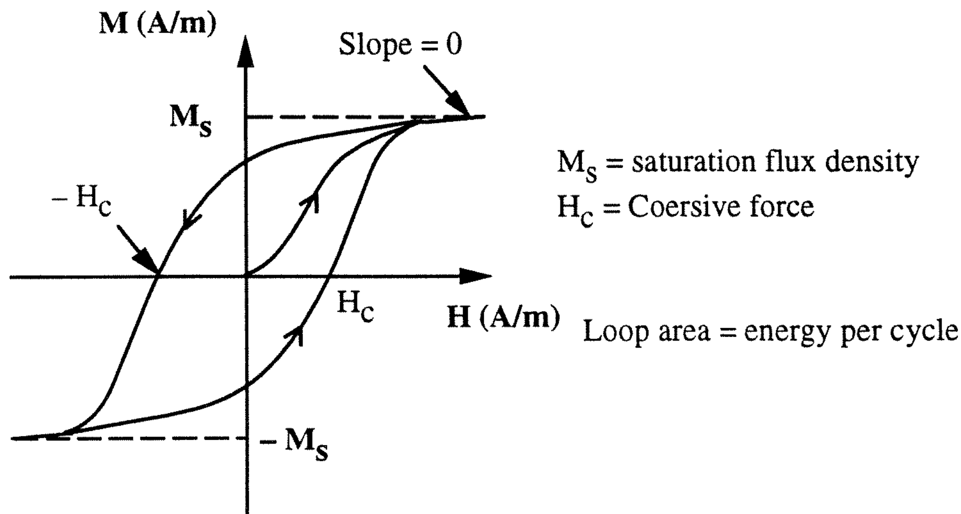
ENGINEERING TRIPOS PART IIB

Monday 28th April 2003 2.30 to 4.00

Module 4C3 : ELECTRICAL MATERIALS SOLUTIONS

1(a) Variation of magnetisation with applied field for a hard permanent magnet material over a full field cycle, such as SmCo or NdBFe;

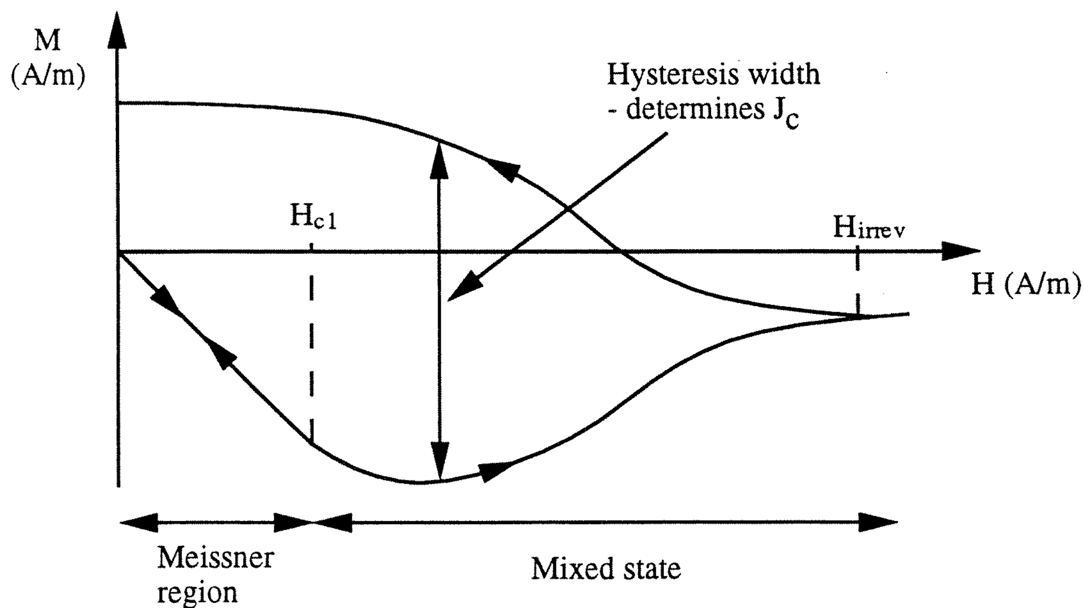


[20%]

Key features; M_s - number of unpaired spins per atom

H_c - strength of domain wall pinning centres (i.e. microstructural imperfections)

Variation of magnetisation with applied field for a type II superconductor that contains magnetic flux pinning centres over a full field cycle; [5%]



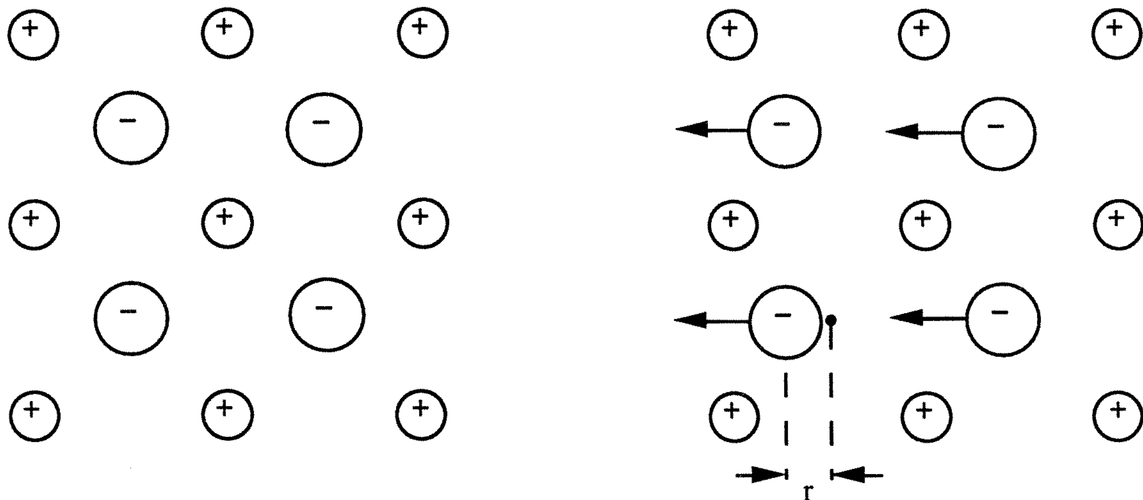
[20%]

Pyroelectricity, on the other hand, occurs in polar dielectric materials whose structure contains at least one *axis* along which an electric dipole moment exists. Only 10 of the 21 dielectric structures, therefore, exhibit pyroelectric properties (orthorhombic, tetragonal and triclinic, for example). A pyroelectric material is necessarily piezoelectric, although the converse is not true.

Pyroelectricity is the change in polarisation that occurs in pyroelectric materials as their temperature changes. Quantitatively this is described in terms of the pyroelectric coefficient, **p**, which is given by the rate of change of $\mathbf{P_S}$, the spontaneous polarisation, with temperature, i.e. the gradient of the $\mathbf{P_S}$ (T) curve;

$$\mathbf{p} = \frac{\Delta \mathbf{P_s}}{\Delta T} = \frac{d \mathbf{P_s}}{d T}$$

Microscopically, P_S originates from a structural transition which results in a displacement of the positive and negative centres of charge symmetry, i.e. ;.



Non-polar lattice **Polar lattice**

The direct piezoelectric effect is the production of a change in dielectric polarisation by the application of a mechanical stress. Conversely, application of an electric field to a piezoelectric will cause it to strain mechanically (indirect effect). The piezoelectric effect can be described microscopically in a similar way to pyroelectricity, but driven by different extrinsic variables.

Majority of useful piezoelectrics and pyroelectrics are ferroelectric, since these have a number of polar axes and are therefore relatively easy to pole. [40%]

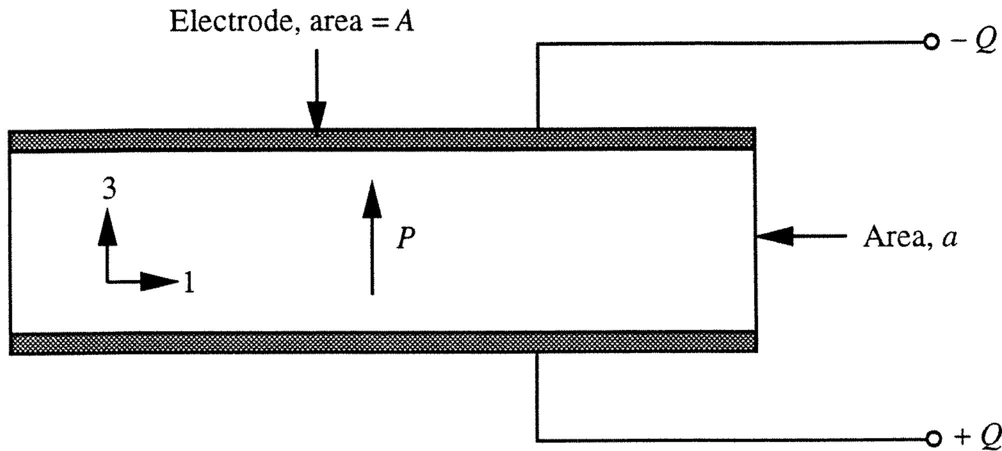
(b) The piezoelectric equations of state describe the basic principles of operation of piezoelectric devices. Most devices operate on the basis of varying stress, σ, or electric field and hence the most useful form of the equations of state are derived from Gibbs free energy considerations;

$$P = \chi E + d \sigma \qquad S = c \sigma + d E$$

where S (strain), P (change in polarisation) E (electric field) and σ are all variable. c is an elastic constant, d is the piezoelectric coefficient and χ is the electric susceptibility, which are all constant. [10%]

In the limit of d = 0, these equations reduce to Hooke's law, $S = c\sigma$, and $P = \chi\varepsilon_0 E$. [10%]

(c)



In longitudinal mode, the coefficient d_{31} couples the polarisation to the applied stress. Define P parallel to direction 3, with direction 1 normal to 3 (i.e. across the page) ;

$$P_3 = d_{31}\,\sigma_1$$

F is parallel to σ_1

$$P_3 = \frac{Q}{A} \text{ and } \sigma_1 = \frac{F}{a} \qquad \text{therefore} \qquad Q = d_{31}\,F\,\frac{A}{a}$$

[20%]

For the dimensions given, $A = 10^{-3} \times 5 \times 10^{-3} = 5 \times 10^{-6}\ \mathrm{m}^2$

$a = 10^{-3} \times 10^{-3} = 10^{-6}\ \mathrm{m}^2$

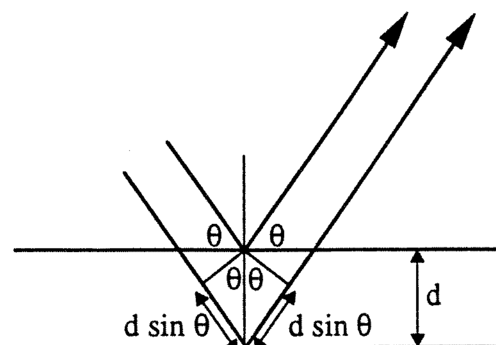
$F = 1\ \mathrm{N}$

$$Q = d_{31}\,F\,\frac{A}{a} = \frac{274 \times 10^{-12} \times 1 \times 5 \times 10^{-6}}{10^{-6}}$$

Hence $\mathbf{Q = 1.37 \times 10^{-9}\ C}$ [20%]

3 (a) (i) X rays are electromagnetic waves. A beam of electrons behaves as a beam of waves with wavelength $\lambda = h/mv$. These waves are scattered by the atoms in a material and in general the phases are such that the resultant amplitude is small. However, if all the waves reach the detector with the same phase, a large signal is detected.

(ii)



From the diagram, path difference = $2d \sin \theta$.

Maximum in scattered intensity occurs when $\mathbf{2d \sin \theta = n\lambda}$.

(b) XRD gives a very accurate measure of the distance between atomic planes and hence the crystal structure of the material. The position of the diffraction peaks can be used to identify the material under investigation, with the intensity of the peaks indicating the amount of material present. There is no restriction on the range of elements that XRD can probe. However, this technique is sensitive only to crystal structure and it can not detect impurities. Electron diffraction is used at glancing incidence in MBE systems to monitor the upper layers of deposited thin film material.

(c) (i) When a high energy electron hits one of the inner electrons in an atom, the inner electron can be knocked out. One of the electrons in the next few orbits then drops into the vacant space, emitting an X-ray with frequency characteristic of that transition of the element as it does so. The EDAX detector measures the frequency and intensity of X rays emitted in this way, thus identifying the element and its concentration.

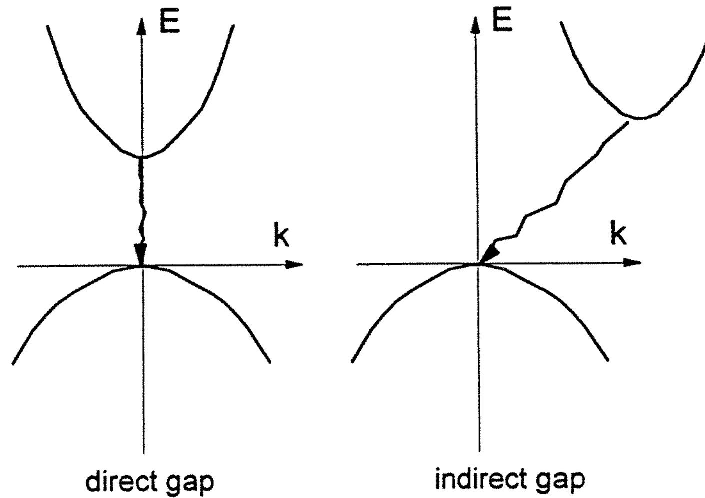
(ii) The spatial resolution of EDAX depends on the spot size of the electron beam and on the sensitivity of the detector. The spot size can be reduced to nanometers by the use of field, rather than thermal, emission sources. In this case, however, the signal is very small and a spot size of $1\mu m$ is more typical. The energy of an electron in orbit round an atom depends on the square of the atomic number, which gives good discrimination between elements. For atoms of low atomic number, however, starting at around carbon, the X rays have a low characteristic energy and are absorbed by all materials. In this case they can not penetrate the window of the detector.

(iii) The energy needed to ionise a hydrogen atom is 13.6 eV, so that for an element of atomic number of 50, the energy required to expel an electron from the inner orbit is $13.6 \times 50^2 = 34$ kV. However, electrons are 1/1000 th of the mass of a single proton so that when they hit the nucleus very little momentum is transferred to the atom and very little damage is done.

(d) Other techniques are secondary ion mass spectroscopy (SIMS), Rutherford back scattering (RBS), Auger spectroscopy and low energy electron diffraction (LEEDS). See lecture notes for details.

4. The following notes are particularly full and give more detail than would be expected in the examination.

(a)



A direct band gap is required since $\Delta k = 0$ for allowed optical transition. Examples of materials with direct and indirect band gaps are GaAs and Si, respectively.

The most important property for optoelectronic devices is the conversion of electricity into light or photons. This typically occurs by the recombination of an electron and a hole in a semiconductor to give energy, which comes out as a photon. Just like in classical mechanics, this process must conserve both energy and momentum. Thus:

$$E(\text{photon}) = E(\text{electron}) - E(\text{hole})$$

$$k(\text{photon}) = k(\text{electron}) - k(\text{hole})$$

Now, photons of a given energy have very small k vectors compared to electrons, because the speed of light is so large.

For photons; $$k = \frac{\omega}{c} = \frac{E}{c\hbar}$$

For electrons; $$k = \frac{(2mE)^{1/2}}{\hbar}$$

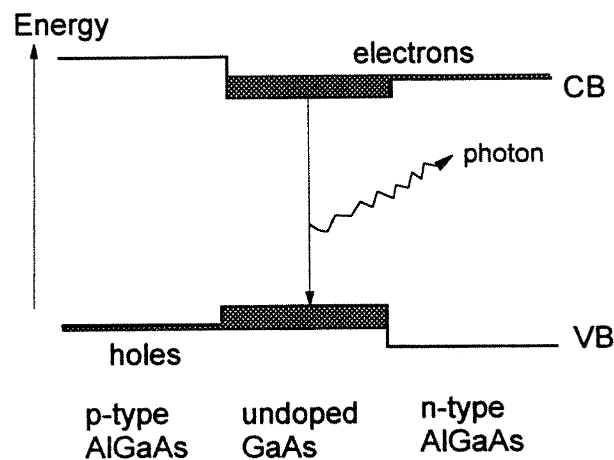
This means that the electron and hole that recombine must have essentially the same k vector. This means that the semiconductor's band gap should be direct (vertical in k-space), and generally this means that it should be at the centre of the Brillouin zone, at (000) or Γ.

Recombination in an indirect gap requires the absorption of phonons, and this strongly lowers the probability and speed of recombination.

(b) Use semiconductors with different band gaps, so their band offsets confine both electrons and holes within the narrow gap, and so increase probability of recombination. The requirement for laser action is 'population inversion', that there are more electrons in higher energy states than in the ground state, so that the rate of stimulated emission of photons from this higher energy state exceeds the rate of excitation into it. The details are beyond this course, but we look at the materials requirements.

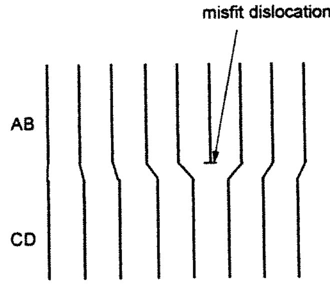
The main requirements are that we get a high concentration of electrons in the conduction band and a high concentration of holes in the valence band. We do this by carrier confinement. The other requirement is to 'confine' the light by surfaces acting as mirrors, but that is not discussed further in this course.

Carrier confinement is accomplished by 'band gap engineering', by making heterostructures of alloys of different band gaps. Consider the following structure:



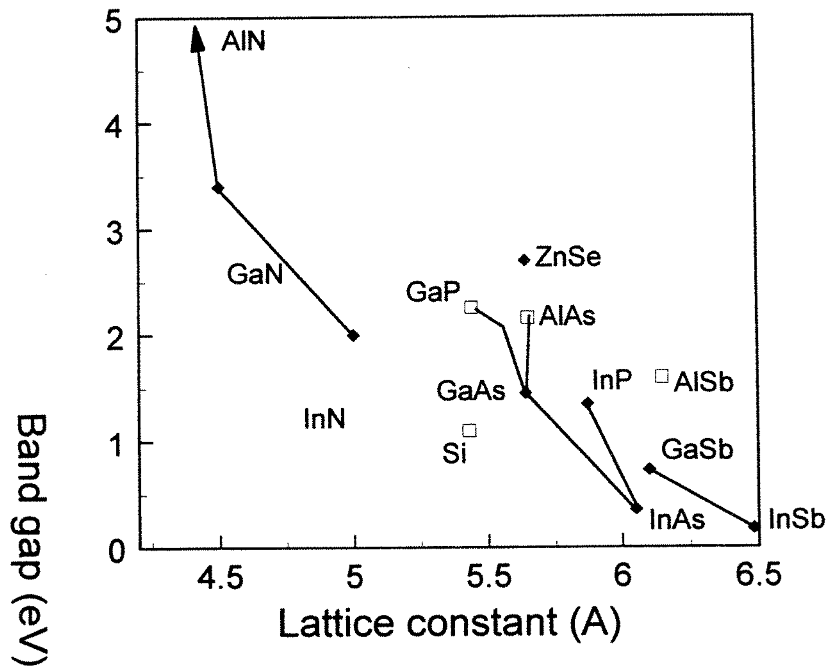
There are three layers. The right AlGaAs layer is doped n. However, its electrons can lower their energy by moving left into the GaAs layer, with the smaller band gap, and falling into its conduction band (CB). The left hand AlGaAs layer is doped p-type. Holes are like bubbles. They gain (potential) energy by rising. So the holes will move into the high valence band (VB) of the GaAs. So the GaAs layer now contains both electrons and holes even though it was not itself doped. The carriers are confined to this layer by the potential barriers of the wider gap AlGaAs layers. The electrons and holes recombine to emit photons. This is the basis of a simple semiconductor laser.

(c) Need lattice matching, otherwise many interfacial defects give non-radiative recombination. To use semiconductors of different band gaps, we must ensure they have the same lattice constant or bond length. Otherwise, their lattices do not match, and we get broken bonds at the interface.



The figure above shows atomic planes of two lattices of slightly different lattice constant. Some of the planes of the smaller lattice must end as misfit dislocations. Dislocations in covalent solids are quite complicated, but in simple terms they are another source of defect states in the band gap. Thus, they are to be avoided as they are carrier recombination centres.

Band gap varies closely with bond length/lattice constant, so semiconductors with lattice matching tend to have same band gap. Cannot so easily choose pairs with different band gap. We must therefore plot band gap against lattice constant to see what is available.



Atomic radii increase as we go down the Periodic Table. The band gaps of semiconductors decrease as the bond length increases and gaps increase as we go more ionic. Compounds like Ge, GaAs and ZnSe of elements all from the same row of the Periodic Table will all have the same lattice constant. Thus, in general we cannot get wider band gaps for the same lattice constant, unless we use more ion compounds like ZnSe.

5. (a) Assume substitutional dopants. Need valence of host +1 for donor, and host −1 for acceptor.

IV, e.g. Si;	Group III as acceptors, group V as donors
III-IV, e.g. GaAs;	Group II on Ga site or group IV on As site as acceptors
	Group IV on Ga site and group VI on As site as donors
II-V, e.g. ZnSe;	Group I on Zn site or group V on Se site as acceptors
	Group III on Zn site or group VII on Se site as donors

(b) Interstitial dopants are group IA alkali metals, such as Li, Na and K. These are small and can occupy interstitial sites. Interstitial dopants tend to be reactive and have high diffusion constants, which are limitations.

(c) Doping efficiency is limited by:

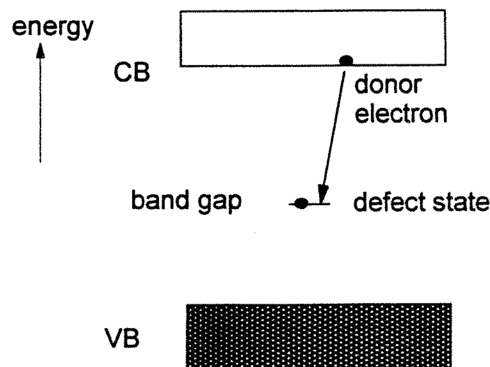
1. Solubility
2. Self-compensation. In this a free carrier falls into a spontaneously created defect state (e.g. a vacancy). As a result, there is no net doping.

Self-compensation is the biggest limitation in wide band semiconductors because the energy gained by falling is higher, whereas the energy cost of creating a defect is relatively low.

The second key requirement, apart from a direct gap, is that you can dope the material n and p type. This is possible for GaAs etc, but is non-trivial for wide gap semiconductors.

Recall that for a III-V compound, we get p-type doping by substituting a group II element at the III site (eg Mg at Ga in GaAS), and we get n-type doping by substituting a group VI element at the V site (eg S at As in GaAs). A II-VI compound needs a I element at the II site or a V element at the VI site for p-doping, and a VII element at the VI site or a III element at the II site for n doping.

There are two problems. Sometimes the dopant elements are not very soluble, and do not want to go in. Another problem is called compensation.



In a perfect crystal there is always a cost to making a defect like a dangling bond – it is the bond energy. In any semiconductor, a donor electron gains energy by falling to a state lower in the gap, e.g. a defect. In a wide gap semiconductor, it can be that the

gain in energy of the donor electron falling down will exceed the formation energy of the defect. It is then favourable to create the defect for the donor electron to fall into. When there, the electron is no longer a carrier. This process is called compensation. In compounds, there are a number of possible defects, not just dangling bonds, such as anti-sites (the Ga on the As site) on DX centres (As atoms next to dopant atoms moving off-site).

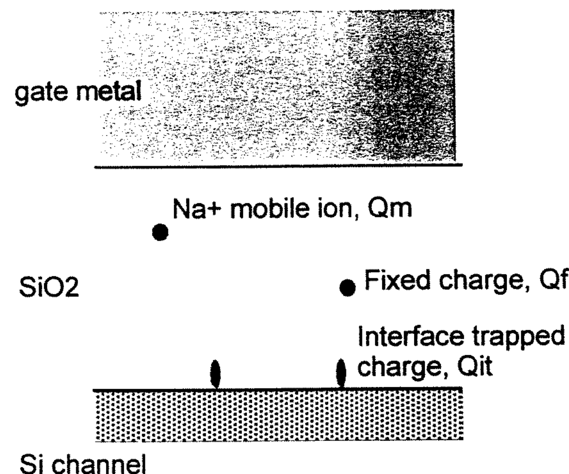
Many wide gap semiconductors suffer from this problem. For example, ZnSe is not easily doped p-type.

(d) There are 3 sources of fixed charge in SiO_2;

1. Mobile ions such as Na
2. Intrinsic defects such as E' centres (e.g. Si dangling bonds)
3. Interface states at the Si/SiO_2 interface (these are defects on the Si side).

Interstitial dopants are not used for silicon devices because they would diffuse into SiO_2 and create trapped charge.

Even high quality gate insulators have some charges inside them. The trapped charge causes a shift of the gate threshold voltage V_T, the voltage at which the FET starts to turn on. These charges can be classified as three types; mobile charge (eg Na^+), fixed charge and interface charge. The mobile charge is detected because V_T will shift with time. This type should be absent in any good device. The fixed charge is trapped at a defect inside the oxide, so that it cannot move to the outside. This is also called 'slow states'. Finally, there is charge trapped at a state at the SiO_2:Si interface, 'interface trapped charge'. This charge can be changed quickly by inter change with the Si channel. These are called 'fast states'. The areal densities of the various types of charge are given by Q_m, Q_f and Q_{it}.



Fixed charge should be small in good quality oxide. It increases only under bombardment, for example in space. Interstitial dopants are bad because they will diffuse into SiO_2 and create trapped charge.

The only poor point about amorphous SiO_2 is its open lattice, which allows ions like Na^+ to diffuse through it. Thus sodium must be rigorously excluded from the process lines. And diffusion barriers like Si_3N_4 are also used in front of the silica.