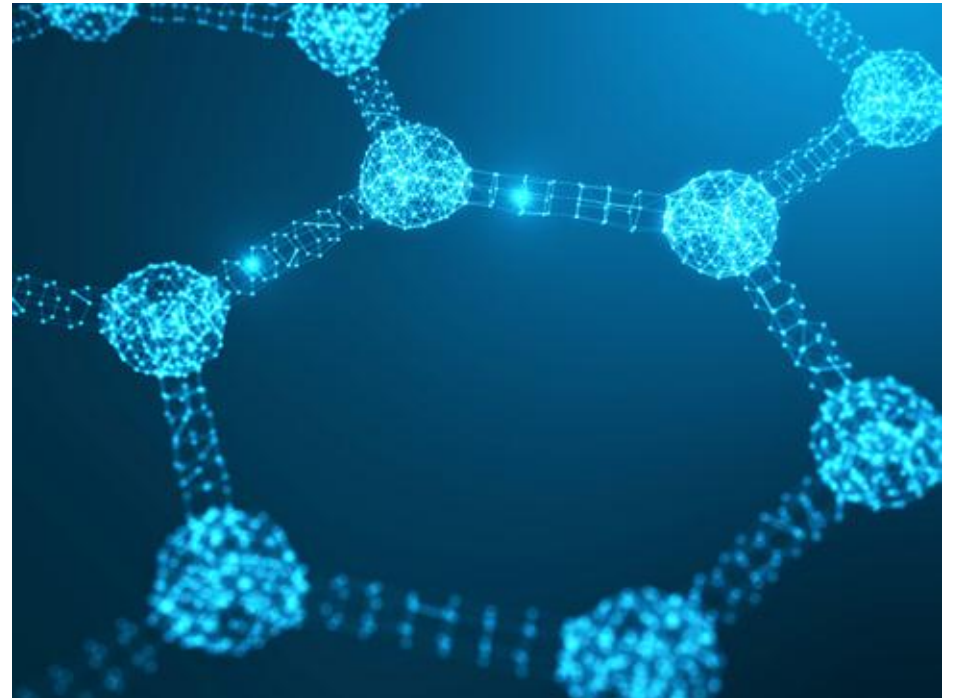


Engineered Materials (SC221)

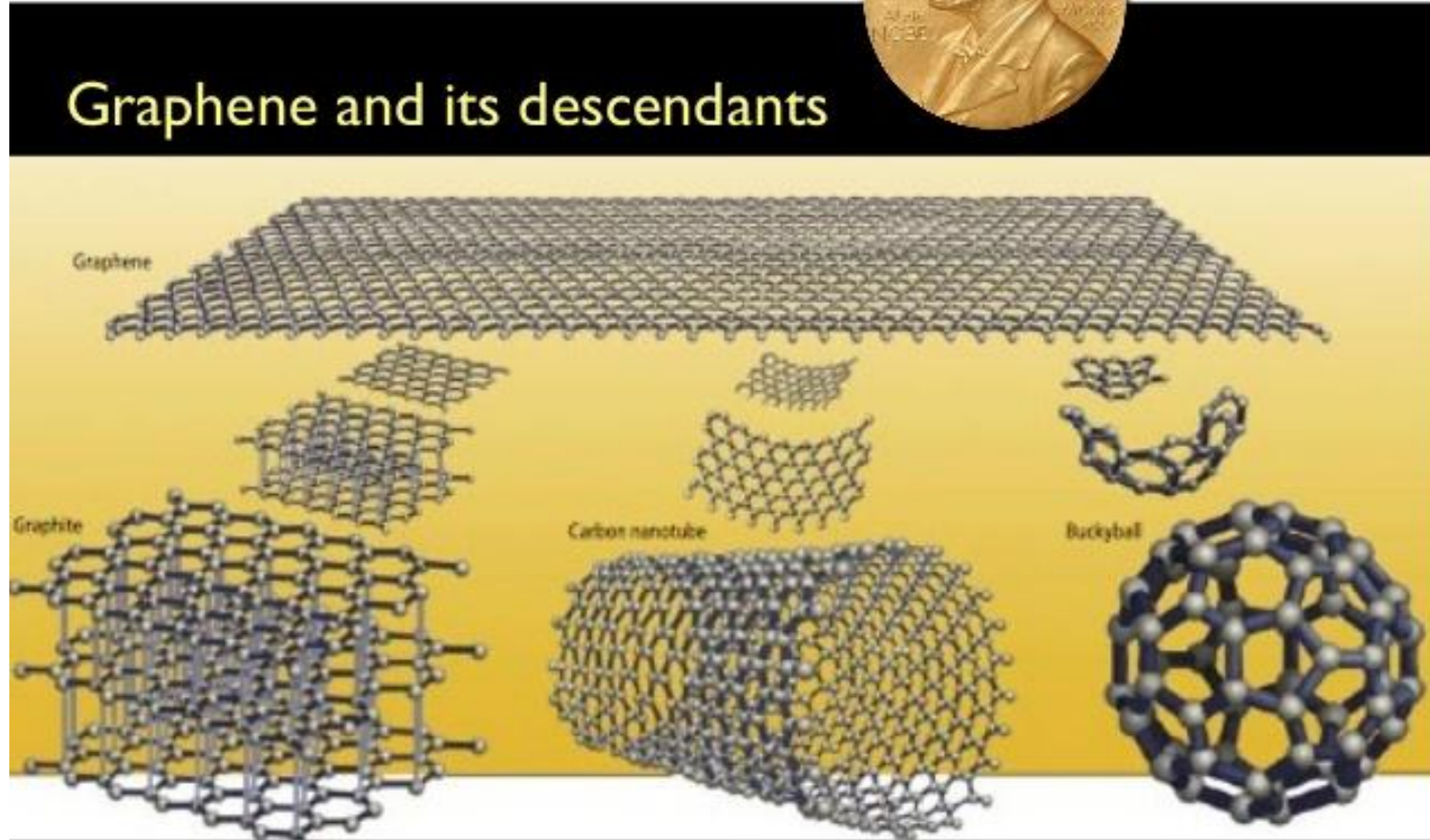
Discovered in 1970s

Andre Geim and Konstantin Novoselov (Univ of Manchester) managed to transfer it to a substrate and did a detailed study. This won them a Nobel prize in Physics, in 2010.

It has hexagonal structure.

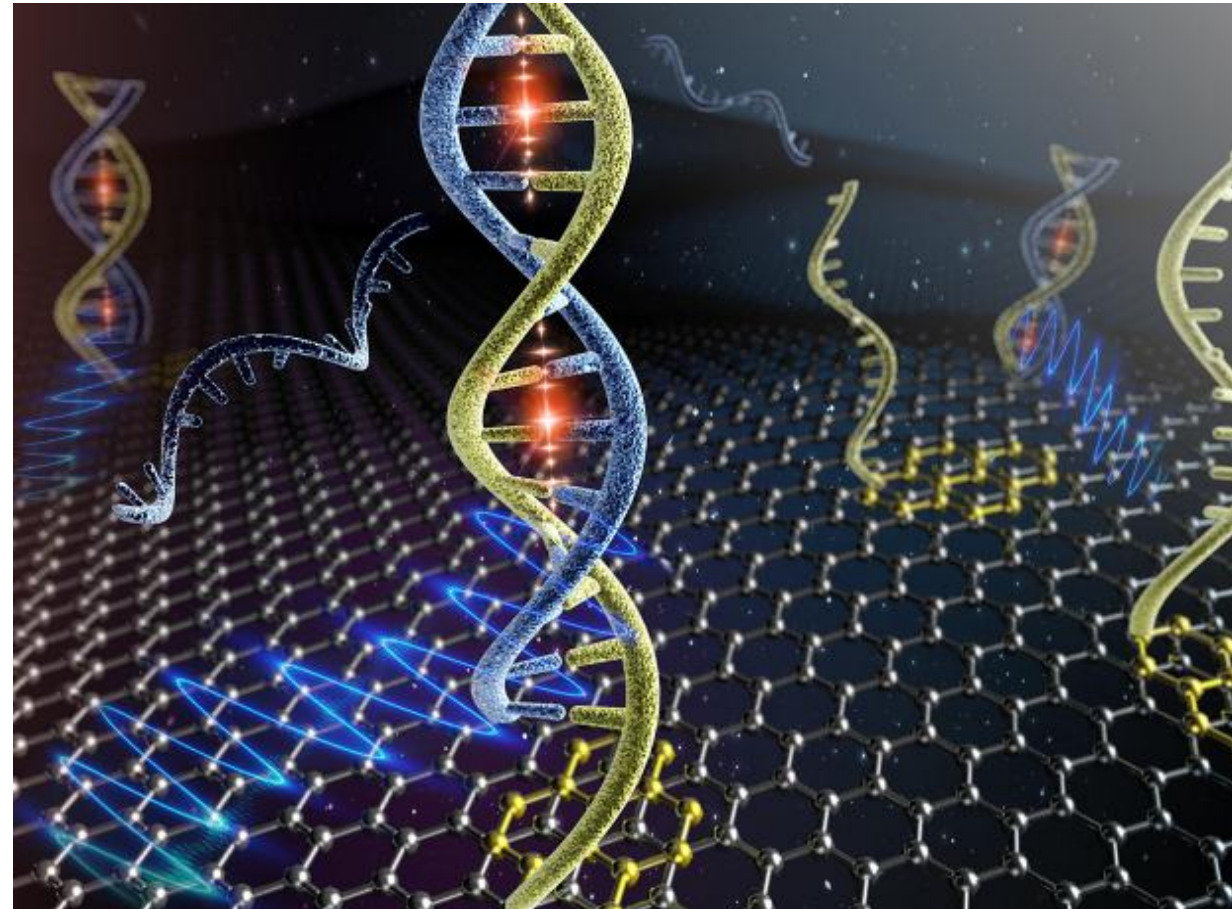


Graphene



It has the ability to detect/sense many chemicals and biomolecules. Therefore it is the best choice for making sensing devices with it. But since it has no energy gap like in case of usual semiconductors, it is too difficult to make switches (on/off device) out of it.

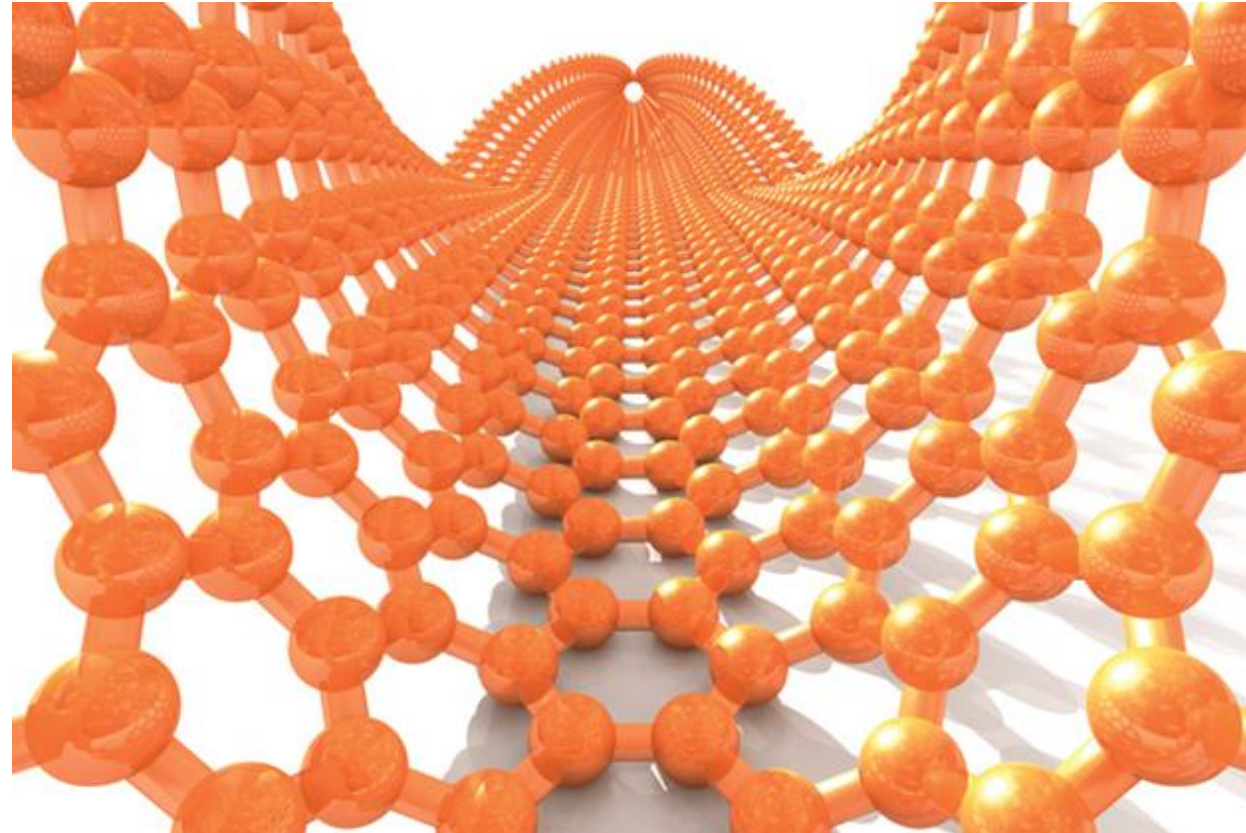
The surface is graphene.



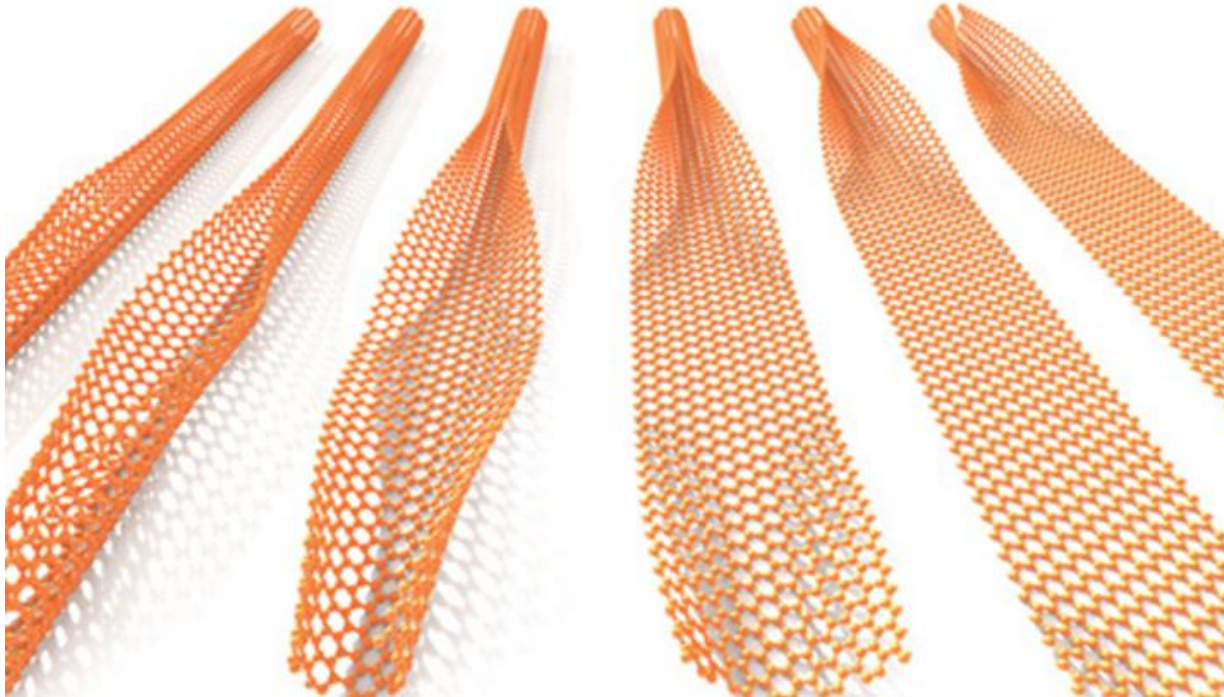
Quantum dots, wires and wells

Fullerene, CNT

When you cut open a CNT,
you will get an infinite sheet
of graphene.



First fabrication of graphene flakes was done simply by peeling them from a graphite crystal using adhesive tape.



When you cut open a CNT, you will get an infinite sheet of graphene.

> 10 stacked graphene sheets make graphite.

Why graphite behaves differently in one dimension than it does in another?

The length of C-C bond in one layer of graphite is only about 0.14 nm. The separation of two layers of graphene in graphite structure is almost around 0.35 nm (2.5 times). Hence the bond strength between two adjacent layers is too weak. Therefore two sheets in graphite slide over each other.

We've been writing with graphene for centuries without appreciating it.

Graphene properties:

- It has a large theoretical specific surface area ($2630 \text{ m}^2\text{g}^{-1}$)
- Very high Young's modulus (1 TPa, does not change its shape considerably)
- It is highly flexible and very light (0.77 mg m^{-2})
- It is chemically stable
- has high thermal conductivity ($5000 \text{ W m}^{-1}\text{K}^{-1}$, better than any metal)
- has ballistic transport over submicron scale ($200,000 \text{ cm}^2/\text{Vs}$ at 5K and $44,000 \text{ cm}^2/\text{Vs}$ at room temp, at very low density it may reach up to $200,000 \text{ cm}^2/\text{Vs}$ at room temp)
- It is highly transparent to visible light (98%)

Graphene properties:

- Strongest 2D material (tensile strength of ~ 130 GPa, for a defect free single layer, 200 times as great as that of steel)
- Even though it is the thinnest material, it is impermeable to gas
- Charge carriers move fastest in it, among all semiconductors known, which could allow for superfast switching in data processing. They (charge carriers) can move up to 2000 times as fast as in silicon, enabling the device or transistor to switch faster.
- Charge carrier concentrations in graphene may go up to 10^{13} cm^{-2}

A charge detector using Graphene has been fabricated that can detect very small amount of charges close to its surface.

Graphene based transistors acquire a unique feature that it exhibits ambipolar (being both n- or p-type) behaviour near the neutrality point.

We need electronics in paper, on walls, and in clothing – and silicon just can't do it. So we are looking for its adjunct.

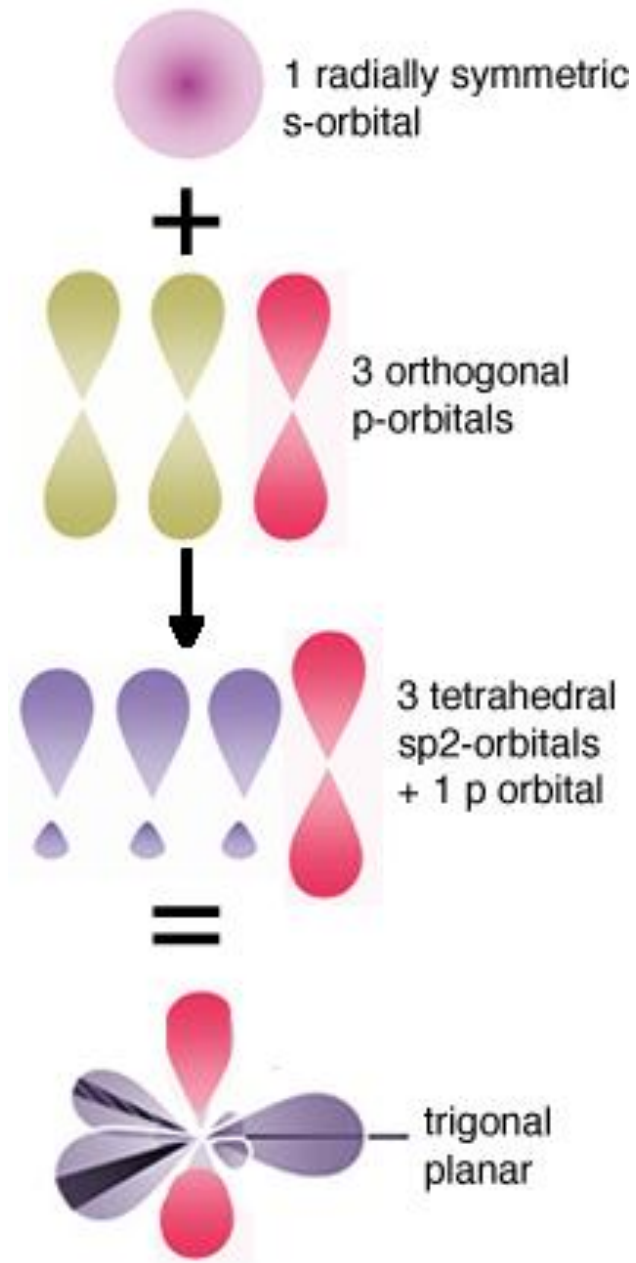
Graphene is just not a replacement, but can do many wonders independently and on mixing with Si in the fabrication of certain devices.

Each carbon atom with an atomic number of six has an electronic configuration of $1s^2 2s^2 2p^2$.

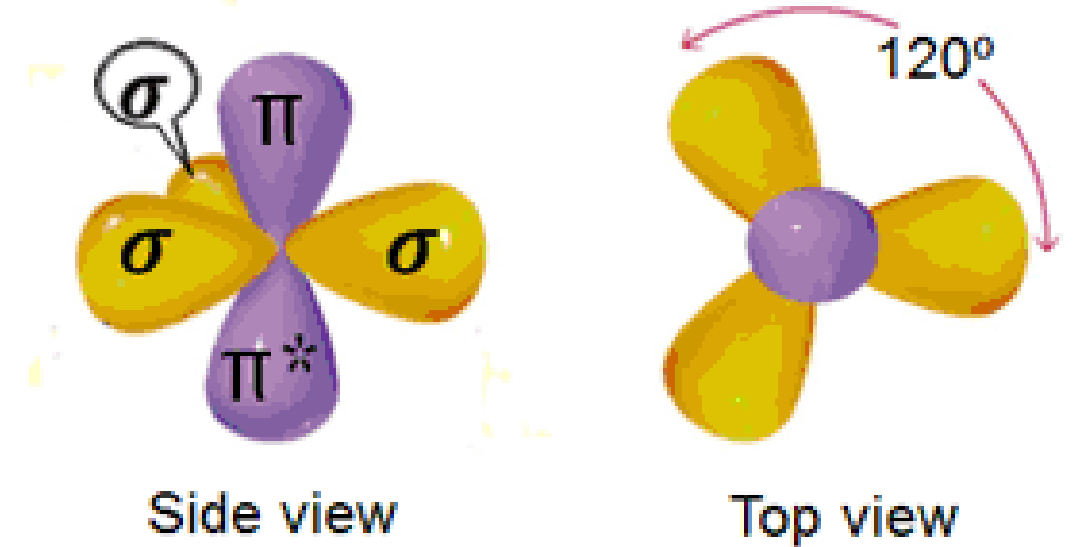
The 1s electrons are essentially inert, close to the nucleus and do not contribute to the chemical bond.

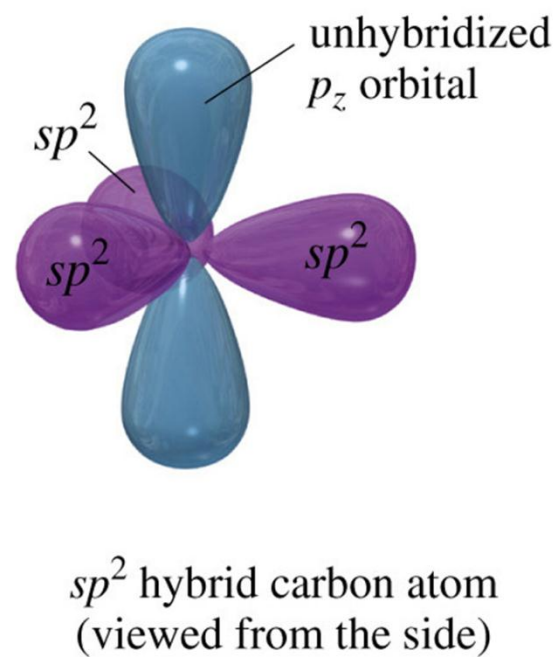
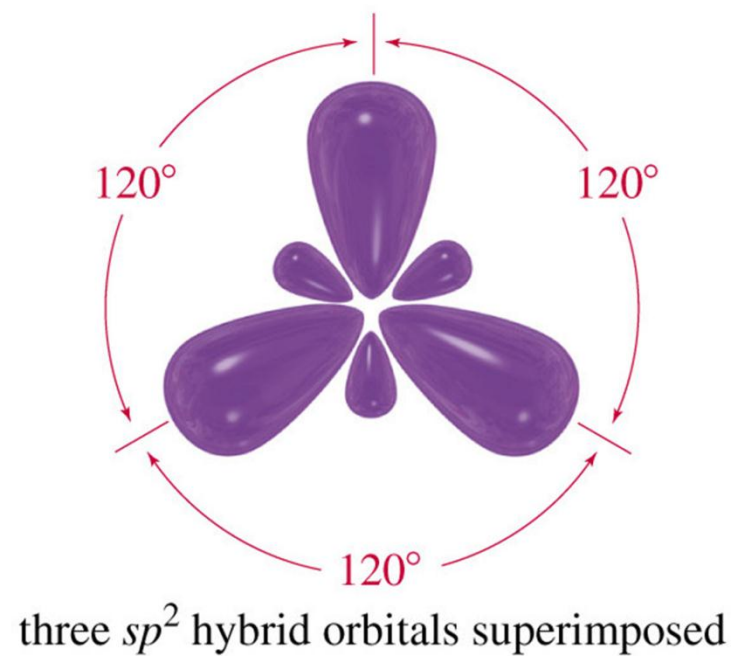
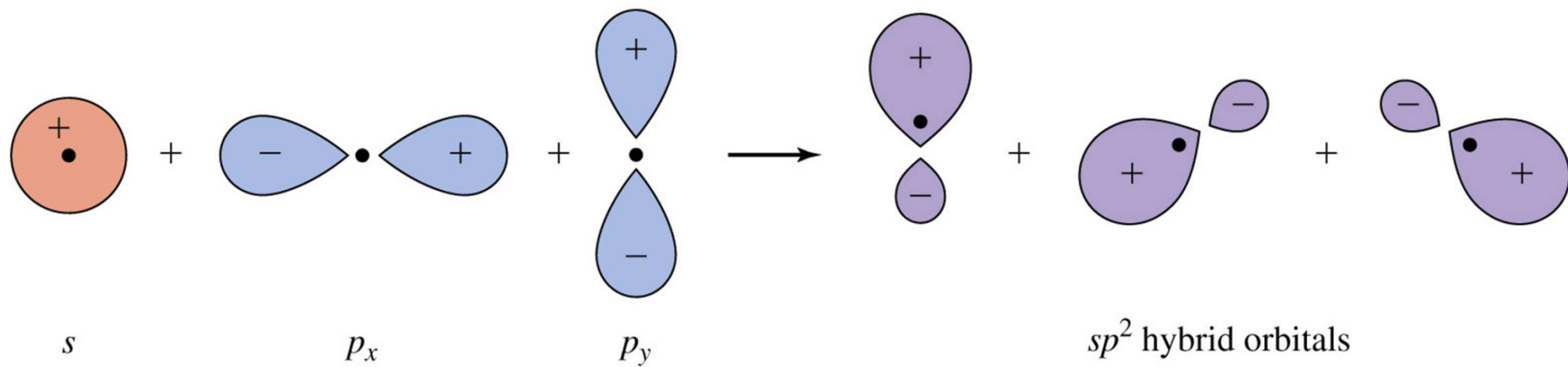
In graphene, the 2s, $2p_x$ and $2p_y$ orbital of carbon atom combine (or hybridize) to form three new planar orbitals called sp^2 hybridization.

The remaining orbital p_z (with 1 electron) is perpendicular to the plane formed by the carbon atoms. The $2 p_z$ orbitals from different atoms combine to form pi bonds, π (valence) and π^* (conduction) bands.



Carbon σ (sigma) and π (pi) Bonds





Each p_z orbital contribute with one electron, therefore graphene is a system with one electron per lattice site. This is called a half-filled system.

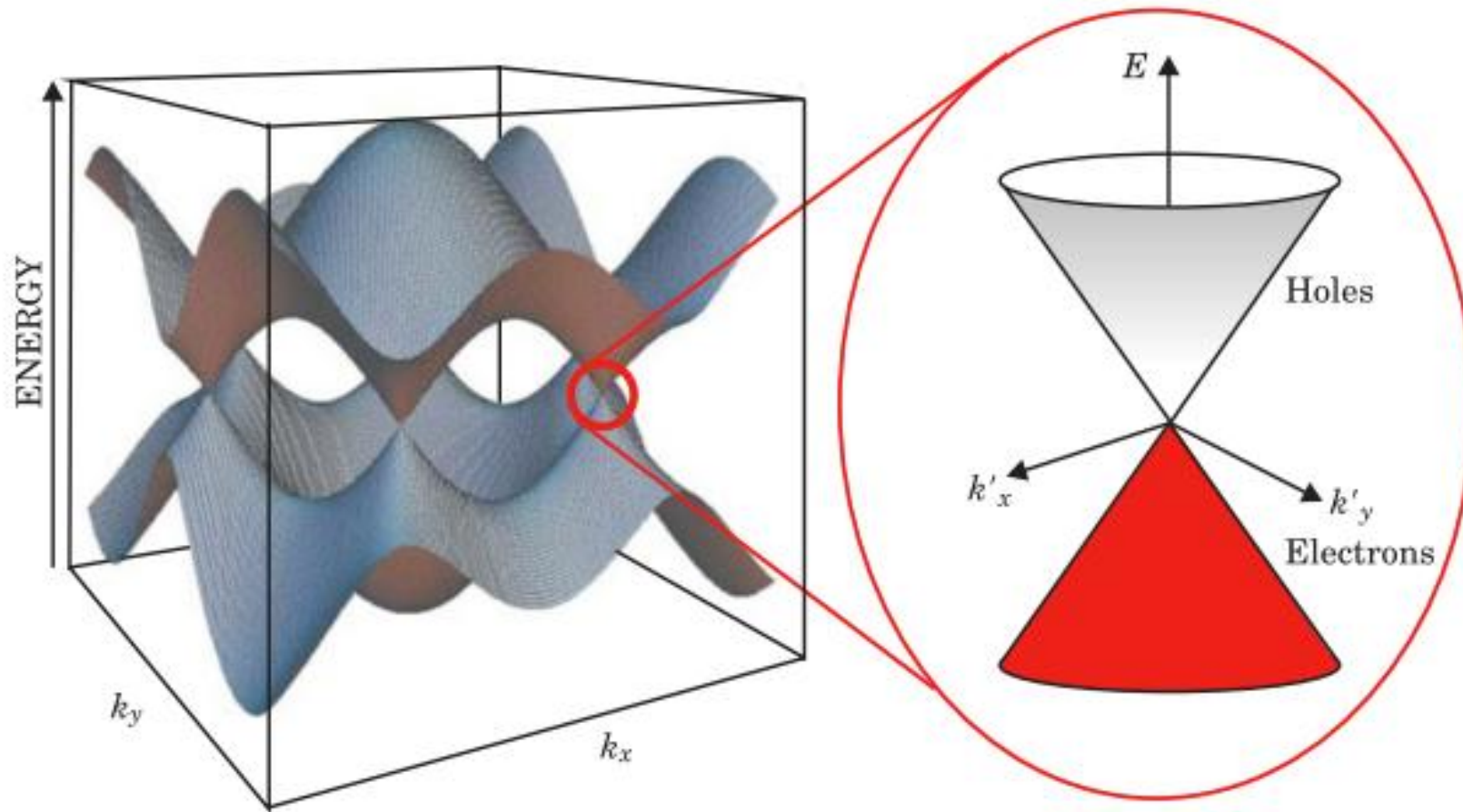
The mechanical properties of graphene are determined by the rigidity of the bond.

The pi-orbitals are responsible for the unusual electronic properties of graphene. A hybridization of character sp^2 leads to hexagonal symmetry as seen in graphite, graphene and carbon nanotubes (CNTs).

The electrons in graphene do not follow Schrodinger's equation, but follow Dirac equation. These are called Dirac fermions.

Reason being the electrons in Pz orbital have almost zero effective mass. So one moves from electrons interacting with a periodic potential (that is explained by Schrodinger's equation) to free massless Dirac particles moving with $v=10^6$ m/s, the Fermi velocity.

The energy dispersion relation (E-k diagram) resembles that of photons, but the velocity is not that of light.

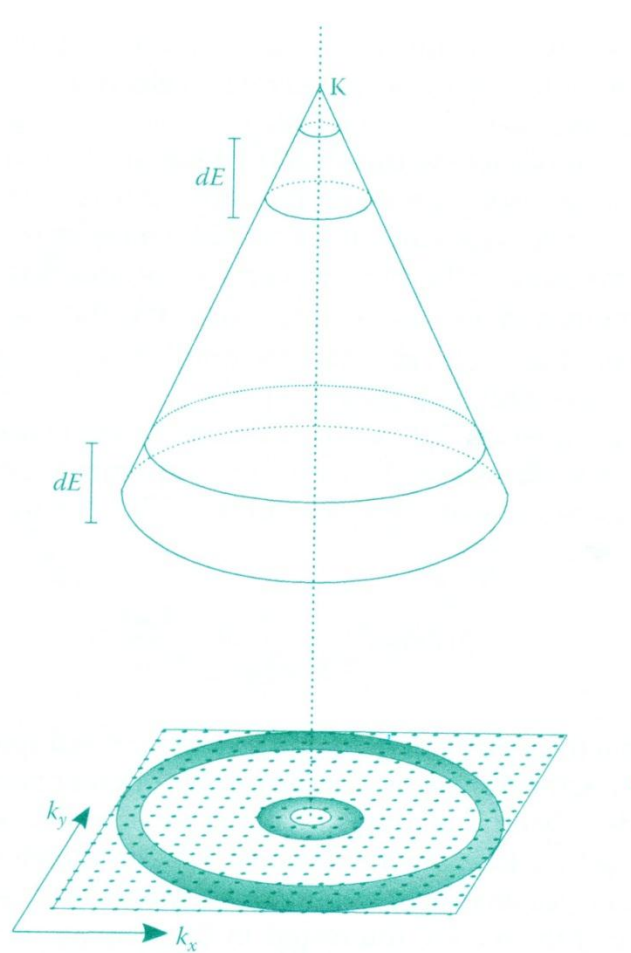


S. Das Sarma *et al.*, **Reviews of Modern Physics** **83**, 407 (2011)

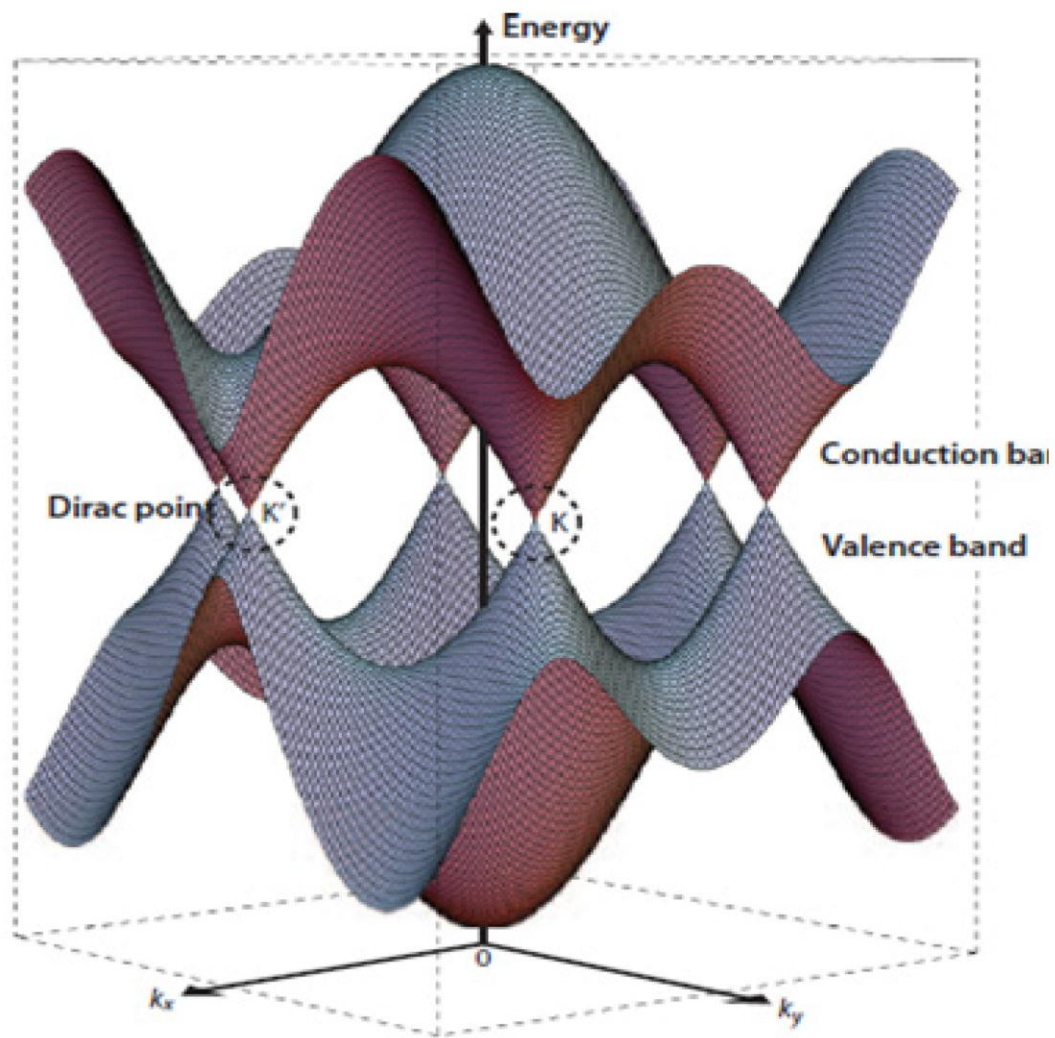
The binding energy spectrum results from solving the Dirac equation for the Hermitian Hamiltonian (whose diagonal elements give the eigenvalues).

- For conductivity we require to know no. of electrons/carriers because flow of these carriers per unit time constitutes current.
- From the quantum theory and Pauli Exclusion principle, we know that electrons can be found only at the allowable energy states (1 energy level has two states representing electrons of opposite spins)
- Therefore, for conductivity, knowledge of no. of states becomes important.

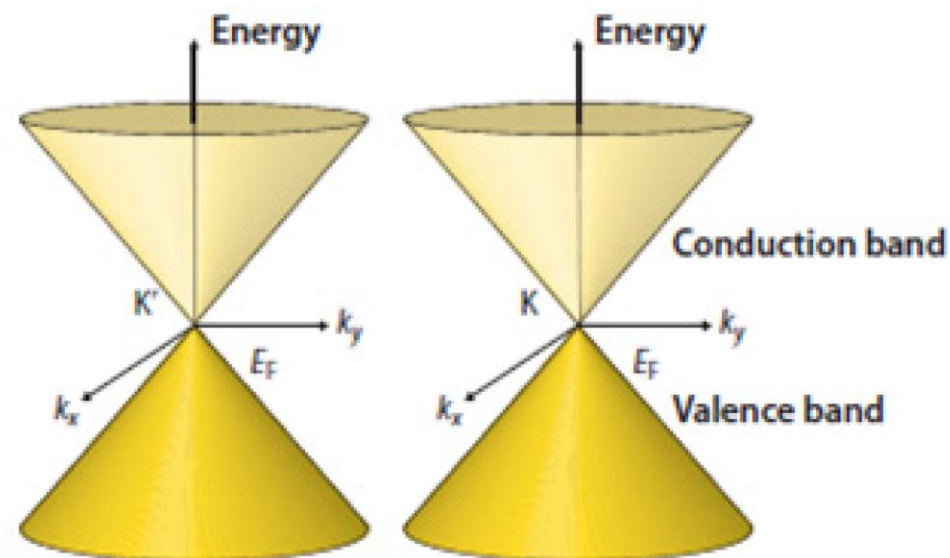
- Usually these no. of states are considered in terms of no. density, i.e., no. of states per unit volume.
- Denoted by $N(E)dE$.
- This is no. density in the energy band of E and $E+dE$.
- It is not always necessary that there is a carrier present at each energy state. Whether an energy state will be filled up by an electron or not is determined probabilistically which is expressed by the probability function $f(E)$.
- At K point, graphene has zero no. density, hence no any room for electrons/holes to be available there.



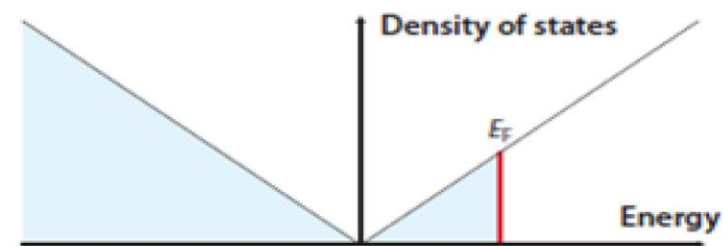
Within a given energy interval dE , the section of the Dirac cone closer to the K-point maps out a much smaller area in \mathbf{k} -space than that within the same energy interval dE further away from the K point. Hence the number of quantum states available within interval dE drops to zero as the K point is approached.



(a)



(b)



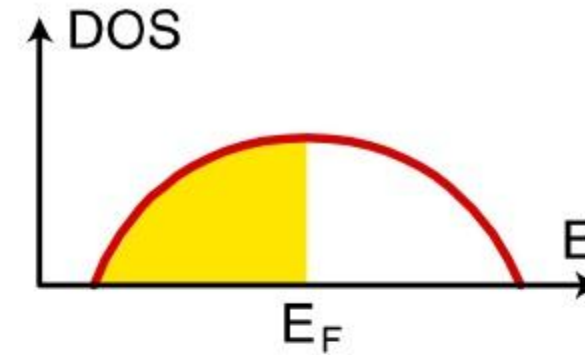
(c)

Source: <http://www.mdpi.com/2079-4991/4/2/267>

Electronic Structure of Graphene

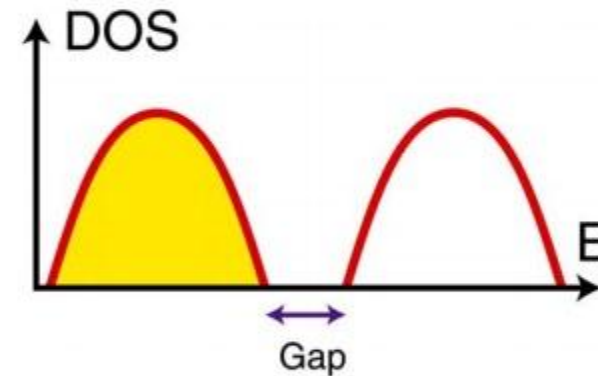
Metal

- Partially filled band
- Finite Density of States (DOS) at Fermi Energy



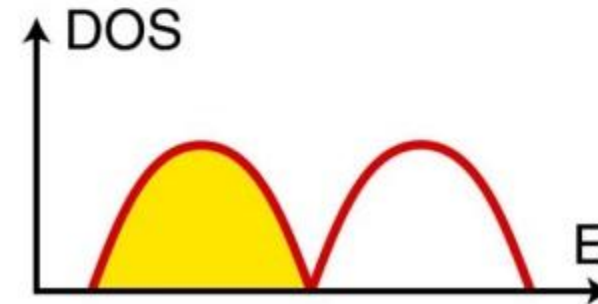
Semiconductor

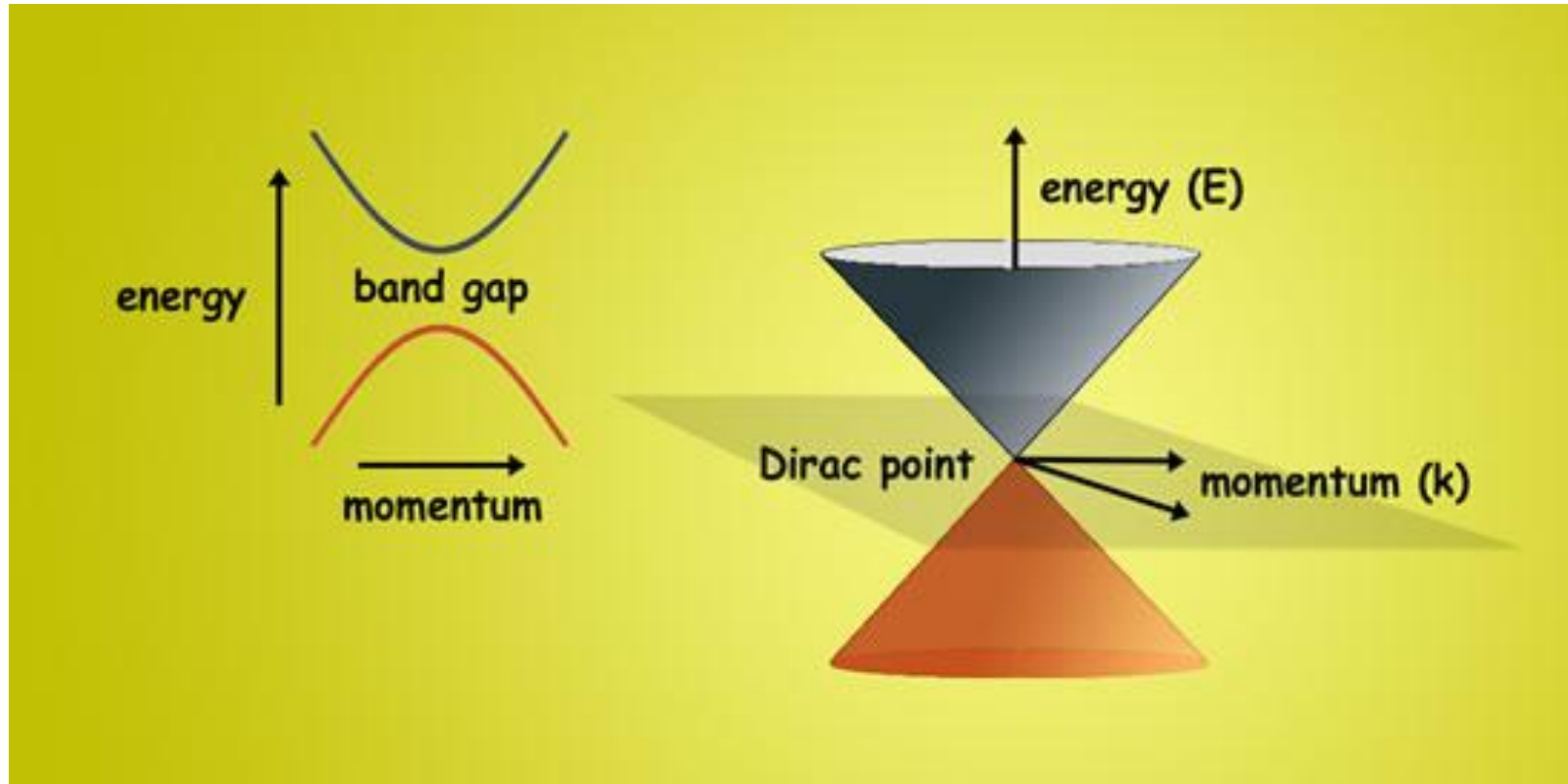
- Filled Band
- Gap at Fermi Energy



Graphene A critical state

- Zero Gap Semiconductor
- Zero DOS metal





Seeing the structure of to bands, we may conclude that graphene is unsuitable as a semiconductor, because there is no band gap, hence no switching is possible, if we make a device out of this. Because of this point contact, it is called semi-metal.

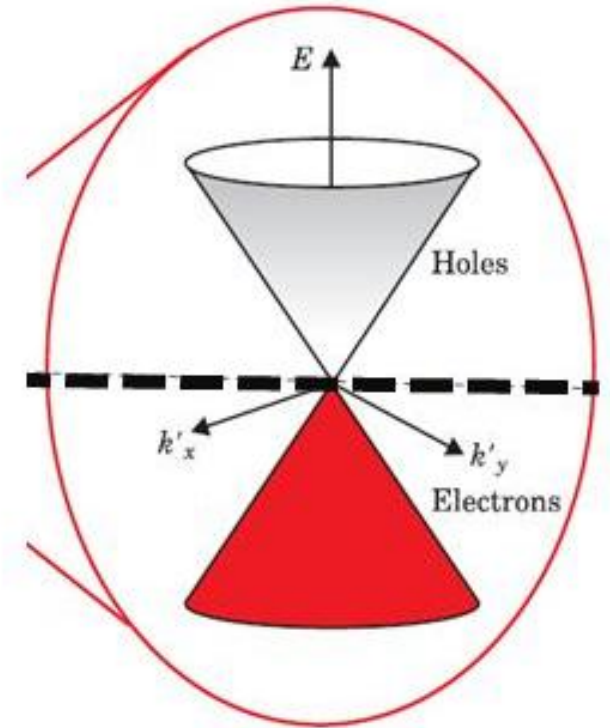
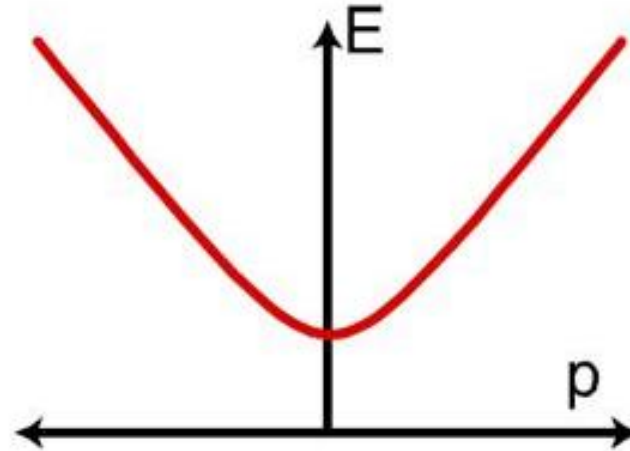
Mathematical model

Massive Particle (e.g. electron)

$$E = \sqrt{(mc^2)^2 + (cp)^2}$$

Nonrelativistic limit ($v \ll c$)

$$E \approx mc^2 + \frac{p^2}{2m} + \dots$$

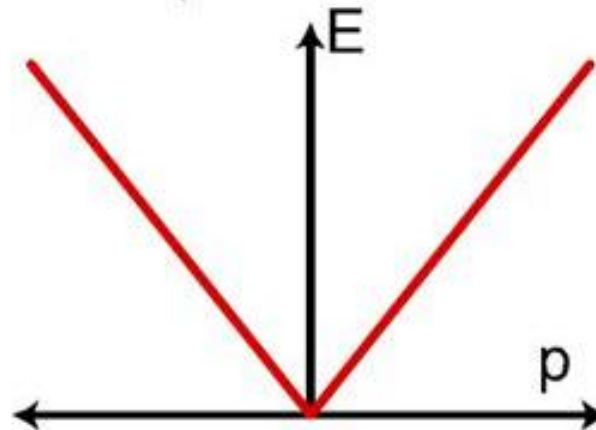


Massless Particle (e.g. photon)

$$m = 0$$

$$E = c |p|$$

$$v = c$$



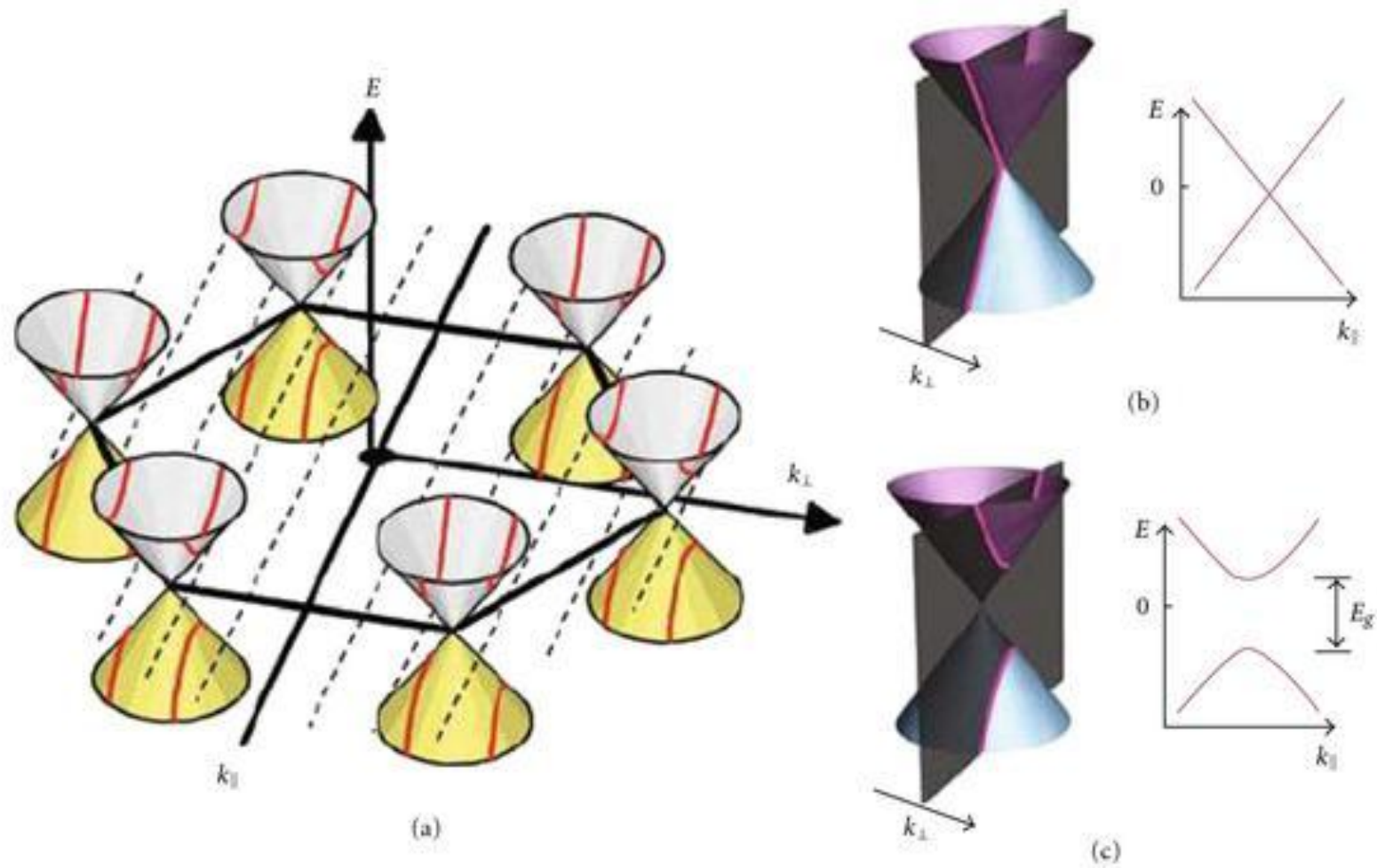
Graphene is an exception: its charge carriers mimic relativistic particles and are easier to describe starting with the Dirac equation rather than the Schrodinger equation.

In neutral graphene sheet, the valance and conduction bands meet at the Fermi energy so that graphene is a semi-metal or zero-gap semiconductor.

But with this comes a limitation and that is it is unsuitable for switching action, if there is no energy gap.

The question is how to create an energy gap in this unique material, which is neither a metal nor a semiconductor.

- The most striking consequence of the lack of a bandgap is that a device made of graphene cannot stop the current.
- One of the most important achievements of Si CMOS technology, along with the ideal signal reconstruction, is the possibility to completely switch off the logic element to reduce the power consumption of the IC.
- A bandgap at least comprised between 400 and 500 meV should be necessary for digital logic operation.



The picture above gives some hint.

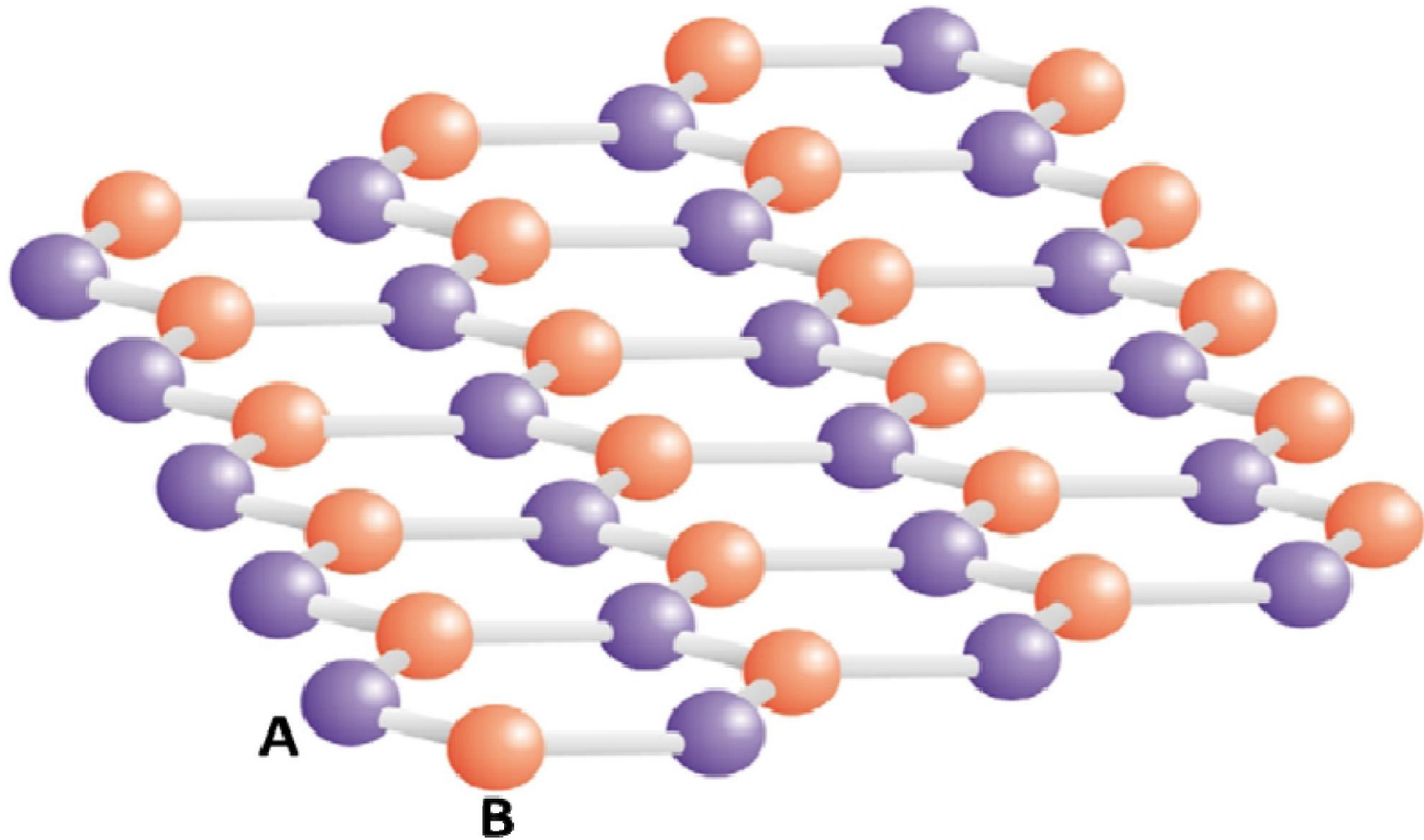


Image Source: <http://www.mdpi.com/2079-4991/4/2/267>

To understand the lattice structure of Graphene. It is a 2-atom hexagonal structure.

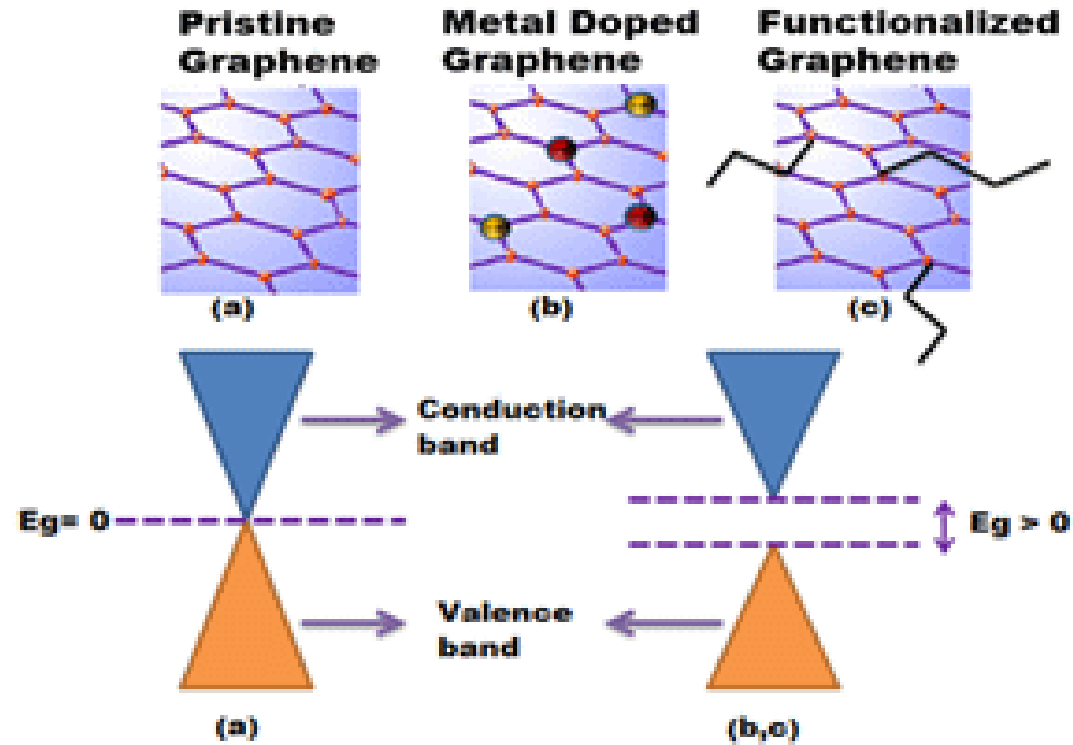
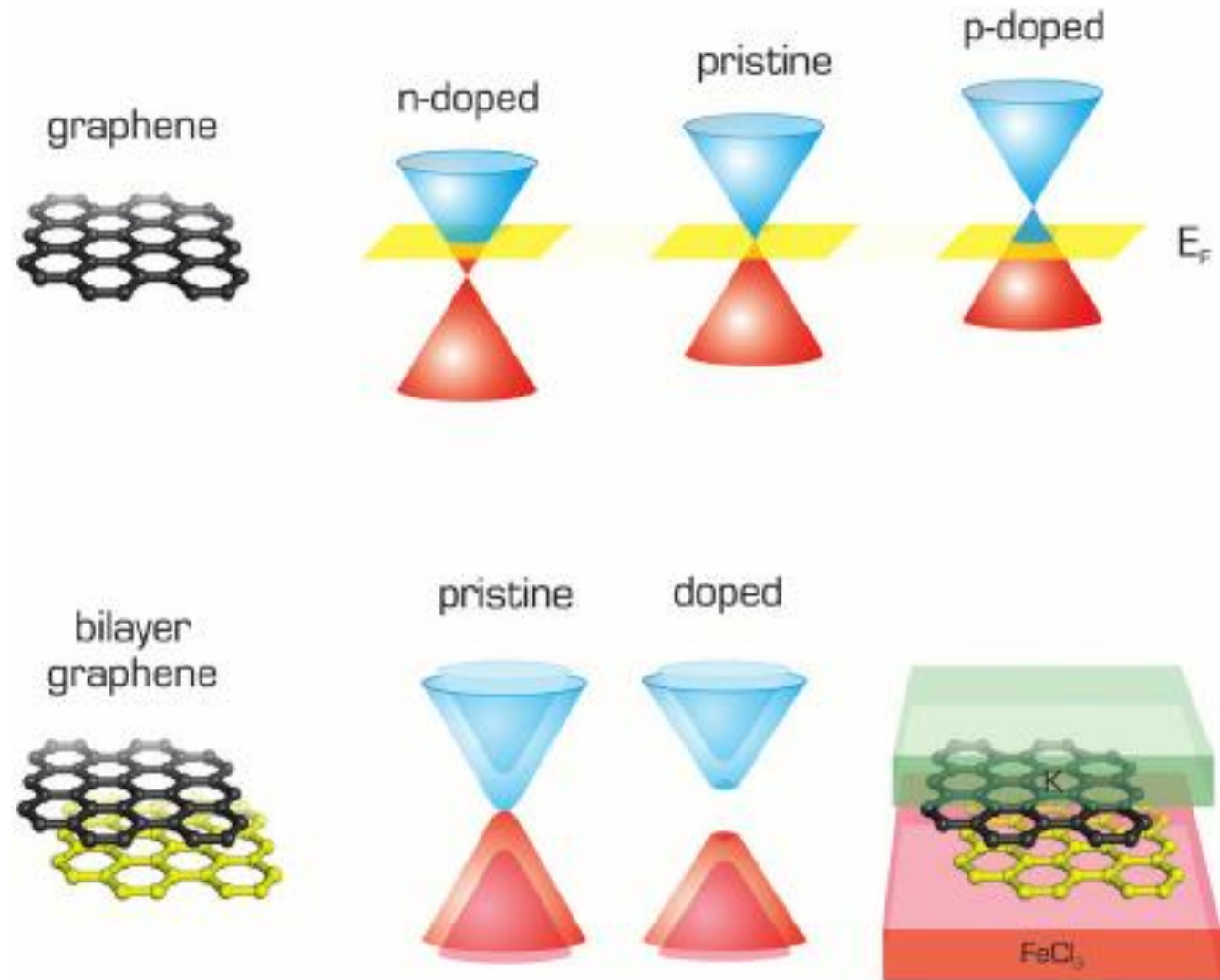


Image Source: <http://www.mdpi.com/2079-4991/4/2/267>

If we replace some C-atoms by Au-atoms, spatial change in interaction (binding) energy creates energy gap.



Source: [https://www.researchgate.net/publication/281539968 Modelling of graphene functionalization/figures?lo=1](https://www.researchgate.net/publication/281539968_Modelling_of_graphene_functionalization/figures?lo=1)

The bilayer arrangement changes the interaction voltage and depending upon its polarity, an energy gap would be created around the Fermi point.

What is mobility?

In solids,

$$I \propto qnv_nA$$

Since, q, n, A are fixed, we may also write

$$I \propto v_n$$

On the other hand,

The applied electric field that causes this 'mobility' in carriers, is

$$E = V/l \Rightarrow V = El$$

$$\text{We also have, } I = V/R \Rightarrow I = El/R$$

$$\Rightarrow I \propto E$$

Therefore, we may also write that $v_n \propto E \Rightarrow v_n = \mu_p E$

$$\text{or } -v_n = \mu_n E$$

where n, p are used for free electrons and holes (carriers).

$\mu_{n,p}$ is called 'mobility' and from here its unit is cm^2 per V per sec.

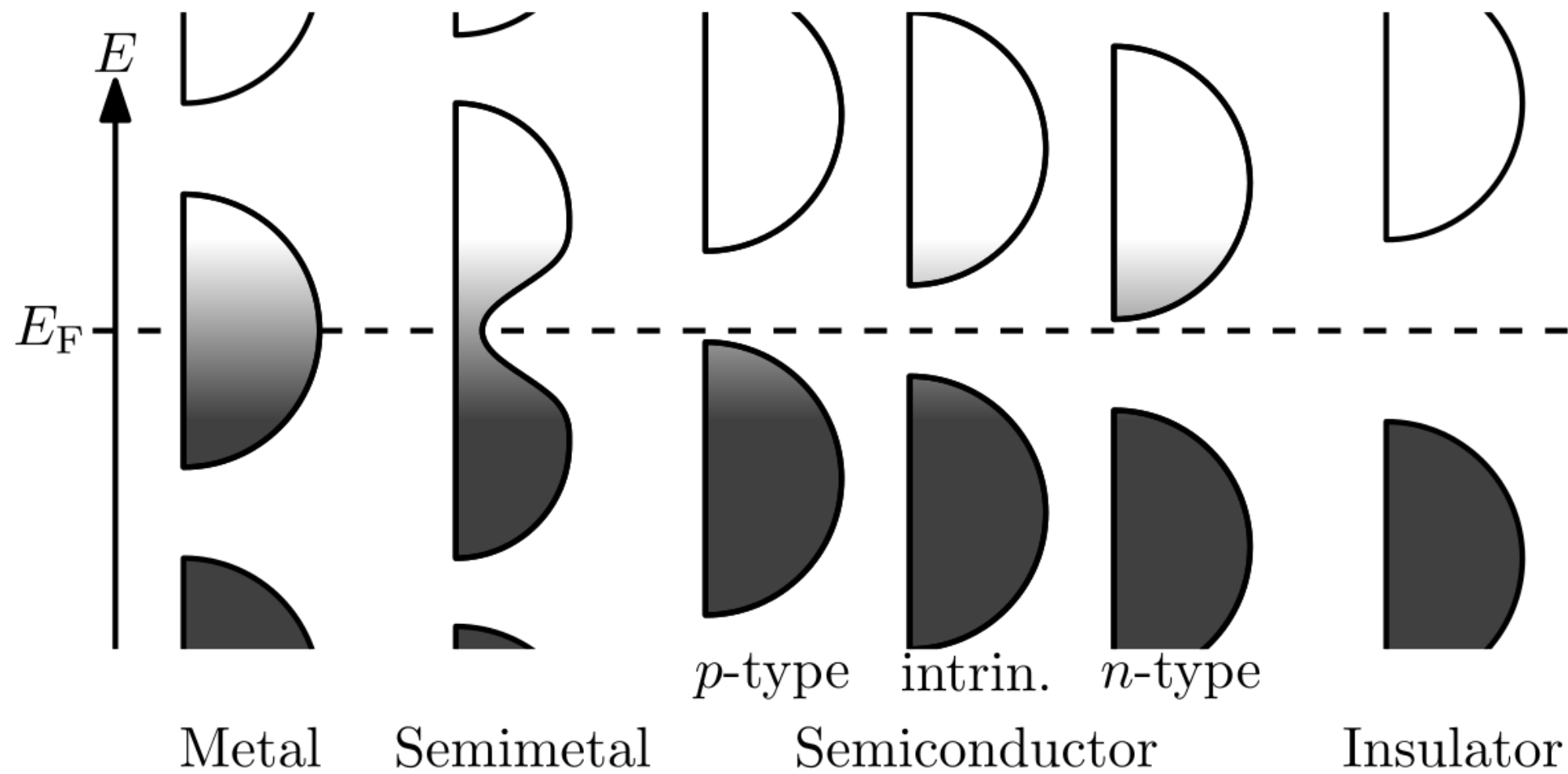
And it is material specific.

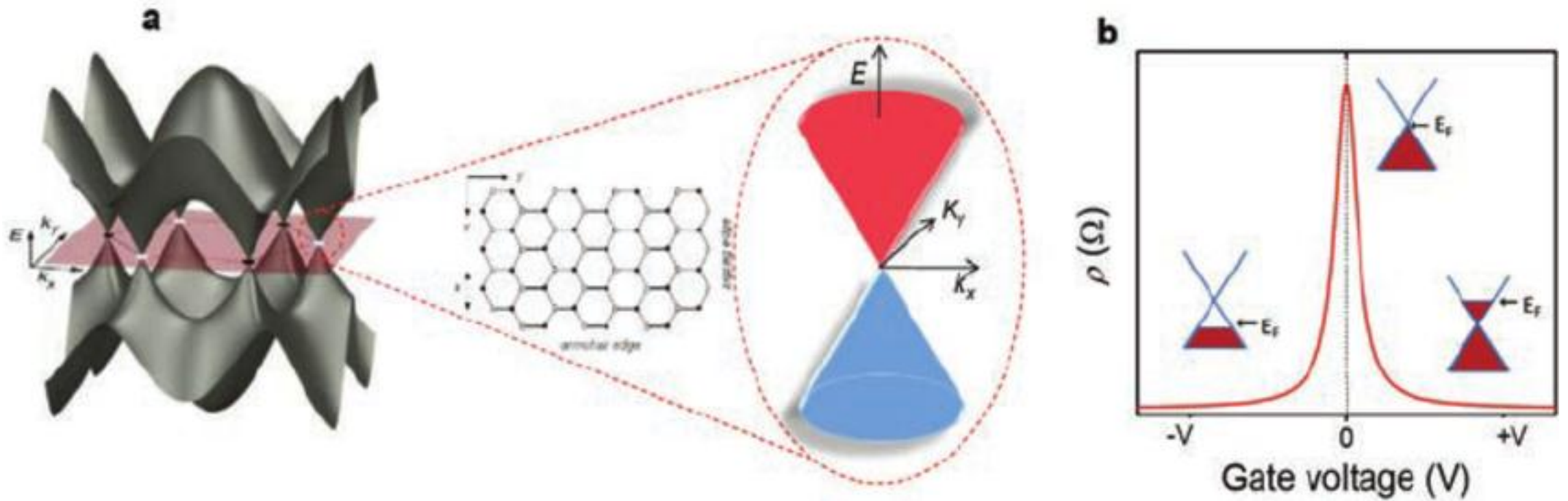
In general, the mobility of holes is lower than that of free electrons.

For silicon,

$$\mu_n = 1250 \text{ cm}^2/\text{Vs}$$

$$\mu_p = 480 \text{ cm}^2/\text{Vs}$$





Compare the previous situation with this picture. In terms of E_F , VB is closer to E_F in p-type semiconductor and vice versa. If we make gate voltage -ve, it creates similar situation. So we can say that graphene will work like a p-type semiconductor.