

Nanotechnology

28 January 2013 16:00

1. What is it?

Manufacture of a structure or device with physical dimensions ~0.1-100nm

2. Examples of current nanotechnology research

1) Micro and nano-electronics

Integrated circuits or individual electronic components on the micro ($10^{-6}m$) and/or nano ($10^{-9}m$) scale.

2) Micro & nano machines → mechanical devices e.g. gears, motors, camshafts etc

MEMs and NEMS: micro and nano electromechanical systems- combination of 1) and 2)

Mechanical portion + transducer- converts mechanical signal → electrical signal

Bio-nanotechnology → manipulation, modification & detection of biological molecules (e.g. DNA)

Atomic manipulation → creation of molecular & atomic assemblies e.g. using scanning tunnelling microscope.

Self-assembly → using chemistry to fabricate nanostructures -often large scale.

Two main approaches

1) Top-down → techniques such as photolithography are used to etch, chisel or sculpt nanostructures onto a surface (Often Si)

Using this method, gears, sensors and ever smaller IC can be made

2) Bottom-up → chemical self-assembly and atomic/molecular manipulation used to build tiny structures

atom/molecule by atom/molecule. Examples of such structures include single electron transistors and ordered arrays of semiconducting nanoscale clusters

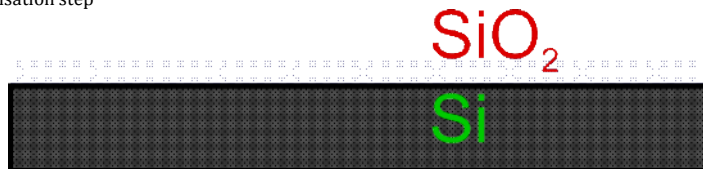
$$(193 \times 10^{-3}) \times 10^{(1/2)} = 1.3892$$

Micro-nano electronics

Micro electronics ($10^{-6}m$): Lithography is the main technique used to fabricate Si- based integrated circuits (IC)

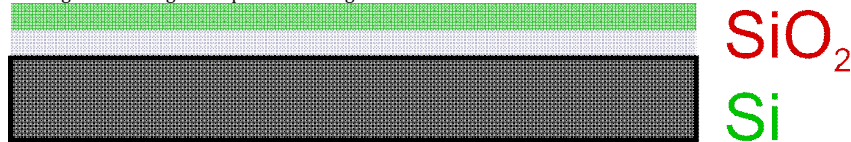
Optical lithography using UV light

1) Oxidisation step

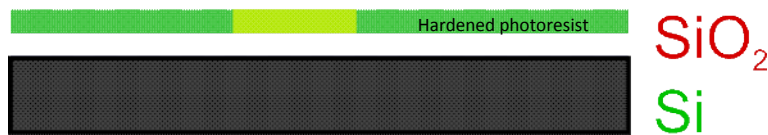
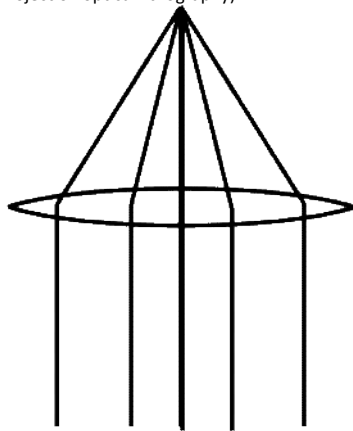


2) Photocast

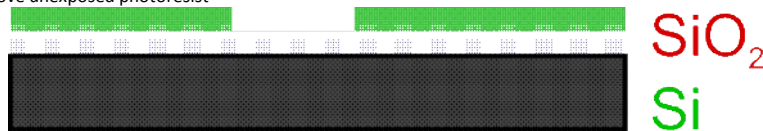
Coating and it changes if exposed to UV light



3) Expose to UV (Projection optical lithography)

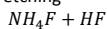


4) Remove unexposed photoresist

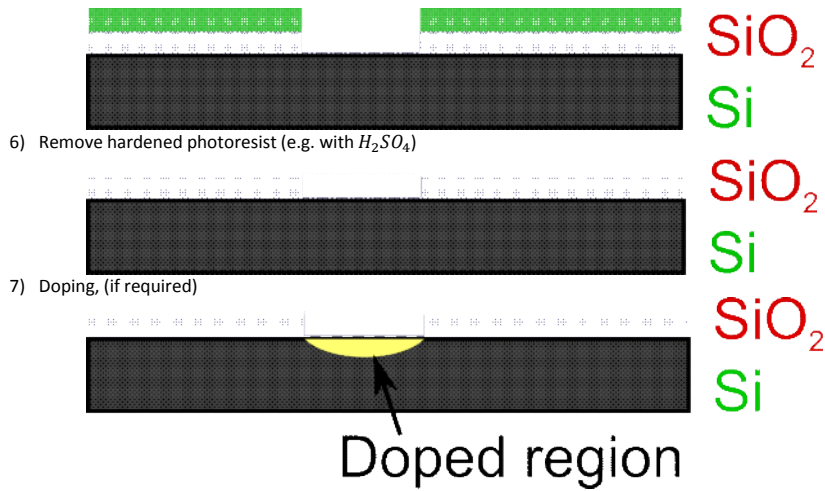


Removed with a "developer"

5) SiO2 etching



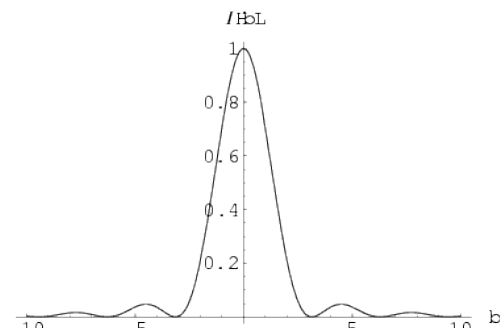
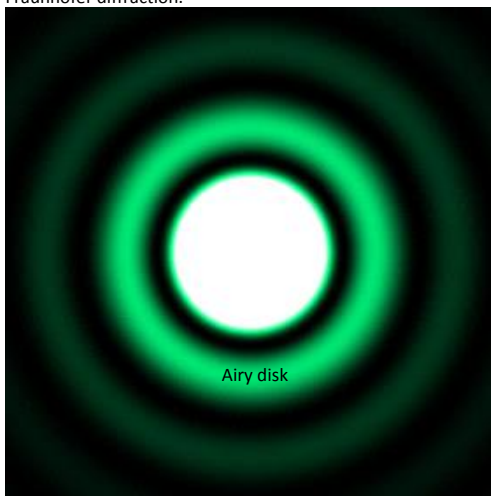
Ammonium bisulphate + Hydrofluoric acid



So is n-type or p-type depending on whether it conducts via (negative) electrons or (positive) holes (missing electrons)
 We can make devices e.g. transistors and diodes by combining p-type and n-type materials in certain configurations
 Doping by adding small amounts of impurities i.e. elements such as boron or phosphorus

Limits of optical lithography - Diffraction

The resolution of the chip produced (i.e. the smallest feature that can be produced) by projection optical lithography by Fraunhofer diffraction.



Diffraction pattern produced by a circular aperture

$$\sin \theta_2 = \frac{2.23\lambda}{d}$$

$$\sin \theta_3 = \frac{3.24\lambda}{d}$$

If we have 2 very close features on a mask they will produce a diffraction pattern that will overlap.
 According to Lord Rayleigh, Rayleigh criterion gives a measure of the limit of which 2 features can be distinguished
 That occurs when the maximum intensity (Airy disk, centre) overlaps with the 1st dark ring of 2nd diffraction pattern
 The minimum size feature or resolution is

$$d = \frac{k\lambda}{NA}$$

For projection based optics, $k \sim 0.63$
 NA is typically ~ 0.6 for large field projection system
 $\therefore d \sim \lambda$

-rule of thumb, changes as function of NA
 Immersion lithography systems used to improve resolution & UV sources of light
 Mercury lamp: $\lambda = 365nm$
 Kr-Fluoride laser: $\lambda = 248nm$
 Ar-Fluoride laser: $\lambda = 193nm$
 Using conventional lenses

However for $\lambda < 120nm$, no optical materials remain transparent to UV light

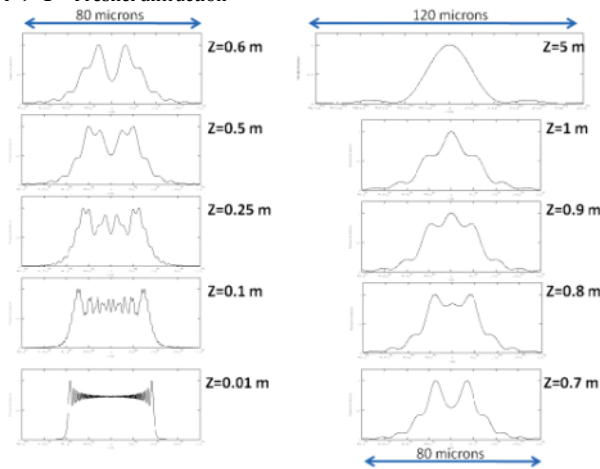
Fresnel number, F is named after Augustine-Jean Fresnel, is dimensionless number used to determine which diffraction theory to use i.e. Fresnel or Fraunhofer

$$F = \frac{a^2}{L\lambda^2}$$

$$(193 \times 10^{-4})^{1/2} = 1,389.2444$$

$$(202.65^2) / 193 = 212.7825$$

a =radius of the aperture
 L =distance to screen
 λ =wavelength of light
 Applies to em radiation, not just light
 $F \ll 1 \rightarrow$ Fraunhofer condition
 $F > 1 \rightarrow$ Fresnel diffraction



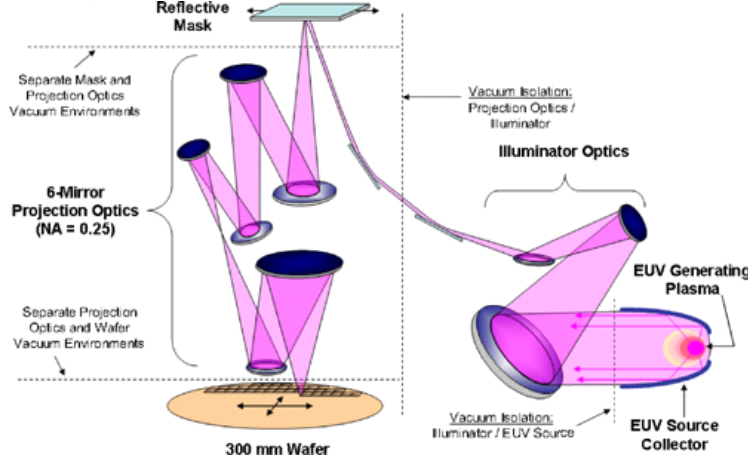
Beyond Optical Lithography

How can we make ever smaller structures?
 5 main alternatives

EUV, x-rays, e-beam, ion beam & LADI

1) Extreme Ultraviolet lithography (EUV)

-reduce $\lambda (< 100nm)$ + reflection optics + masks



- 2) *
- 3) *
- 4) *
- 5) LADI

Laser Assisted Defect Imprint

Advantages:

- No expensive focusing optics
- No photo-resist

Potential problems or drawbacks:

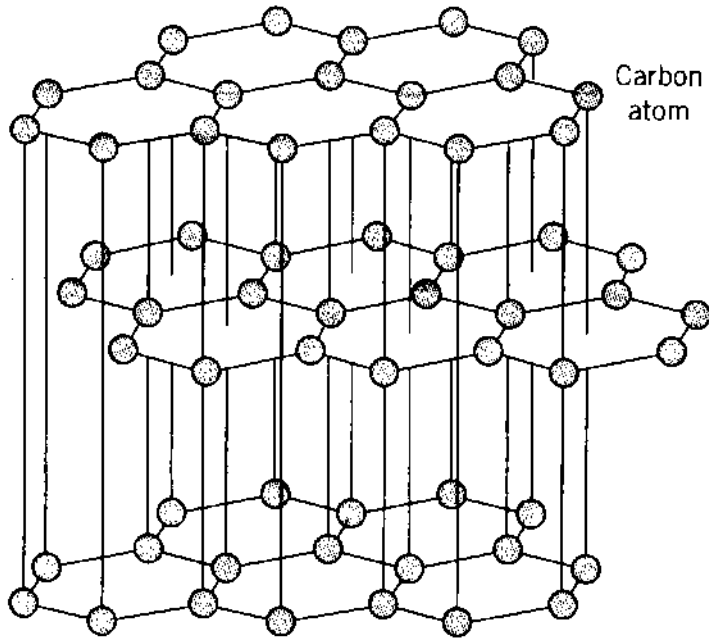
- Defects caused to propagate by contact with the quartz mask

Nanoelectronics ($10^{-9}m$)

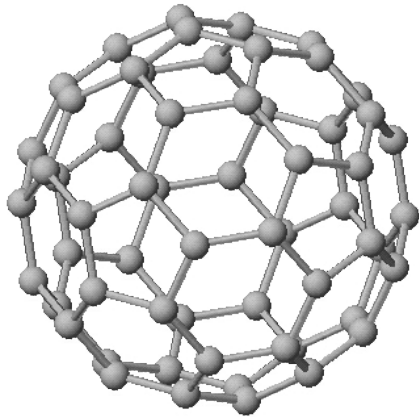
There are limits to how small we can make structures using lithography (etc). To reach dimensions of a few nm ("Nanoelectronics") a more promising approach is to fabricate devices from molecular structures which are already on the nanoscale. One example (with enormous potential) is a form (allotrope) of carbon called a carbon nanotube.

Allotropes of carbon (See handout/blackboard)

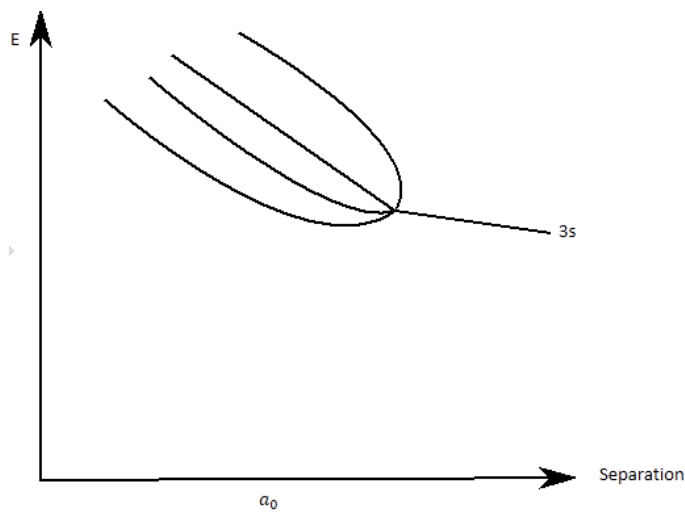
- 1) Diamond: c-c bonds, 3D 4 bonds \equiv 4-fold coordination c-c=1.54Å
- 2) Graphite: c-c=1.42Å, A-B stacking van der Waals bonding between layers (weak)
 3-fold coordination \rightarrow remaining electron (Van der Waals)



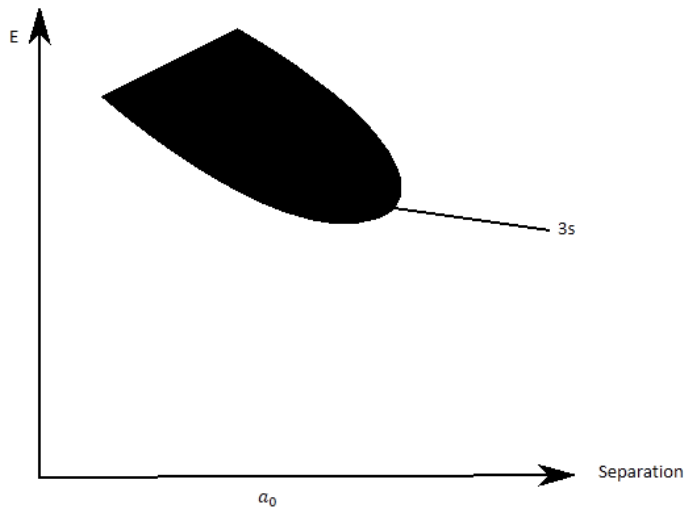
- 3) Graphine → single layer of graphite
- 4) Fullerenes: buckyball C_{60}
 Discovered in 1985 by Harry Kroto (Sussex) + team in Houston, Texas - Rice



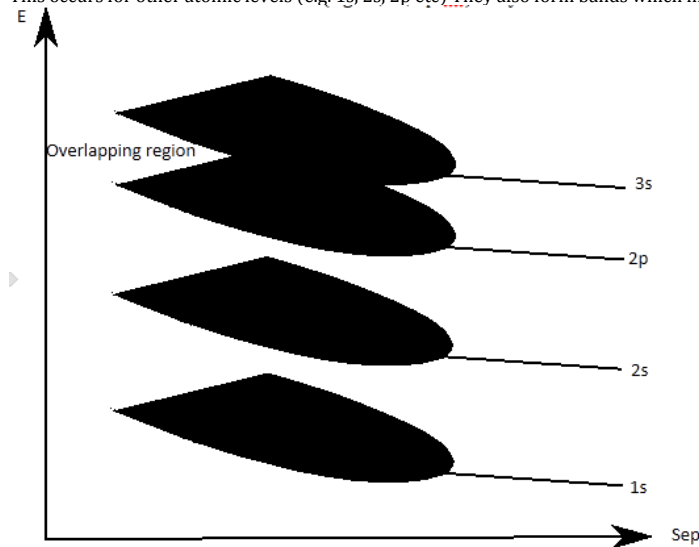
For N atom → N discrete levels



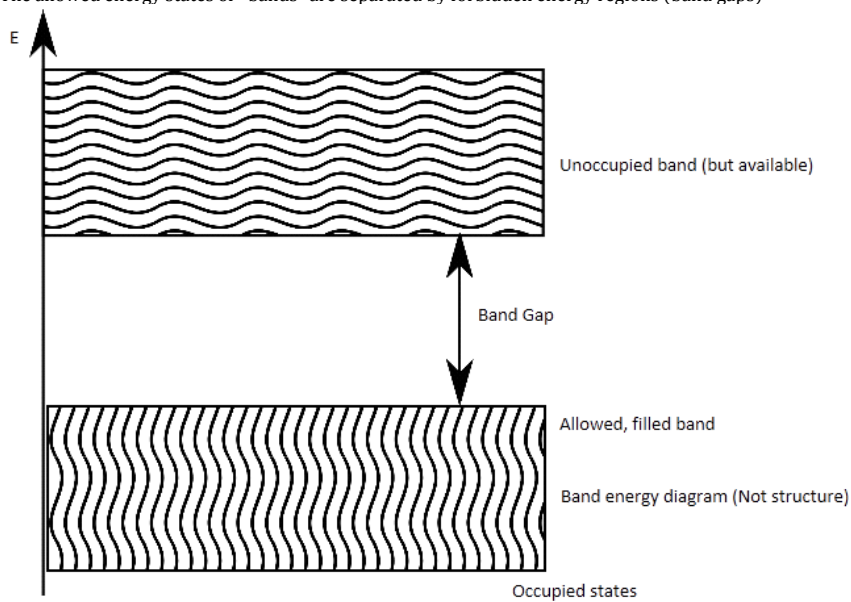
For large N → Band of allowed energies



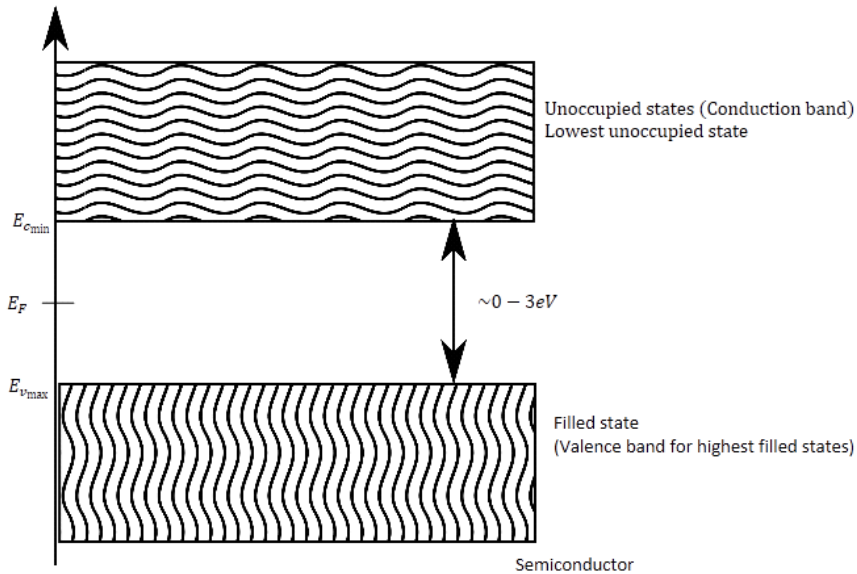
This occurs for other atomic levels (e.g. 1s, 2s, 2p etc). They also form bands which may start to overlap in energy



The allowed energy states or "bands" are separated by forbidden energy regions (band gaps)



Partially filled state E_F defines cut off between filled and empty states
 e^- full states in ascending order of energy up to a maximum (Known as the Fermi Level)
 If E_F lies inside a band, the material is metallic
 If E_F lies inside a band gap, it is either a semiconductor or an insulator



If band gap > 3eV, material conduction is more difficult, hence insulator

Metals conduct electricity easily because there are so many unoccupied states easily accessible to e^- just below the E_F fermi level

Semiconductors require an input of energy (e.g. thermal or light or electricity) to promote e^- across the band gap to the unoccupied conduction band (leaving holes in the valence band) The no of electrons in the bands varies strongly with temperature T.

The bands vary with the crystal properties i.e. with direction. And thus in reciprocal space, the wavevector k) Can illustrate them with band structure

Metal

~~~~

Assuming conductive  $e^-$  are free

$e^-$  gas in a metal,  $E = \frac{p^2}{2m}$ . Free electron  $e^-$ ,  $p = \hbar k$   
(In general, solution will not be symmetric)

~~~~

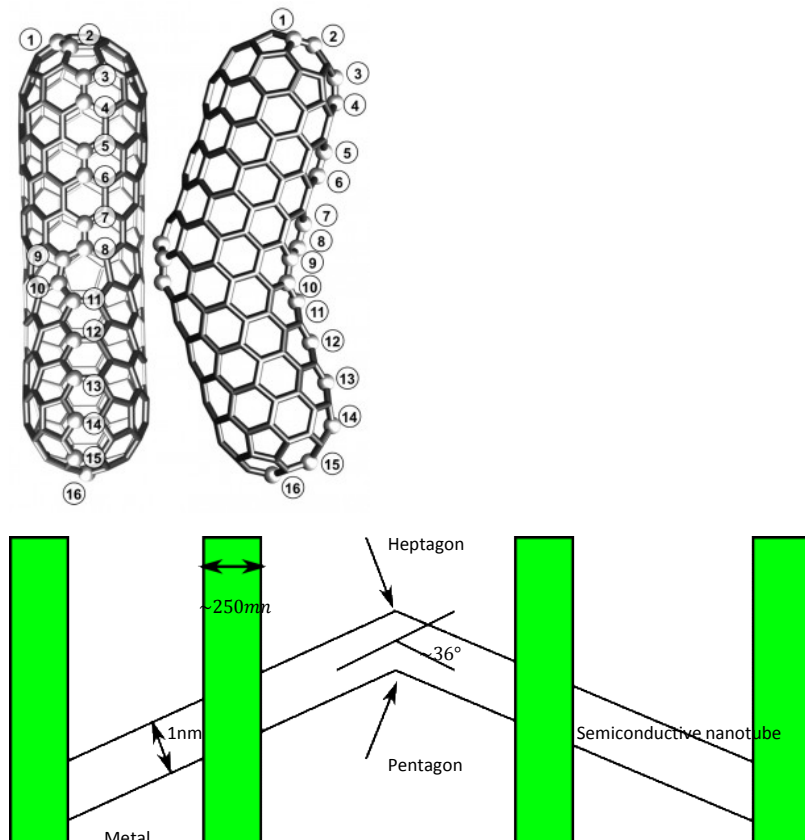
Examples of electronic nano-devices (Carbon nanotubes)

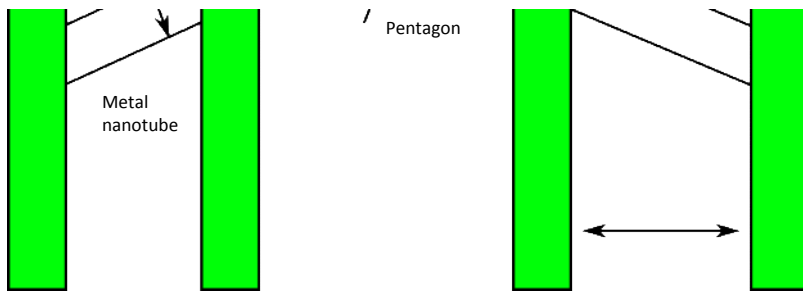
We can grow carbon nanotubes with specific diameters and manipulate them with fabrication techniques, we need to make electrical connections to them so that we can build nano-scale electronic devices

Example 1: Diode

Join metallic & semiconducting nanowires \Rightarrow their different chirality means we need to introduce defects at the join, e.g. heptagons & pentagons

Kinky nanotube





Device will allow electrons to flow in 1 direction only
 When the metal side has a +ve bias, current flows above a threshold voltage $\sim 1\text{V}$

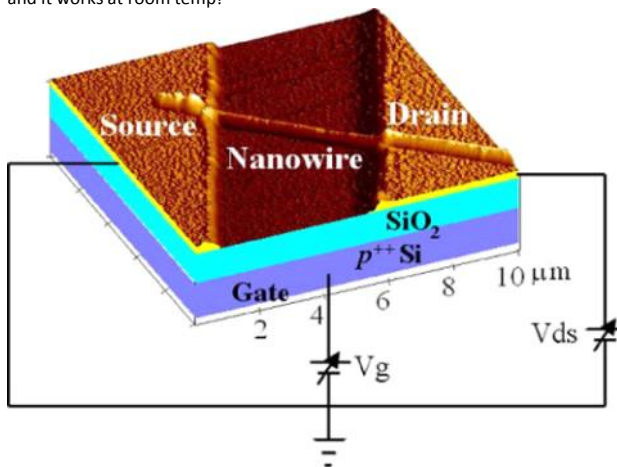
Example 2: Field effect transistor (FET)

This can be made from a SC nanotube

A FET can be made when the output current is controlled by an applied gate voltage

Current flows along the tube when a negative bias voltage is applied to Si substrate (gate), making the gate -ve, draws e^- away from the tube producing holes (Unoccupied states) which then conduct in a similar way to e^- except that they are +ve carriers

The resistance (or conductance) of this device changes by many orders of magnitude when the bias voltage is applied and it works at room temp!



Example 3: Metal wires

Traditional wires on a nanochip are made from metal evaporated on a Si substrate

Problems with making wires smaller than 20-50nm high and 50-250 nm wide

- 1) No easy way to remove heat particularly when smaller wires are packed together tightly: leads to overheating
- 2) Pulse of e^- can cause atoms in thinner wires to move around. \rightarrow the wire can electrically fail- like a fuse

Nanotubes can solve both the problems highlighted due to their heat conduction properties and strong c-c bond

Can transport high currents $\sim 10^9 \text{A cm}^{-2}$. CF Au contacts 10^5A cm^{-2}

Electron transport in carbon nanotubes

e^- in nanotubes are confined to length scales (& dimensions) that are smaller than the electron mean free path. (Λ_{MFP})

\Rightarrow Ballistic sections

e^- are confined to small diameters ($\sim \text{nm}'s$)- this is smaller than the electron mean free path (mfp)

Λ_{mfp} typically 10-100nm, but affected by purity, defects and temperature

Mean free path can $\sim \sim \sim$

Mean free path is related to resistance and resonance in nanofibres (metallic)

Electron can move with little stuttering and are called ballistic \Rightarrow relatively low $\sim \sim \sim$

A perfect metallic carbon nanotube $\sim \sim \sim$

We should see quantised conductance in 1-d structures (metallic)

A single walled nanotube is almost like a single mode optical fibre, but for electrons not light, i.e. Large transmission

The electrical conductance G, (increase of resistance) can be quantised

The fundamental quantum of conductance,

$$G_0 = \frac{2e^2}{h}$$

It can be shown theoretically that the electrical conductance of a 1-d nanotube $= 2G_0$

This means that nanotubes are predicted to have a resistance $(1/G) = 6500\Omega$, independent of length

Testing ballistic behaviour

Walt de heer expt (handout)

$\sim \sim$

The conductance is observed (t_0)

As the bundle is lowered further the conductance appears independent of the length $\sim \sim \sim$

Spintronics

It is also seen that the e^- spin is maintained as electrons move along a carbon nanotube

Development of electronic devices which are controlled by e^- spin \rightarrow "Spintronics"

Coulomb blockade

Nanotubes also display a property known as coulomb blockade in which it is very difficult to insert more than one electron into the nanotube

These properties are exploited in building a single electron transistor

This type of behaviour is also seen with other nano systems/junctions e.g. quantum dots

So how does it work?

a) Single charge

At time t=0, net surface charge =0 (due to arrangement)
 At some time later, t
 At time t, e^- moves towards surface, surface has a net -ve charge
 But the magnitude depends on all -ve charges + +ve charges
 \Rightarrow surface charge= fractional amount of electric charge
 = $0.1 e^-$, or $0.5e^-$
 Etc
 And can vary continuously

Consider what happens if we bring two conducting surfaces together (on surface a thin insulating inside layer \Rightarrow "Junction")
 Tunnelling \rightarrow macroscopic system

e^- tunnel across the thin insulating barrier and a (tunnel) current flows.

We are combining the conductive flow of charges in the conductor with the discrete tunnelling of the insulator system

In a macroscopic system, this has little effect because lots of e^- tunnel across together. But if we reduce the dimensions of the system it becomes a different scenario.

In a nanoscopic system:

Now the surface charge is much smaller and the discrete flow of e^- across the junction is more noticeable

So if 1 electron were to tunnel across the junction, the difference in the surface charge increases to $2e$.

Thus we can see the energy of system increases and thus it is energetically unfavourable for this process to occur
 \Rightarrow coulomb blockade & electron transport across the junction is suppressed

How can we overcome the blockade?

Lets apply a voltage and wait for the surface charge to increase.

Once the surface charge Q reaches $-e/2$ on the left electrode (and $+e/2$ in the right electrode), the transfer of $1 e^-$ by tunnelling produce a difference in charge of $+e$

- \therefore the energy of the system is the same before and after tunneling
- \therefore tunnelling is allowed and the coulomb blockade lifted \rightarrow and $1 e^-$ flows across the junction

Note; we cant transfer more than one electron at a time, energetically unfavourable

e.g.

$$\Delta Q_z = 3e \left(if + \frac{3e}{2}, -\frac{3e}{2} \right)$$

So if we have a constant current flowing in a nanoscopic junction, it induces a voltage (due to the surface charge) which oscillates in time (as each e^- tunnels)

Freq of oscillation of the voltage=

$$= \frac{I}{e}$$

(note dependent on 'junction parameters')

Nanomaterials:

Nano powders, nano crystals, nanowires, nanosheets are materials that behave differently due to their dimensions. Typically we see big changes as the physical dimensions are reduced to $\sim \leq 10nm$

This can be due to a number of factors including surface area/volume ratio and quantum confinement

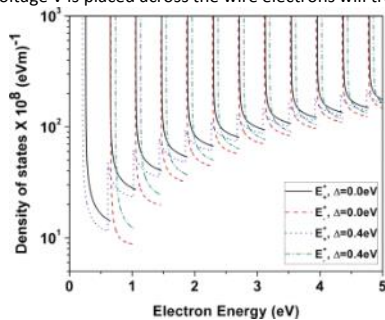
Quantum Confinement:

We have seen that electron transport is modified once a material is reduced to the scale of the electron mean free path (mfp $\sim 10-100nm$)

Similarly if the size is reduced to the order of debroglie wavelength then we have

Consider two electron reservoirs connected by a 1-D wire in which electrons can travel ballistically, from left to right and right to left.

If a voltage V is placed across the wire electrons will travel in the sub-bands.



If I_t is the current from left to right, the total current in the sub-band starting at energy E_i is given by:

$$I_t = - \int_{E_i}^{E_L} \frac{D(E)}{2} eV(E) dE$$

(1/2 left \rightarrow right carriers only)

$$I = \Delta n q V$$

Δn = carrier density

Remember for a 1-D structure

$$D(E) = \frac{4}{hv}$$

$v = \text{electron velocity in the sub-band}$

$$I_+ = -\frac{2e}{h}(E_L - E_i)$$

$$I_- = -\int_{E_L}^{E_R} \frac{D(E)}{2} ev dE$$

$$= -\frac{2e}{h}(E_R - E_i)$$

Total current = $I = I_+ + I_-$

$$= -\frac{2e}{h}(E_L - E_R)$$

$$(E_L - E_R) = -e\Delta V$$

$$\therefore I = \frac{2e^2}{h}(\Delta V)$$

$\Delta V = \text{Voltage applied across 2 contacts}$

Conductance

$$G = \frac{I}{\Delta V} = \frac{2e^2}{h}$$

For the sub band

For all sub-bands

$$\Rightarrow G = N_c \frac{2e^2}{h} T$$

Landauer Formula

N_c = number of occupied sub-bands

T = transmission probability of each channel

Peaks in sub-band density of state called Van Hove Singularities

For further examples: see later editions of Kittel's Book on solid state physics (Pg 530, ed9)

Notice the effect of the singularities on the density of states calculated for a semiconducting carbon nanotube
If we perform scanning tunnelling microscopy/spectroscopy on the CNT, then density of states shows the singularities.

Optical properties

→ these depend upon the spacing between energy levels, and these in turn depend upon confinement i.e. the size

e.g. nanoparticle (\equiv quantum dot) average level spacing $\propto \frac{1}{\text{volume of the particle}}$

Similarly if we consider insulating or semiconducting nanoparticles with band gaps, the widths of these are changed by quantum confinement.

\therefore we can tune a materials optical properties by varying its size.

~~~~

Band-gap energy spacing is modified by confinement, but we need to take account of the electron-hole pair (exciton)- coulomb attraction (reduce energy spacing)

~~~~

As particle size reduces, band gap increases λ at which absorption & emission occurs is reduced and the material appears more yellow

~~~~

Previously looked at Si-based MEMS devices- made by optical lithography & e-beam lithography,  
Another approach is to build NEMS devices (10s of nm) from individual molecules or atoms

Biomolecular motors are particularly interesting because they have a built-in power source (chemical, light etc)

NEMS → Biomolecular motor

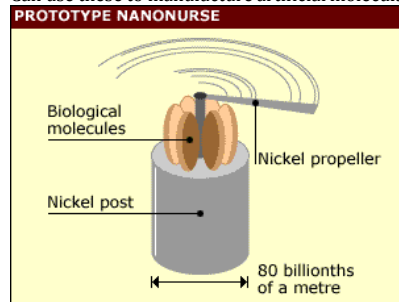
There are a number of natural biomolecular motors in biological systems eg

Enzymes

- Kinesin
- RNA polymerase
- Myosin
- Adenosine triphosphate

These can either produce linear or rotational motion

Can use these to manufacture artificial molecular motors



When the ATPase enzyme is immersed in a liquid mixture containing ATP it begins to rotate. If this is affixed to a metal, and a metal rotor is attached then that too will rotate

Each ATPase molecule produces  $\sim 100$  pN nm of rotary torque which in turn gives  $\sim 8$  rev/s

Reducing the size further has been achieved with DNA (single strand) based motors

~~~~

The inner one springs back and forth with very little friction and no sign of wear and tear

Nanotubes are atomically smooth → so no wear & tear

Static friction $f_s \sim 6.5 \times 10^{-15} N \text{Å}^{-2}$

Dynamic friction $f_d \sim 4.3 \times 10^{-15} N \text{Å}^{-2}$

~1000 times less than frictional forces found in conventional macroscopic materials

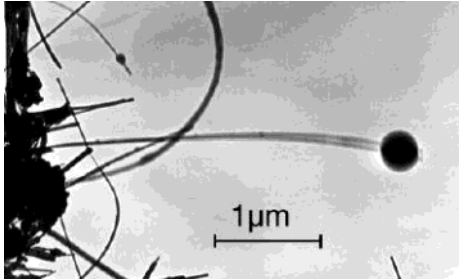
Note

$$fd = \mu_d N$$

μ_d = coefficient of dynamic friction

N = normal reaction force

Nanobalance



When an oscillating voltage is applied to a pinned carbon nanotube it begins to vibrate. By varying the frequency of the voltage and studying the amplitude of the oscillations, the natural frequency can be found

$$\omega_0 = \frac{\beta^2 D}{8\pi L^2} \sqrt{\frac{E_b}{e}}$$

D = diameter of tube

L = length

E_b = bending modulus

e = density of the tube

$\beta = 1.875$ 1st harmonic

4.694 2nd harmonic

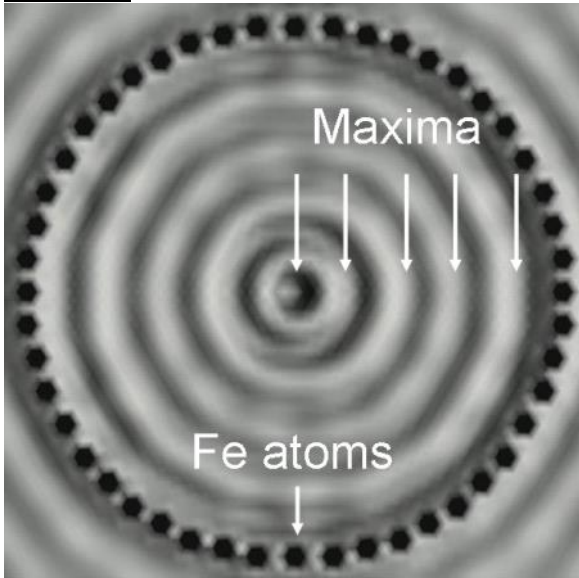
If an additional mass is now added to the end of the nanotube, the natural frequency will drop, if by more than 40% then mass of the order of 22fg ($1fg = 10^{-15}g$) have been measured

This is the most sensitive mass balance in smallest produce

-can be used to measure viruses

Atomic Manipulation

Quantum Corral



Copper surface

e^- on surface of a metal form a 2d free e^- gas.

When they are confined on length scales approaching the de Broglie wavelength ($\lambda = \frac{h}{\sqrt{2mE}}$) their behaviour is dominated by quantum mechanics

A STM can be used to move atoms around on a surface (at low temperature) to create structures which confine the electron wavefunctions ⇒ quantum corral

In addition the STM can be used to characterise the e^- trapped inside the corral

As well as measuring atom topology, the STM measures the local density of states (LDOS) at a given energy (Typically E_F)

LDOS = probability of finding an e^- with energy E at a point r in space

$$LDOS(r, E) = \sum_n |\chi_n(r)|^2 \delta(E - E_n)$$

δ = non zero when $E_n = E$

E_n = energy of nth state

In the case of a quantum corral as a 2d circular box, and the e^- being a "particle in a box", (QM modules)

The result is as follows,