3 9EW, United Kingdom*

[2]*Departamento de Física, Universidad de Santiago de Chile, Avenida Ecuador 3493, Casilla 307, Correo 2, San*

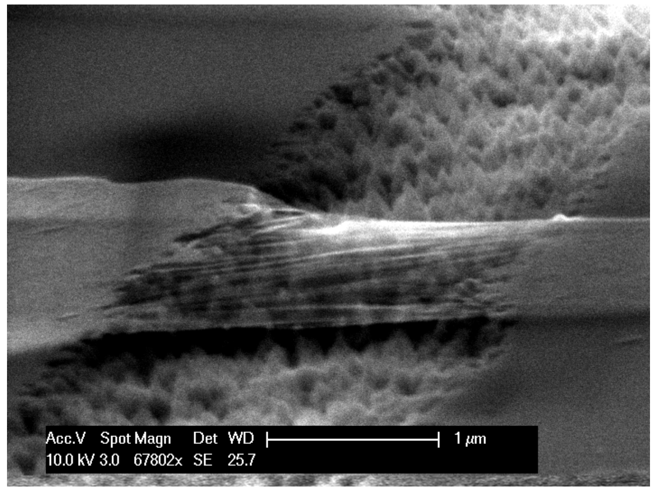
(Received 25 June 2002; published 19 February 2003)

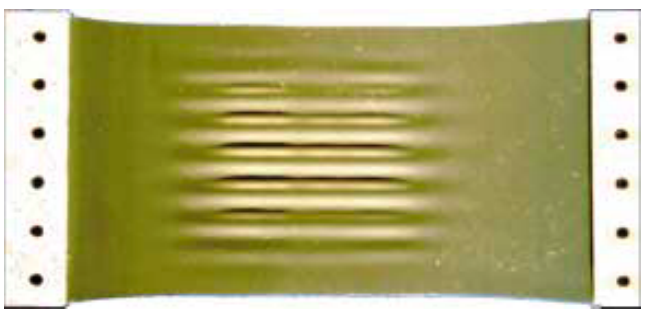


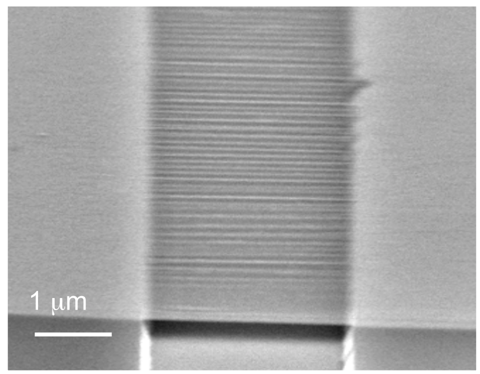
Graphene as the World's thinnest Saran Wrap

macroscopic

mesoscopic

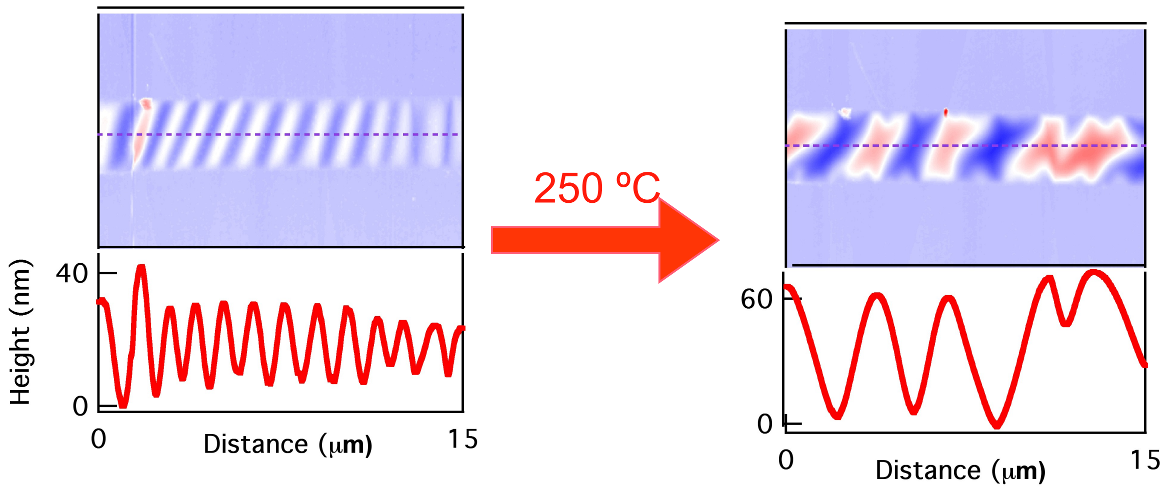


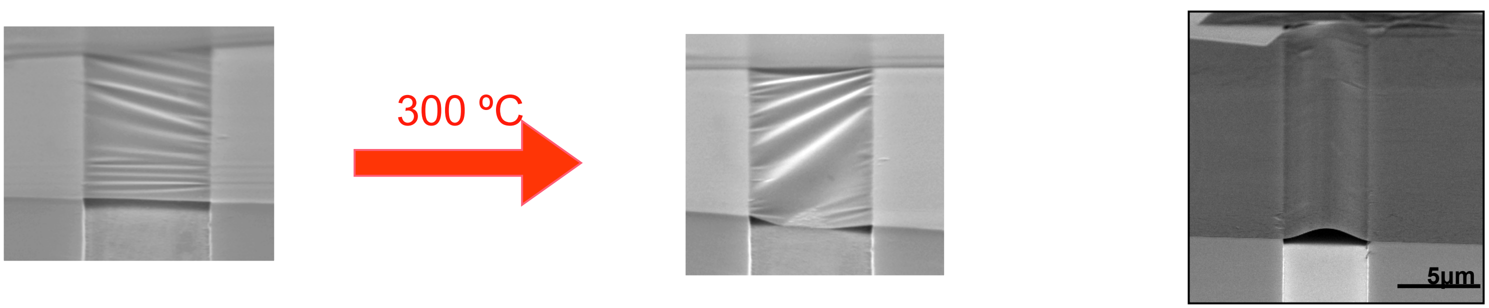




W. Bao, F. Miao, Z. Chen, H. Zhang, W. Jang, C. Dames, C.N. Lau, Nature Nanotechnology, 2009..

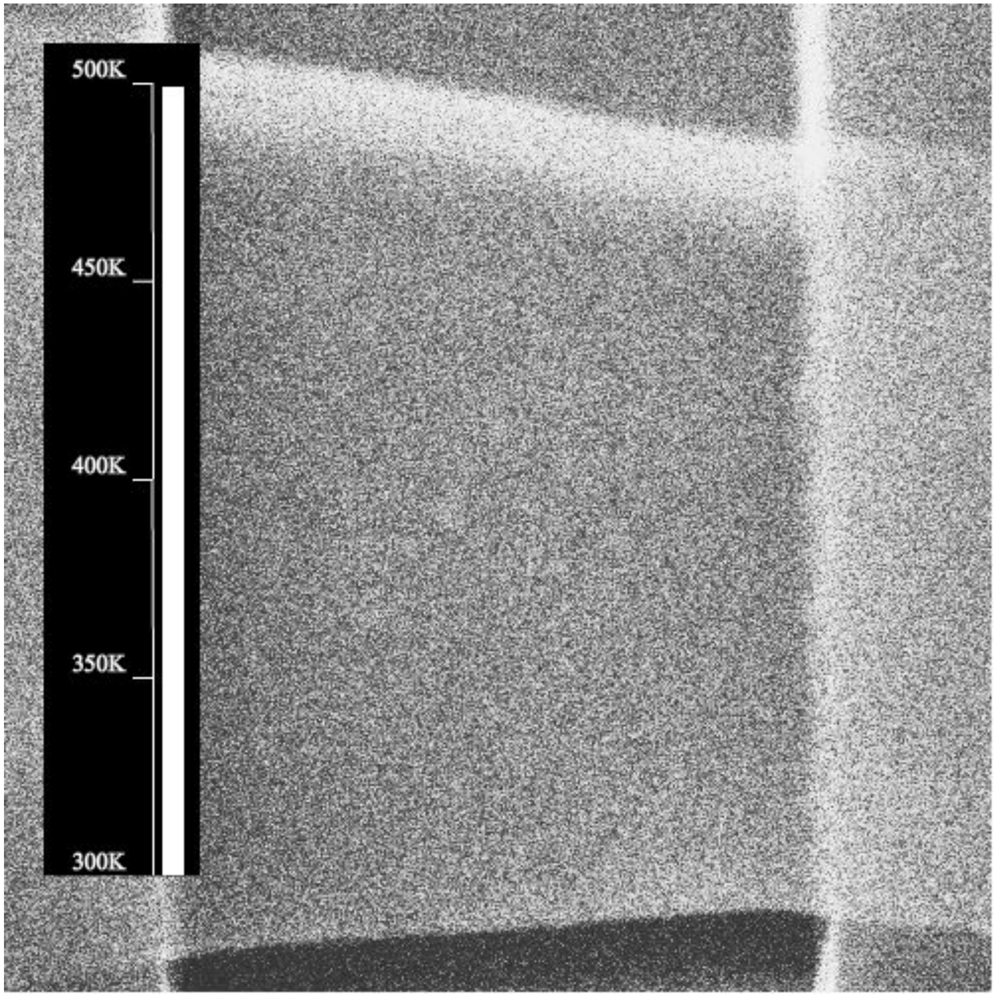
Thermal Effect on Ripples





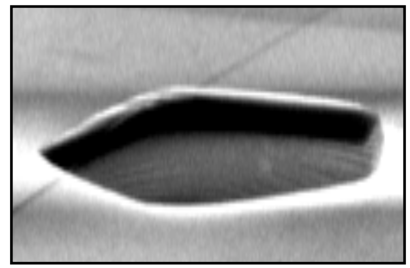
- Ripples have larger wavelengths and amplitudes
- Membranes buckles upward or towards the bottom of the trench

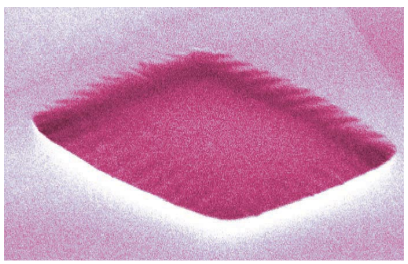
Movie of ripple formation

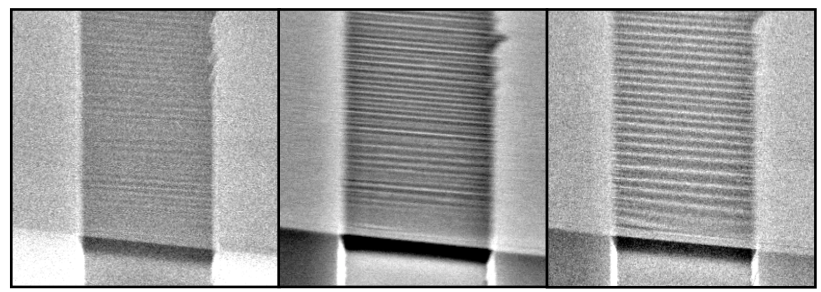


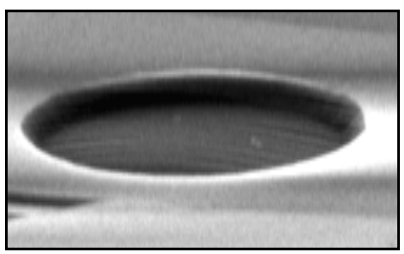
Graphene -- the ultimate Saran wrap

Graphene contracts when heated
Like putting Saran wrap into an oven



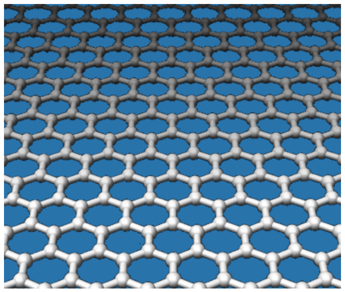


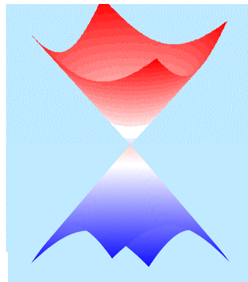




Graphene's Double Identity

<u>Extraordinary Conductor</u>

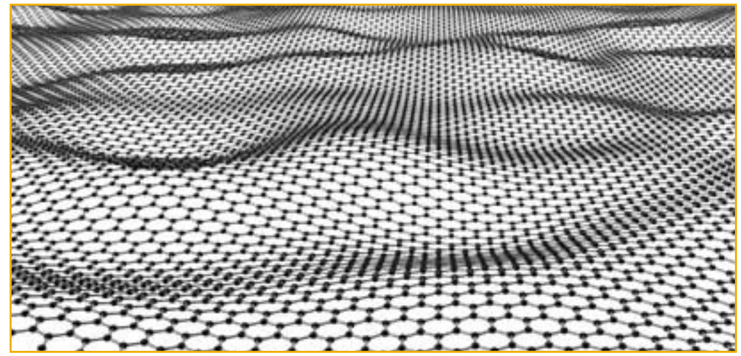




New model system for condensed matter research and electronic materials

Linear dispersion, tunable carrier, surface 2DEG, high thermal and electrical conductivity ….

<u>2D Elastic Membrane</u>



Thinnest isolated membrane with exceptional mechanical properties

Castro Neto, Guinea, Katsnelson, Brey, Louie, etc

Exploit Electrical Properties of Rippled Graphene?

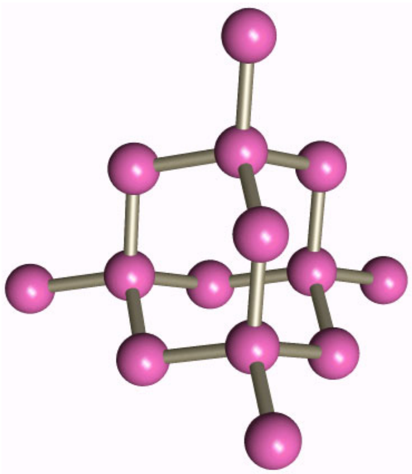
superlattices, strain-based engineering…

The Softer Side of Graphene

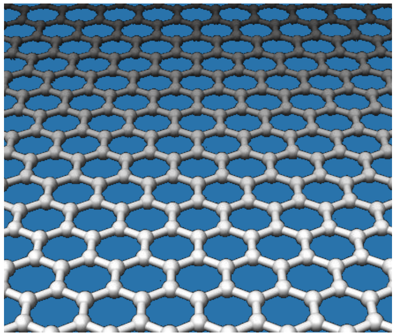
Collaborator: Chris Dames, ME@UCR

- Thinnest isolated membrane with exceptional mechanical properties
- Easy to deform
- Wrinkles in graphene can significantly alter its electrical properties which depend on the local atomic arrangement

Insulating Diamond



Conducting graphene

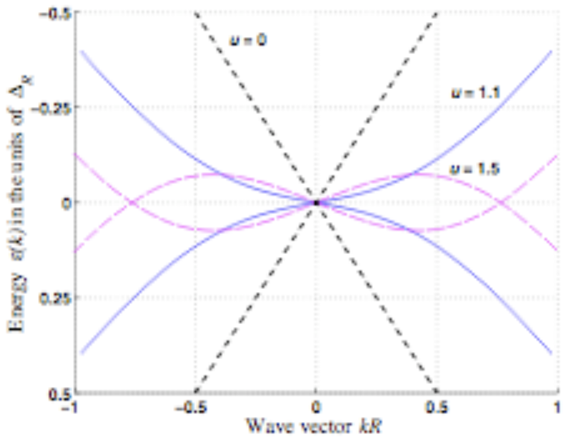


- can produce effective local magnetic field or electric field without external voltage or magnet

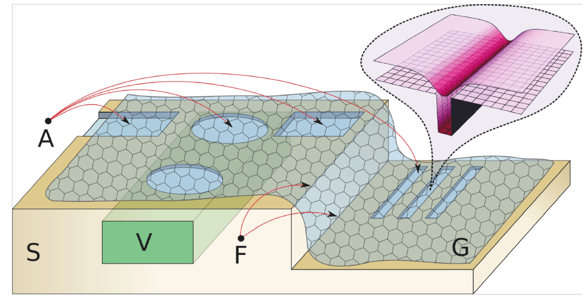
Theories: Louie, Castro Neto, Katnelson, Guinea, Herbut *et al*, Juan *et al*…

Expt: Meyer *et al*, Nature (2007)

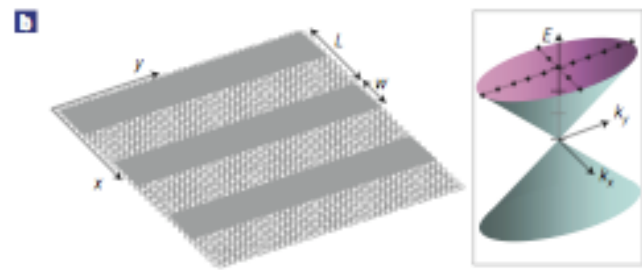
Engineering Based on Strain and Ripples



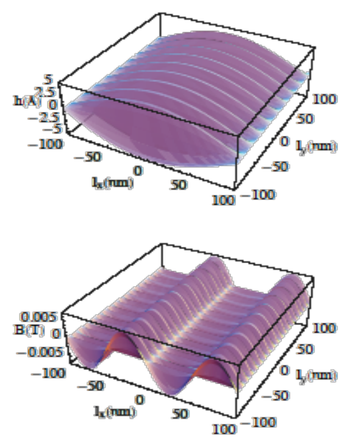
Novikov & Levitov, PRL (2006)
Brey & Fertig, arxiv (2009).



Pereira & Castro Neto, 2008



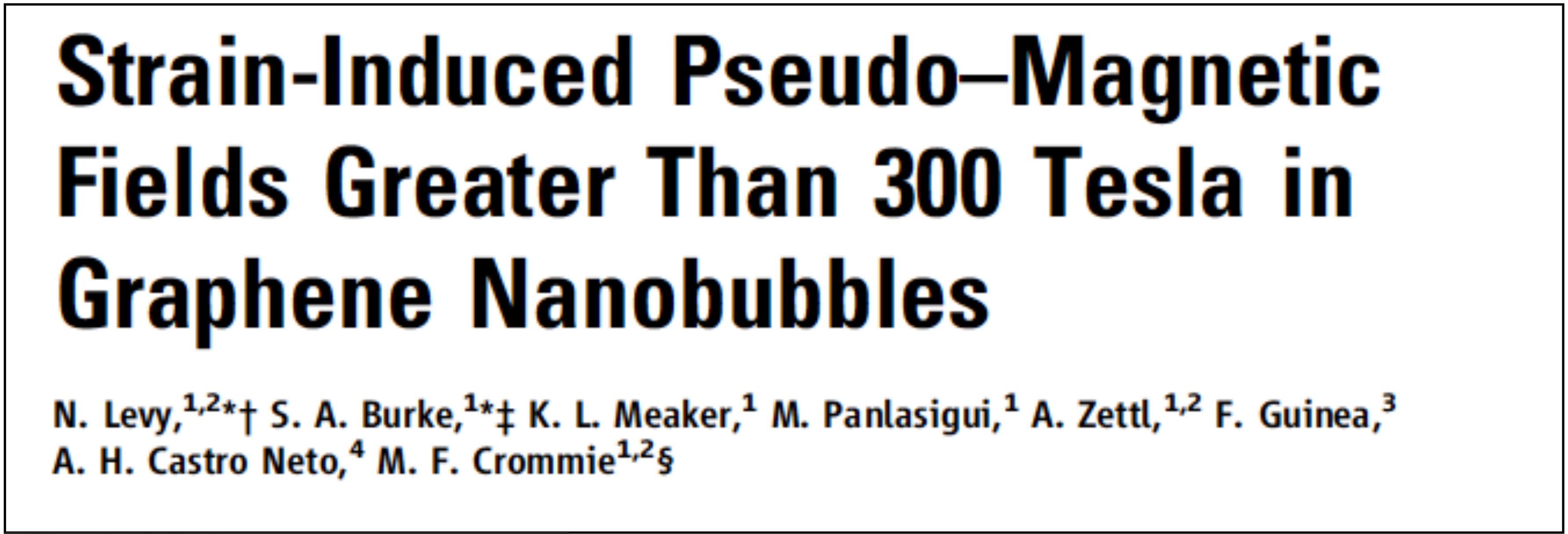
Park, Yang, Son, Cohen, Louie, *Nature Physics* (2008)



Paco Guinea,
Katsnelson and co.

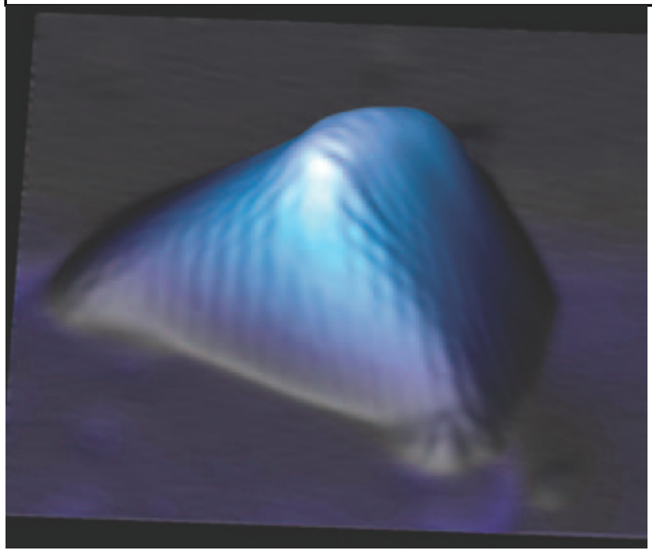
- Modified band structure
- Anisotropic transport
- Supercollimation
- Inducing effective magnetic field

Engineering Based on Strain and Ripples



Strain-Induced Pseudo–Magnetic Fields Greater Than 300 Tesla in Graphene Nanobubbles

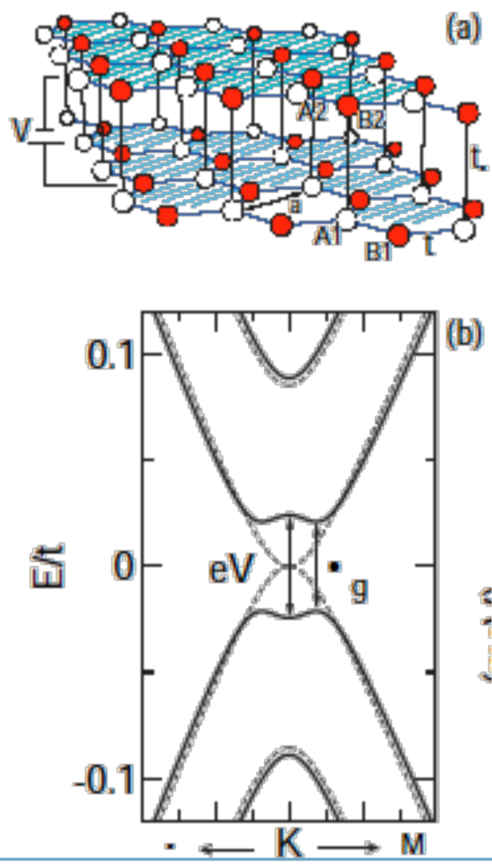
N. Levy,[1,2*†] S. A. Burke,[1*‡] K. L. Meaker,[1] M. Panlasigui,[1] A. Zettl,[1,2] F. Guinea,[3] A. H. Castro Neto,[4] M. F. Crommie[1,2§]

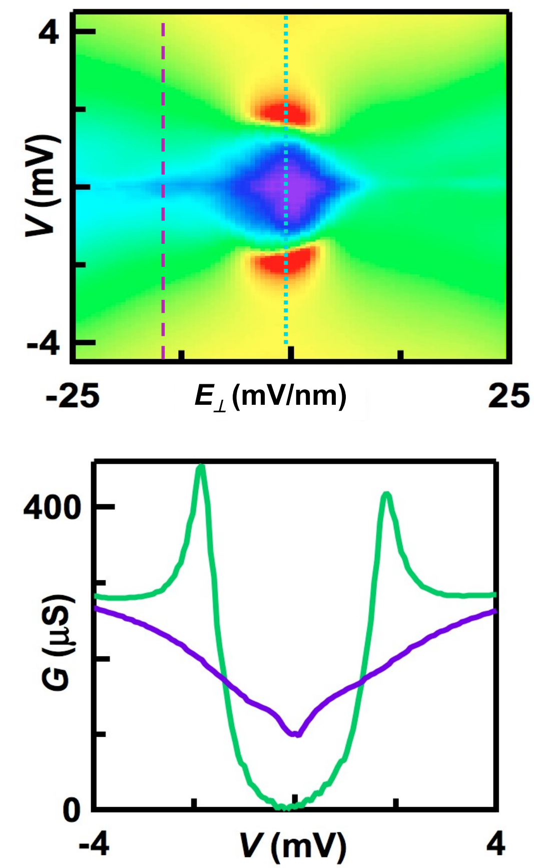


Highest steady magnetic field on earth: = 45T in National High Magnetic Field Lab, Tallahassee, FL.

Bilayer graphene

- Band gap engineering for digital electronics
- Fundamental understanding of nature (e.g. spontaenous symmetry breaking, "Higgs bosons"?)

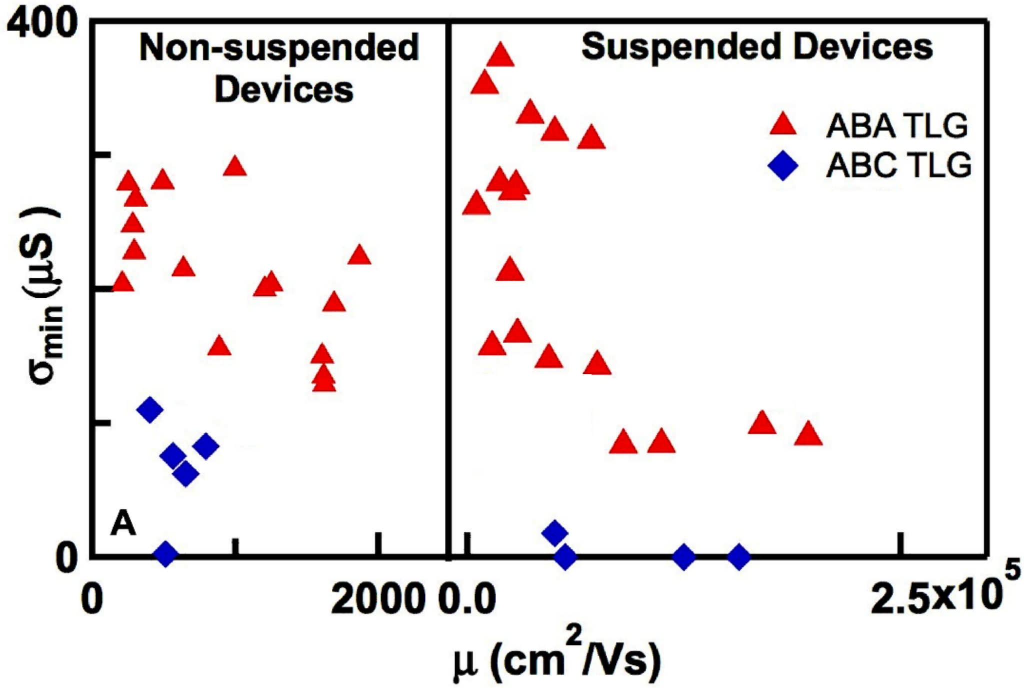




1, 2, 3… infinity

- Bilayer graphene
  - Band gap engineering
  - Fundamental understanding of nature (e.g. spontaenous symmetry breaking, "Higgs bosons"?)
- Trilayer graphene
  - Shifting the top sheet by 1 atomic position cause the change from conductor to insulator
- n-layer graphene (graphite?)
  - There are 2^{n-2} different ways to stack the layers
  - Different band structures
  - Tune the electronic properties by stacking?

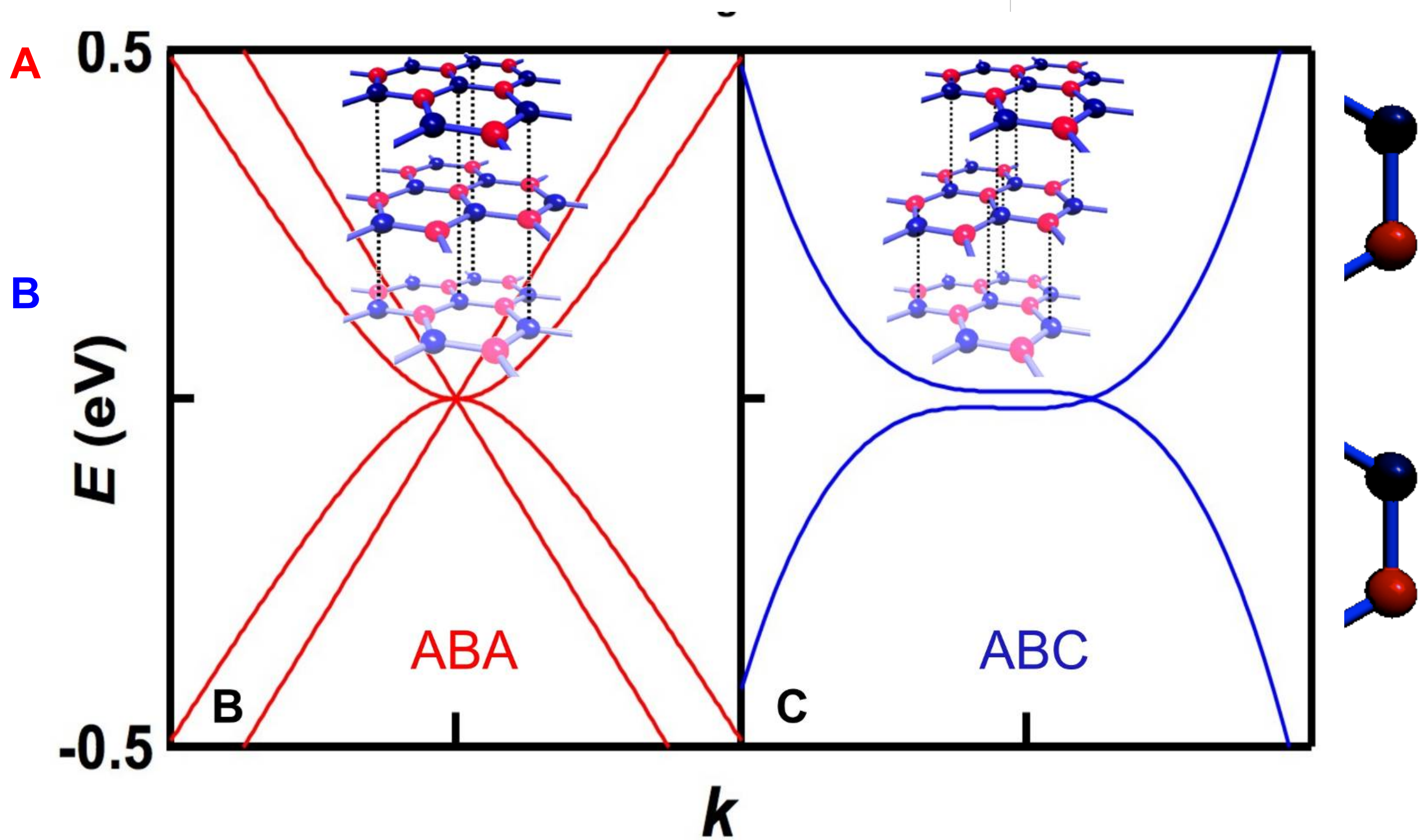
Minimum conductivity (σ_{min})



- σ_{min} decreases with increasing sample mobility for ABA-stacked devices, but remains finite >100 μS.
- σ_{min} of ABC-stacked trilayer is significantly smaller, ~0 for suspended devices.

manuscript submitted

Stacking orders of trilayer graphene



- ABA (Bernal) stacking
- ABC (rhombohedral) stacking, slightly higher energy

1, 2, 3… infinity

- Bilayer graphene
  - Band gap engineering
  - Fundamental understanding of nature (e.g. spontaenous symmetry breaking, "Higgs bosons"?)
- Trilayer graphene
  - Shifting the top sheet by 1 atomic position cause the change from conductor to insulator
- n-layer graphene (graphite?)
  - There are 2^{n-2} different ways to stack the layers
  - Different band structures
  - Tune the electronic properties by stacking?

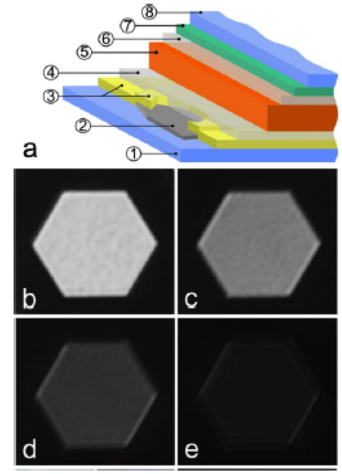
Graphene, the new wonder material

- ✓ Truly 2D, only a single atomic layer thick
- ✓ Compatible with current silicon-based technology
- ✓ Stronger than steel, softer than silk
- ✓ Conducts heat 20 times better than copper
- ✓ Conducts electricity 20 times better than silicon
- ✓ Carry 100 times more current than copper
- ✓ Transparent like plastic
- ✓ Chemically stable and inert
- ✓ Fascinating physics abound: electrons lose their mass…

Graphene holds tremendous promise for post-silicon electronics.

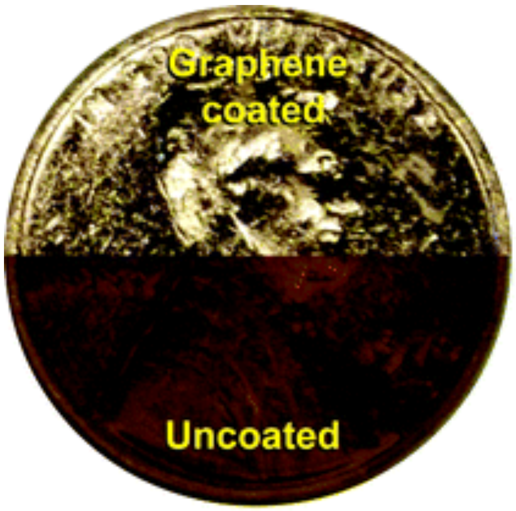
Applications

- Post-silicon electronic material
  - •With advantages of carbon nanotubes
    - ✓ high thermal conductivity (~5000 W/mK) Balandin *et al*, Nano Lett. (2008)
    - ✓ high current density (~ mA/μm width)
    - ✓ high mobility (~10,000 cm^2/Vs in as-prepared samples)
  - •2D → compatible with lithographic techniques, e.g. nanoribbon FET
    Han *et al*, PRL (2007); Chen *et al*, Physica E (2007); Li *et al*, Science (2008)
  - •Potential for large scale synthesis (e.g. Berger *et al*, *Science* (2006))



Blake *et al*, cond/mat (2008)

- Transparent electrodes for solar cells, LCD, etc
- Robust, non-volatile, atomic switches
  (Bockrath+Lau+Bruck group, see also Echtermeyer *et al*, cond/mat 2008)
- Chemical and biological sensors
- Ultra-capacitors for energy storage (Ruoff group, 2008)
- Flexible Electronics, Spintronics, and Valley-tronics
- Anti-Oxidation coating



Source: Ruoff Group

(OLD) Challenges for Technological Applications

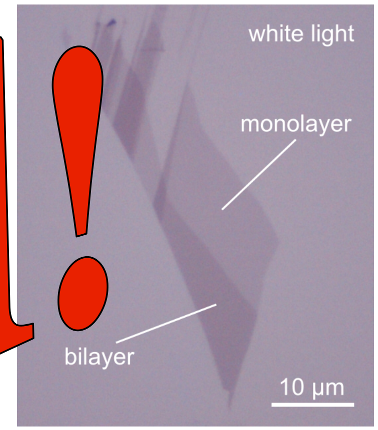
3. Precision crystallographic edge control

2. Band Gap engineering

1. Large Scale Synthesis & Production

GRAPHENE INDUSTRIES

Expired!



Pricing gui

≈ £ 0.50 -- µm² a

1 £ ~ 2 US

1 µm² cont ns 3 ^{7} atoms

1g contain ^{22} atoms

Cost per gram: ~ US $ 10^{15}

Cost of Bailout ~ 7 x 10^{11}

US National Debt ~ $ 9.6 x 10^{12}

Do you take payment in graphene?!

Large Scale Graphene Synthesis

Epitaxial Graphene growth on insulating SiC substrates

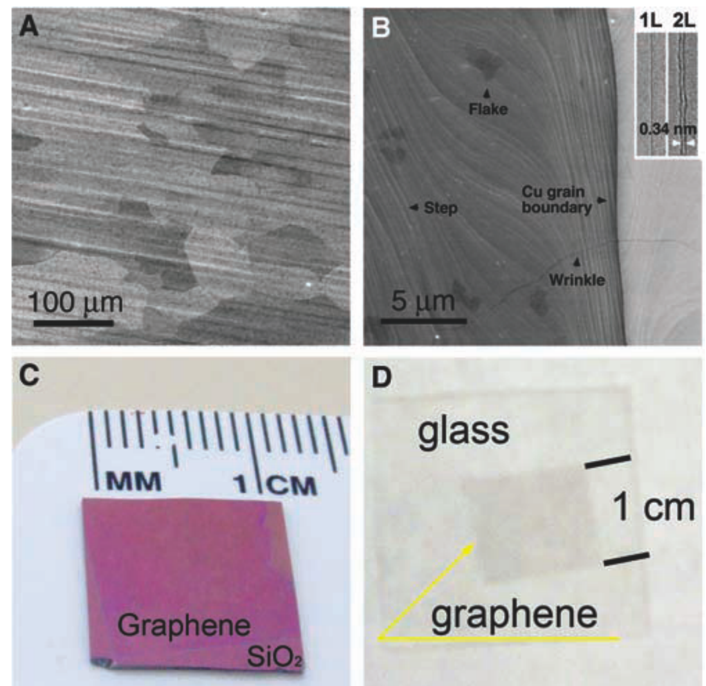
- “evaporate” Si atoms from SiC, leaving carbon (graphene) behind
- pioneered by Walt de heer
- presence of a “buffer” layer prevents gating via back gate

Berger *et al*, Science 2006

Epitaxial Graphene growth on metallic substrates, e.g. Ru, Cu, Ni

- chemical vapor deposition
- decomposition of carbon onto metal substrates at high temperature
- wafer-scale graphene sheets (up to 95% are single layer)
- mobility up to 3500 cm^2/Vs (quantum Hall effect observed)
- can be transferred onto insulating substrates by PDMS stamping or dissolving the underlying substrates

Ruoff group, Science 2009; Kim *at al,* Nature 2009; Reina *et al* Nano Lett. 2009, Bae *et al,* Science 2009.



Solution Chemistry Processing

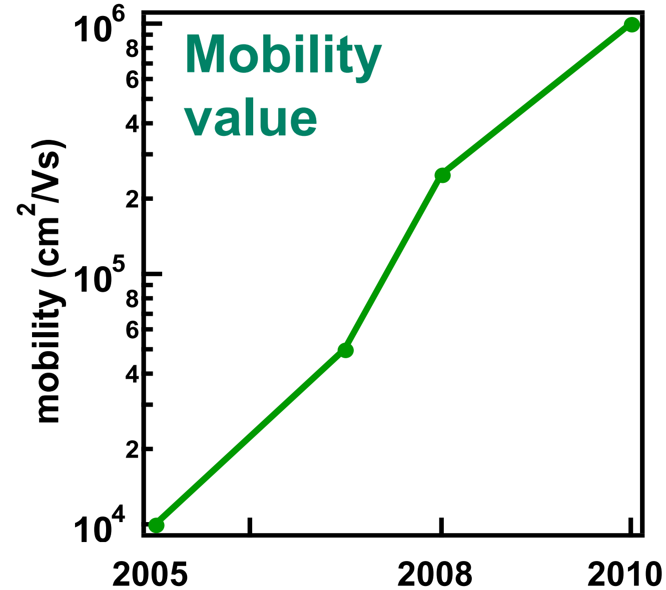
Kaner group

Current Challenges

"Moore's Law" for Graphene

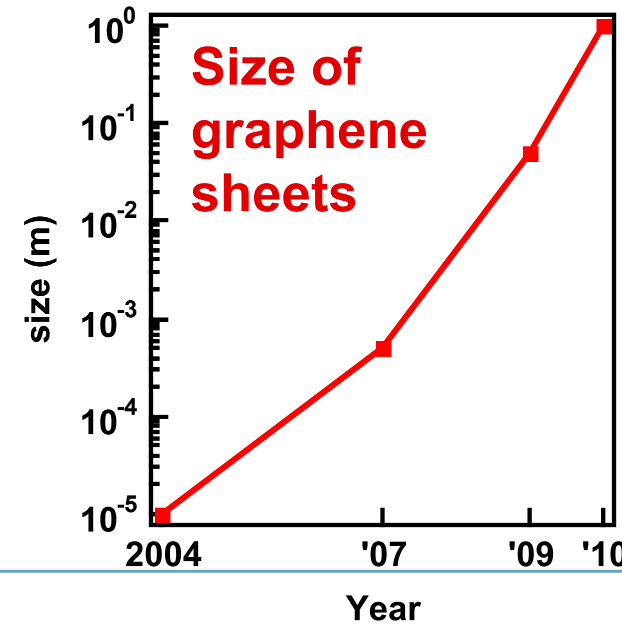
3. Mobility and doping control

- substrate control
- ambient condition control
- annealing/treatment



2. Precision crystallographic edge control

- Chemical modification
- Nanoparticle etching

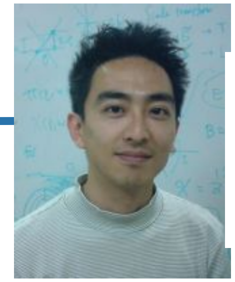


1. Band Gap engineering

- nanoribbon
- chemical modification
- strain
- biased bilayer

Collaborators

Ed
McCann



Mikito
Koshin
o

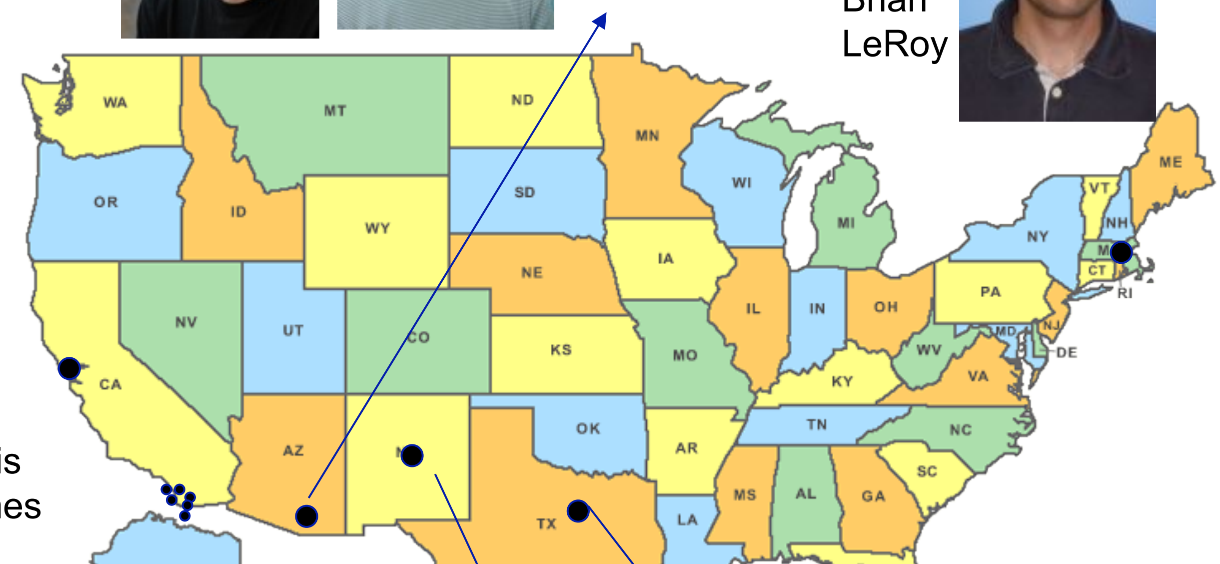
Brian
LeRoy

Nai-chang Yeh

Robert Haddon

Steve Cronin

Chris
Dames



Jing Shi

Roland
Kawakami

Nikolai Kalugin,

Allan
MacDonald

Dmitry
Smirnov

Chandra Varma

Vivek Aji

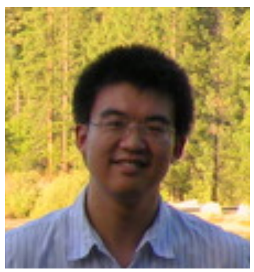
Acknowledgments

Graduate Students

Jairo Velasco

Wenzhong Bao

Hang Zhang

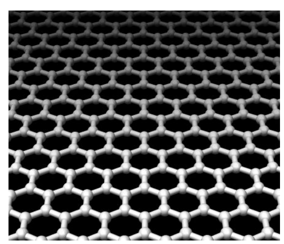


Lei Jing

Adam Zeng Zhao

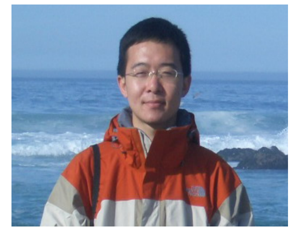
Yongjin Lee

Jhao-wun Huang



Fenglin Wang

Former Graduate Students



Feng Miao
(Now at HP Labs)

Gang Liu
(Now at UCLA)

Undergraduate Students

Philip Kratz
Kevin Myhro
David Tran

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