An Introduction to Graphene and the 2010 Nobel Physics Prize

(for senior secondary school students)

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2010 Nobel Physics Prize



Andre Geim (Born 1958 and educated in Russia, Dutch, University of Manchester UK)



Konstantin Novoselov (Born 1974 in Russia, educated in the Netherlands, Russian & British, University of Manchester UK)

"for groundbreaking experiments regarding the twodimensional material graphene"

http://nobelprize.org/nobel_prizes/physics/laureates/2010/press.html

So, what is graphene?



Take-home message 1 – It is all about carbon! Graphene is a **single layer** of carbon atoms forming a honeycomb lattice.

Graphene – The perfect atomic lattice [Picture taken from Nobel Prize Announcement (public information)]



A single sheet of carbon atoms forming a honeycomb lattice!

Questions...

- How to fabricate graphene?
- Old Physics?
- New implications to physics?
- Why is it important?
- Properties?

[Thinnest, strongest, transparent, nice/tunable semiconductor, good thermal conductor, etc.]

Nice properties for future applications?

All is about carbon!



http://image.wistatutor.com/content/p-block-elements/diamond-structure.gif

Diamond is a form of carbon 3D structure



www.diamondvues.com/84%20Carat%20Diamond.jpg

Graphite – layers of graphene



http://mrsec.wisc.edu/Edetc/nanoquest/carbon/images/pencil.jpg

The problem over many years is:

How to peel a layer of graphene off graphite?

History of Graphite – a "not-too-old" material

Discovery of graphite deposit: ~ 16th century (England)





• The mine was discovered in the 16th century and in those early days was used only for marking sheep.

• It was called "Plumbago" (lead ore). Scheele (1779, Swedish) showed that plumbago is CARBON, not lead

• Werner (1789, German) called it GRAPHITE (Greek meaning "to write")

- 17th Century: Casting moulds for cannon and musket balls
- 18th Century: Pencil industry

Applications:

Steel industry, refractory crucibles, electrodes, lubricant, brake linings, ...

Modern graphite mine



<u>Applications:</u> Steel industry, refractory crucibles, electrodes, lubricant, brake linings, ...

World Production of graphite US: 1,110 Kt/yr

China: 800 Kt/yr India: 130 Kt/yr

US (Synthetic): 198 Kt/yr

Applications based on Graphitic Carbon



Steel company: coke



Rubber/plastic: carbon black





Graphite electrode



Pencil: graphite+clay

Domestic Production and Use: Although natural graphite was not produced in the United States in 2002, approximately 200 U.S. firms, primarily in the Northeastern and Great Lakes regions, used it for a wide variety of applications. The major uses of natural graphite remained the same as in 2000: refractory applications led the way in use categories with 22%; brake linings was second with 21%; dressings and molds in foundry operations, 8%; lubricants, 5%; and other uses made up the remaining 44%.

Graphitic Composite Materials: Carbon Fiber



Weigh ~ ¼ of aluminum Strength ~ 10 times of steel Electrical conductor Thermal conductor



Graphene – the mother of all graphites





Simple Physics of Carbon Atoms

6th element in periodic table => 1 nucleus + 6 electrons

Quantum Physics (Schroedinger, Heisenberg and Dirac, Nobel Physics Prize 1932 & 1933) tells us how the 6 electrons behave under the influence of the carbon nucleus



C Carbon $1s^2 2s^2 2p_x^1 2p_y^1$

2 electrons in 1s atomic orbital (full)

2 electrons in 2s atomic orbital (full)
1 electron in 2px atomic orbital (not full)
1 electron in 2py atomic orbital (not full)
0 electron in 2pz atomic orbital (empty, not full)

Quantum Physics (3 compulsory + 1 elective) courses are a major part of our physics 4-year curriculum!

1s has very low energy, but 2s and 2p orbitals are very close in energy



2s and 2p are very close in energy
2s, 2p_x, 2p_y, 2p_z together can hold 8 electrons
there are only 4 electrons in a carbon atom *Take-home message 2 –* the 4 electrons in 2s, 2p_x, 2p_y, 2p_z are responsible for bonding (chemistry), conduction and other physical properties

[1s (2 electrons) => very low in energy because they are closer to the nucleus] (very stable => the 2 electrons don't participate in bonding and conduction)

http://invsee.asu.edu/nmodules/carbonmod/bonding.html

Basic Questions in 20th century physics...

Why do electrons and nucleus form atoms?

Why do atoms form molecules and solids?

Why do protons and neutrons form nuclei?

Why do quarks form protons and neutrons?

Basically, what is matter and why is there matter? Answer is again provided by Quantum Physics! *Gain stability (lower energy) by doing so!* To prepare for bonding with other atoms, each carbon atom mixes the 2s and 2p orbitals

- Why is it possible?
 2s and 2p are close in energy (don't need much energy to do the preparation)
- What for?

To stretch out in space so as to avoid Coulomb repulsion between electrons -- when electrons from other atoms come in they form bonds!

• Clever move – spend a bit of energy (in mixing) and then gain back a lot (when forming a bond)!

One-dimensional example: s and px mix to form highly directional Hybridized orbitals





Highly dimensional => expected to form honeycomb lattice



The remaining p_z orbital is perpendicular to the x-y plane. There is 1 electron in p_z.

http://www.chemistryland.com/CHM151W/09-CovalentBonds/Covalent.html



Strong bonds on the plane provide the structure.

There is 1 electron in each p_z orbital. These electrons are relatively free to move around (above and below) the plane.

Graphene – the mother of all graphites



"Graphene: Exploring Carbon Flatland," A. K. Geim and A. H. MacDonald, Physics Today, August 2007, p. 35

Take-home message 3 – Structure

• Each carbon atom has 4 electrons that can affect bonding and physical properties

• 3 of them are used to form the rigid honeycomb framework (strongest material)

 Each atom has 1 electron residing in pz, it lives above and below the plane

• Much physics has to do with these pz electrons

How to get graphene? The idea is to rub a tiny piece of graphite against another surface, just like writing.

Mechanical exfoliation



--Pencil drawing --Scotch tape Method

Advantage

- --Simple and easy
- --High quality, good for fundamental physical study

Disadvantage

-Low efficient and laborious

Towards Graphene: Nano-Pencil

Writing using a graphite microcrystal at the tip of an atomic force microscope [P. Kim (Columbia U)]





Nanopencil could write down thin pancakes!



[Picture: Taken from Geim and Kim, in Scientific American (2008)]

But these pancakes are still THIN graphite, not a single layer!

In physics, there was also the question of whether a strictly 2D ordered structure could exist or not.

Atomic Force Microscope



Gerd Binnig 1986 Nobel Physics Prize

One of the inventors of AFM (1985) is Gerd Binnig, who won the 1986 Nobel Physics Prize for his invention of the Scanning Tunneling Microscope (STM)

And then...came the Nobel Prize winning work of Geim and Novoselov (2004)!

First Experimental Extraction of Graphene (2004)

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,¹ A. K. Geim,¹* S. V. Morozov,² D. Jiang,¹ Y. Zhang,¹ S. V. Dubonos,² I. V. Grigorieva,¹ A. A. Firsov²

We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conductance bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to 10¹³ per square centimeter and with room-temperature mobilities of ~ 10,000 square centimeters per volt-second can be induced by applying gate voltage.

The ability to control electronic properties of a material by externally applied voltage is at the heart of modern electronics. In many cases, it is the electric field effect that allows one to vary the carrier concentration in a semiconductor device and, consequently, change an electric current through it. As the

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semiconductor industry is nearing the limits of performance improvements for the current technologies dominated by silicon, there is a constant search for new, nontraditional materials whose properties can be controlled by the electric field. The most notable recent examples of such materials are organic conductors (*I*) and carbon nanotubes (*2*). It has long been tempting to extend the use of the field effect to metals [e.g., to develop allmetallic transistors that could be scaled down to much smaller sizes and would consume less energy and operate at higher frequencies

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than traditional semiconducting devices (3)]. However, this would require atomically thin metal films, because the electric field is screened at extremely short distances (<1 nm) and bulk carrier concentrations in metals are large compared to the surface charge that can be induced by the field effect. Films so thin tend to be thermodynamically unstable, becoming discontinuous at thicknesses of several nanometers; so far, this has proved to be an insurmountable obstacle to metallic electronics, and no metal or semimetal has been shown to exhibit any notable (>1%) field effect (4).

We report the observation of the electric field effect in a naturally occurring twodimensional (2D) material referred to as few-layer graphene (FLG). Granhene is the

name given to a single layer (densely packed into a bent ture, and is widely used to c ties of many carbon-based mat graphite, large fullerenes, nank carbon nanotubes are usually graphene sheets mlled up intocylinders) (5–7). Planar graj heen presumed not to exist i being unstable with respect to curved structures such as soot nanotubes (5–14).





Geim & Novoselov (2004)



Graphene Preparation (using plastic adhesive tape!)



Mechanical exfoliation

Scotch Tape Method



[Then we need some microscopes (electron microscope, atomic formce microscope) to select the single sheet graphene. A DIY guide to prepare graphene is given in Scientific American (April 2008).]

A Few Layers of Graphene on SiO₂/Si Substrate





graphite

graphene

fullerene



nanotube

Graphite (3D) – stacking up graphenes

Graphene (2D) – the mother of graphites

The basic block for carbon nanotubes (1D) (folding up graphene) and C60 (0-D) bucky ball

DAim liste/ the Royal Swedish Academy of Sciences





C60 – 1996 Nobel Chemistry Prize





Sir Harold W. Kroto



Richard E. Smalley

Nobel Prize in Chemistry 1996 "for their discovery of fullerenes"




Scientists also tried other ways to get graphene...

- Chemistry route [graphite oxide reduction, graphite intercalation]
- Start with SiC ("burn" Si away)
- Chemical vapor deposition
- Start with carbon nanotubes unzip into graphene ribbon



Take Home message 4:

The breakthrough in graphene came when the Manchester University group found an easy way to fabricate them!

Properties of Graphene

Take-home message 5

Thickness – With only one layer of carbon atoms, graphene is the thinnest material ever found! The thickness is about 0.335 nm.

Density --Each hexagon contains 2 carbon atoms

 \Rightarrow 2 carbon atoms in 0.052 (nm)² \Rightarrow density = 0.77 mg/m²

Bonus -

2 electrons (wandering electrons) in each hexagon, one from pz orbital of atom A and another from pz orbital of atom B



Important idea: Carbon atom A and Carbon atom B have different local environments!

Optical Properties: Almost Transparent



One atom thick membrane -> nearly transparent (useful in devices)

R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, & A. K. Geim, Science **320**, 1308 (2008).

Strength (mechanical properties) of Graphene: Strong and Tough

C. Lee, X. Wei, J. W. Kysar, & J. Hone, Science 321, 385 (2008)



200

150

Indentation Depth (nm)

Graphene vs (scaled down) steel film of the same thickness

Take-home message 5

=> Graphene is more than 100 times stronger than the strongest steel!



[Can put a 4Kg mass (e.g. a cat) on a 1 m² graphene (if one can make it). Cartoon taken from Nobel Prize announcement]

Chemical Property: Impermeable Membrane

Graphene Lattice



Electron density

Not permeable even for proton!

Graphene Balloon

(McEuen group, 2009)







Graphene Bubbles

(P Kim, Columbia group, 2009)



Chemical reaction:

 $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

Graphene is ideal one atomic thick Impermeable membrane!

Electronic Properties of Graphene

For physicists and device engineers, the most behavior of graphene comes from its electronic properties!

How do the pz electrons (1 for each atom, 2 for each hexagon) in graphene behave?

Like electrons in atoms, Quantum Physics tells us that electrons can occupy states that are grouped in energies, i.e., energy bands! [This is Solid State Physics, also a compulsory course in our 4-year physics curriculum.]

Standard shape of energy bands Why are there conductors and insulators?



[Consequence of quantum physics]



Silicon [best selling and money-making semiconductor]



http://upload.wikimedia.org/wikipedia/commons/e/e2/Silicon_single_crystal.jpg





Historical Note: Dirac (1928) suggested the existence of **antiparticle**. In addition to looking for antiparticles in cosmic ray and huge particle accelerators, semiconductors provide a table-top realization of antiparticles in the form of holes (missing electrons) in the valence band! [Crossover of relativistic quantum physics and solid state physics!]

x-axis is proportional to momentum p y-axis is energy $E = \frac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{p^2}{2m}$ p = mv = momentumCompare $E = \frac{p^2}{5m}$ with $y = Ax^2$ ⇒ parabola



[Lighter electron **effective** mass, higher curvature, faster electronics! Key idea behind the whole semiconductor industry! Electrons in semiconductors behave as "free electrons" but with a different mass!]

Graphene has unusual energy bands



The pz electrons (2 in each hexagon) completely fill the lower band. The upper band is empty. One can introduce (or take away) electrons into the upper (lower) band by various methods.



Take-home message 6 – Graphene is a semiconductor with zero gap or a gapless semiconductor Scientists are developing methods to make useful devices out of graphene

Implication – possible to use semiconductor *device physics* (well developed in silicon industry) in graphene and to integrate with devices derived from graphenebased structures, e.g., carbon nanotubes!

Graphene: Extremely Good Semiconductor

Electrons move without much "resistance" on the plane of graphene!



High mobility materials have been under intensive research as an alternative to Silicon for higher performance mobility: Si (1,400 cm2/Vsec), InSb (77,000 cm2/Vsec)



Graphene is the basic material for nanoscale devices

[Analogy - cloth to make different dresses!]



Transparent, conducting and flexible electrodes



Era of Semiconductor Devices





The world's first transistor (Bell Lab, 1948-50), Nobel Physics Prize 1956



Computer Chips (Intel)

[Circuits are packed (integrated) in one chip!]

Graphene based transistor



Scientific American, 2008 April, P.96

All in nanometer scale!

Graphene Electronics: Challenging to Silicon





Making a transistor out of graphene

100-GHz Transistors from Wafer-Scale Epitaxial Graphene

Y.-M. Lin,* C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu,

(IBM Watson Lab, USA)



Fig. 1. (**A**) Image of devices fabricated on a 2-inch graphene wafer and schematic cross-sectional view of a top-gated graphene FET. (**B**) The drain current, I_D , of a graphene FET (gate length $L_G = 240$ nm) as a function of gate voltage at drain bias of 1 V with the source electrode grounded. The device transconductance, g_{m} , is shown on the right axis. (**C**) The drain current as a function of V_D of a graphene FET ($L_G = 240$ nm) for various gate voltages. (**D**) Measured small-signal current gain $Ih_{21}I$ as a function of frequency f for a 240-nm-gate (\diamond) and a 550-nm-gate (\triangle) graphene FET at $V_D = 2.5$ V. Cutoff frequencies, f_T , were 53 and 100 GHz for the 550-nm and 240-nm devices, respectively.

Integrated Circuit on Graphene Wafer-Scale Graphene Integrated Circuit

(IBM Watson Lab, USA)

Yu-Ming Lin,* Alberto Valdes-Garcia, Shu-Jen Han, Damon B. Farmer, Inanc Meric,† Yanning Sun, Yanging Wu, Christos Dimitrakopoulos, Alfred Grill, Phaedon Avouris,* Keith A. Jenkins





Fig. 1. (A) Circuit diagram of a four-port graphene RF frequency mixer. The scope of the graphene IC is confined by the dashed box. The hexagonal shape represents a graphene FET. (B) Schematic exploded illustration of a graphene mixer circuit. The critical design aspects include a top-gated graphene transistor and two inductors connected to the gate and the drain of the GFET. Three distinct metals layers of the graphene IC are represented by M1, M2, and M3. A layer of 120-nm-thick SiO2 is used as the isolation spacer to electrically separate the inductors (M3) from the underlying interconnects (M1 and M2).

1294

10 JUNE 2011 VOL 332 SCIENCE www.sciencemag.org

Very simple Integrated Circuit built on Graphene, reported in Science two weeks ago - it is just the beginning!

What to expect from Graphene --Major Applications



Source "Carbon Nanotubes and Graphene for Electronics Applications" IDTechEx 2010

Graphene and Fundamental Physics --Graphene, relativistic quantum mechanics, Dirac equation, and table-top experiments for QED (Quantum electrodynamics)

Take-home message 7– Electrons in Graphene behave as if they are relativistic particles with zero mass (massless)! Graphene provides tabletop (inexpensive) tests on quantum electrodynamics (QED)!

Thus, another crossover of relativistic quantum mechanics and solid state physics!

Unusual energy bands in Graphene



The pz electrons (2 in each hexagon) completely fill the lower band. The upper band is empty. One can introduce (or take away) electrons into the upper (lower) band by various methods.



Electrons in Graphene behave as if they are massless!

[Expect fast electronic devices from graphene!]

And more...



The come-shaped bands are described mathematically by $\mathcal{V}\begin{pmatrix} 0 & \hat{p}_{x} - i\hat{p}_{y} \\ \hat{p}_{x} + i\hat{p}_{y} & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \mathcal{E}\begin{pmatrix} a \\ b \end{pmatrix}$ which happens to be the <u>Dirac Equation</u> for massless particles! relativistic Quantum Mechanics Leads to QED (Quantum Electrodynamics)

Electrons in Graphene behave as if they are massless Dirac particles!



Nobel Prize in Physics in 1933 with Erwin Schrödinger, "for the • discovery of new productive forms of atomic theory."

[Dirac also "required" the existence of antiparticles (proven to be true later), based on the viewpoint that his equation is too beautiful to be wrong!]

Electrons in graphene are still electrons.

But electrons moving in the special environment of graphene lead to the special effect that they behave as if (i) they are massless; and (ii) they obey the Dirac equation!

Implications...

• Use graphene (cheap – pencil and tape!) as a tool to test predictions of QED!
CERN (ring passes through two countries -- underground!)



BIG, EXPENSIVE PROJECTS!

http://www.dis.anl.gov/images/cern_overhead.jpg



Graphene provides an inexpensive small-lab table-top system to study QED!

E.g. Klein tunneling => easier to tunnel through when the barrier is higher! Now confirmed in graphene experiments!

Summary

- Single Sheet of Carbon atoms
- Thinnest (about 1/3 nm thick)
- Light (0.7 mg for 1m²)
- Tough (tougher than steel of the same thickness)
- Yet flexible (doesn't break easily, can support 4kg for 1m² graphene)
- Transparent
- Impermeable membrane

- Electrons in pz show unusual behavior
- Gapless (zero gap) semiconductor
- High mobility (high speed electrons)
- Electrons behave as if they are massless and they obey the Dirac equation
- Table-top test bed for QED



2010 Nobel Physics Prize



Andre Geim (Born 1958 and educated in Russia, Dutch, University of Manchester UK)



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"for groundbreaking experiments regarding the twodimensional material graphene"

http://nobelprize.org/nobel_prizes/physics/laureates/2010/press.html

A Rapidly Growing Field



Source: M. Taghioskoui, Materials Today, 12, 34 (2009)

Many works waiting for YOU (young people) to do!

- mass production of big piece of graphene?
- applications?
- electronics based on graphene and carbon nanostructures?
- replacing silicon!



http://www.krisbattles.com/images/Fig_3.7_Hand_with_Pencil_Writing.JPG



http://www.krisbattles.com/images/Fig_3.7_Hand_with_Pencil_Writing.JPG

Supplementary Pages for Future Talks

Tunneling - Klein "paradox"





Figure 4 | **QHE for massless Dirac fermions.** Hall conductivity σ_{xy} and longitudinal resistivity ρ_{xx} of graphene as a function of their concentration at B = 14 T and T = 4 K. $\sigma_{xy} \equiv (4e^2/h)\nu$ is calculated from the measured dependences of $\rho_{xy}(V_g)$ and $\rho_{xx}(V_g)$ as $\sigma_{xy} = \rho_{xy}/(\rho_{xy}^2 + \rho_{xx}^2)$. The behaviour of $1/\rho_{xy}$ is similar but exhibits a discontinuity at $V_g \approx 0$, which is avoided by plotting σ_{xy} . Inset: σ_{xy} in 'two-layer graphene' where the quantization sequence is normal and occurs at integer ν . The latter shows that the half-integer QHE is exclusive to 'ideal' graphene.

Source: "Two dimensional gas of massless Dirac fermions in graphene", Novoselev et al., Nature 438, 197 (2005).