2008

PROF D.A. CARDWELL

ENGINEERING TRIPOS **PART IIB**

Thursday 1st May 2008 **2.30 to 4**

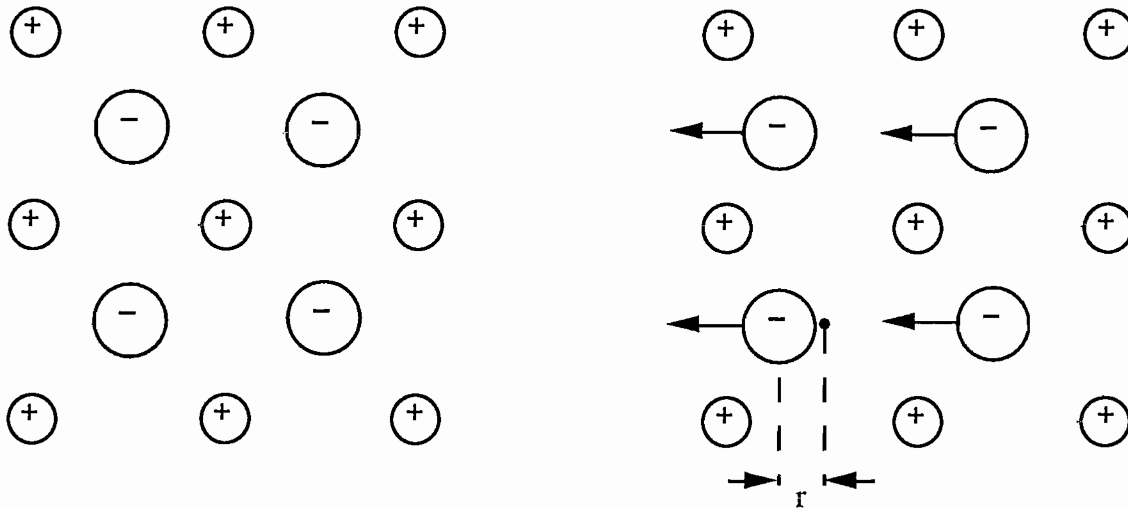
Module 4C3 : ELECTRICAL AND NANO MATERIALS **SOLUTIONS**

1(a) Pyroelectric and piezoelectric materials are sub-classes of dielectrics, and are characterised by an asymmetry in their crystallographic structure, which leads to polar properties. The crystal structure of piezoelectric materials is characterised by the lack of a centre of symmetry (i.e. they exhibit point or axial asymmetry). As a result, 20 of the known 21 dielectric structures are piezoelectric. 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 is driven by different extrinsic variables (e.g. tremperature). [40%]

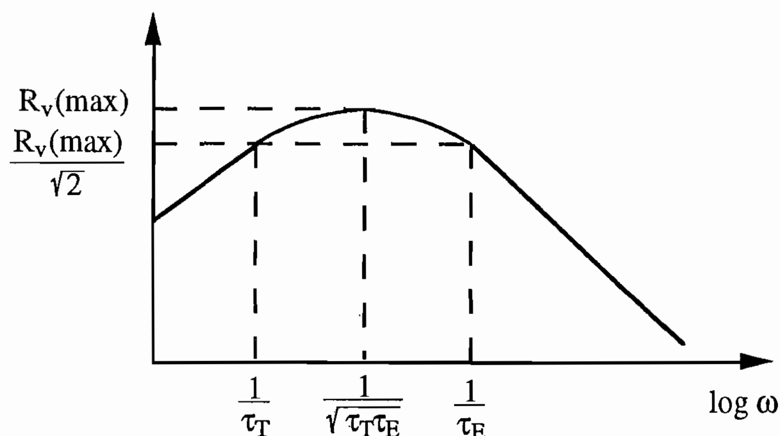
(b) Only *brief* explanations of the following are required.

(i) Piezoelectric materials are classified as either hard or soft based on their mechanical properties. Hard piezoelectric materials contain microstructural imperfections or second phase inclusions that resist the formation and propagation of cracks, which makes the material hard mechanically. Soft piezoelectric materials, on the other hand, contain relatively few such inclusions and are mechanically much softer than hard materials. Hard piezoelectric materials are used generally in passive applications in which an applied stress causes a change in polarisation (i.e. the direct piezoelectric effect). Soft piezoelectric materials are used generally in active applications in which an applied electric field causes a change in strain (i.e. the indirect piezoelectric effect), with softer materials giving larger changes in geometry. [10%]

(ii) The three non-zero piezoelectric coefficients in practical piezoelectric devices are d_{33}, d_{31} and d_{15}. In total there are 27 d_{ij} coefficients relating tensile and shear stresses to electric displacement. Symmetry considerations reduces this to 18. Piezoelectric elements in practical devices are usually formed in thin plates which means that a large field is developed across the element thickness. This reduces the number of d_{ij} coefficients further to 5. Of these $d_{31} = d_{32}$ and $d_{15} = d_{24}$. i.e. leaving 3 non-zero coefficients for practical devices. [10%]

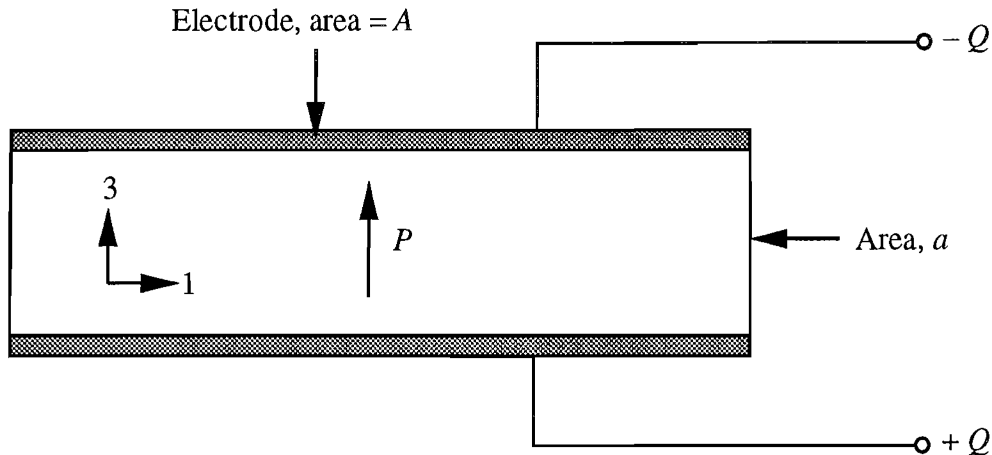
(iii) Ferroelectrics are particularly suitable for the fabrication of practical pyroelectric devices since the direction of the dipole moment in these materials can be changed by the application of an electric field. The main advantage of this is that ferroelectrics can be fabricated in polycrystalline (ceramic) form and poled accordingly with a large electric field ($E_p \sim 1$ - 5 $V\mu m^{-1}$). Ferroelectrics contain more than one polar axis in their crystal structure. As a result the polar axes are effectively oriented randomly in the different grains within a ceramic before poling (the as-manufactured material does exhibit polar properties overall). Although the pyroelectric coefficient is generally smaller in ferroelectrics than, for example, in single crystal materials such as $LiTaO_3$, the can be poled in any direction. [10%]

(iv) The frequency response of pyroelectric detectors varies significantly with frequency due to the thermal (τ_T) and electrical (τ_E) time constants of the element and interface amplifier circuit. τ_T lies between 0.01 and 1 s and determines the low frequency response of the detector. τ_E lies between 0.1 and 10^{-6} s and determines the high frequency response of the detector. The 3dB points in the response occur at frequencies of $1/\tau_T$ and $1/\tau_E$.



The low and high frequency responses of a pyroelectric detector determine the current and voltage mode operating characteristics of the device, respectively. [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

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

Piezoelectric devices based on longitudinal mode operation are used generally for passive applications (i.e. an applied stress generates a change in polarisation in devices such as telephone microphones). As a result, a hard piezoelectric material would be most suitable for this application.

[20%]

For the dimensions given, $A = 1 \times 10^{-3} \times 10 \times 10^{-3} = 10^{-5}\ \mathrm{m}^2$

$a = 1 \times 10^{-3} \times 1 \times 10^{-3} = 10^{-6}\ \mathrm{m}^2$

$F = 1\ \mathrm{N}$

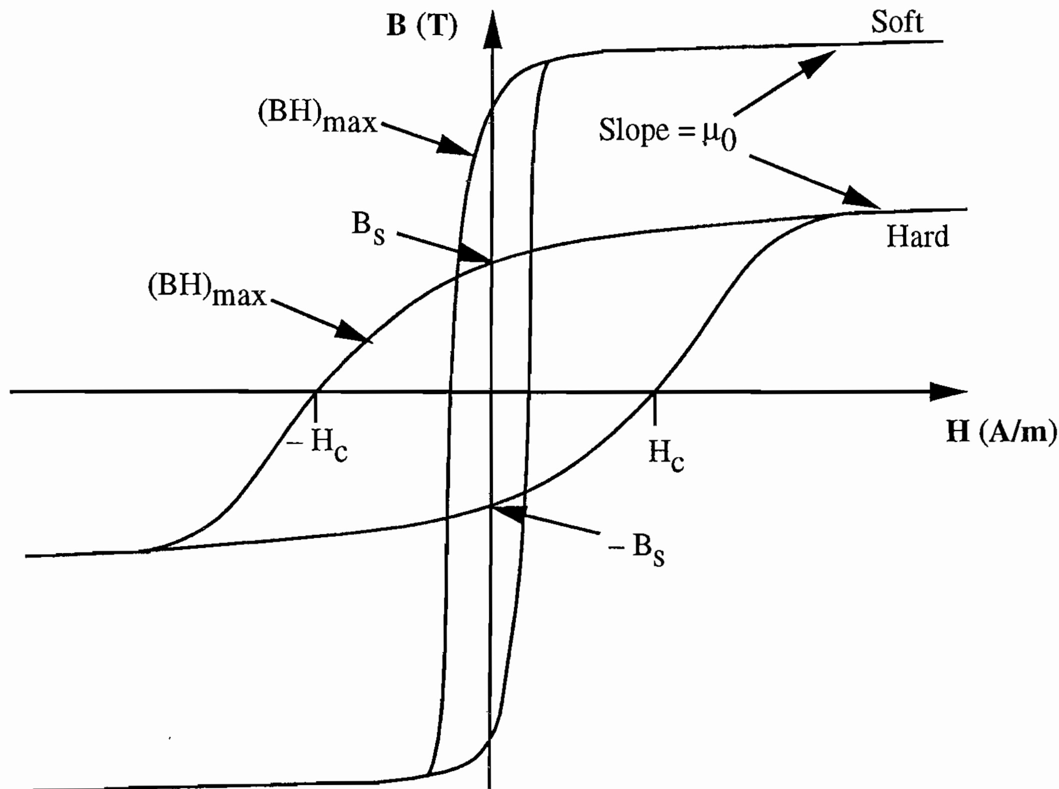
$$Q = d_{31}\,F\,\frac{A}{a} = \frac{123 \times 10^{-12} \times 1 \times 10^{-5}}{10^{-6}}$$

Hence $\mathbf{Q = 1.23 \times 10^{-9}\ C}$ [20%]

2(a) Only *brief* explanations of the following are required.

(i) Magnetic flux density is generated in permanent magnets by the alignment of unpaired electron spins associated with specific ions. An ordered array of spins may be approximated by a surface current although this does not flow throughout the material, as is the case for a homogeneous superconductor which carries current everywhere. The magnitude of the net magnetic moment is directly proportional to the sample volume. Hence the volume magnetisation does not vary with increasing sample volume.

Variation of flux density with applied field for hard and soft permanent magnet materials over a full field cycle of applied field, H (only the variation for a hard permanent magnet is required to answer the question).;



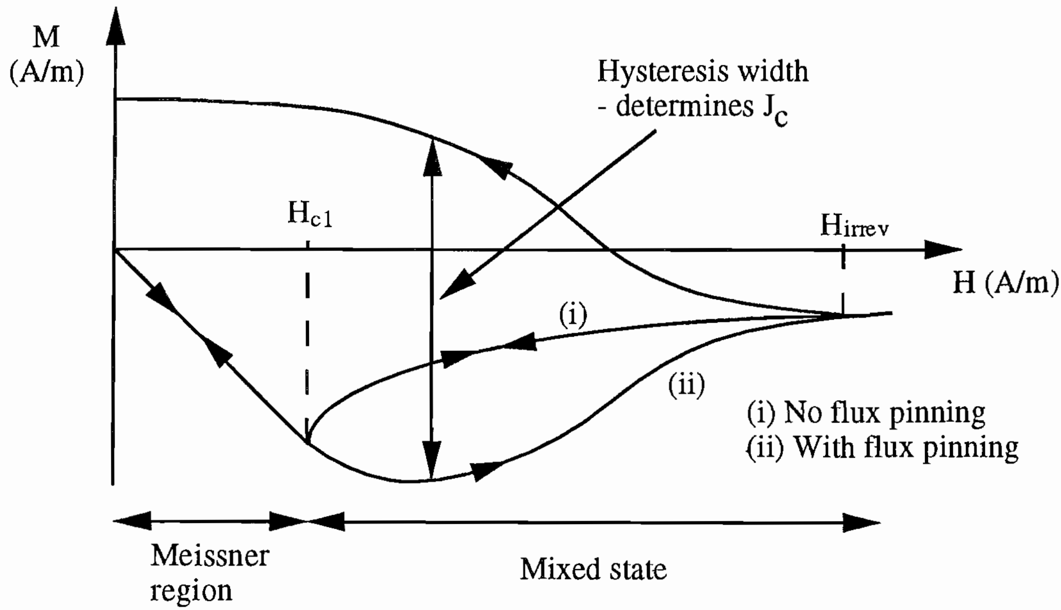
Key features; B_s - saturation flux density

H_c - coeercive force, determoned by the strength of domain wall pinning centres (i.e. microstructural imperfections)

Loop area = energy loss per cycle per unit volume

$(BH)_{max}$ occurs closer to the B axis for soft materials and closer to the H axis for hard materials.

(ii) Magnetic flux density is generated in bulk superconductors by the Faraday effect. This involves applying a changing magnetic field to the superconductor, which induces an e.m.f., which causes an Eddy current to flow throughout the bulk material, which, in turn, generates magnetic flux. As a result, bulk superconductors generate fields in a way analogous to a wire-wound solenoid. The magnitude of the net magnetic moment depends on the magnitude of these induced currents and the area over which they flow. Hence the volume magnetisation, M (defined as the net magnetic moment per unit volume) increases in direct proportion to the cross sectional area of the sample, normal to the direction of applied magnetic field (i.e. in proportion to r). M-H hysteresis curve is as follows;



[30%]

(b) The assumption of slab geometry is particularly suitable for analysis by the Bean model since this simplifies the algebra significantly. The relationship between the flux density gradient and critical current density for a type II superconductor is derived from Maxwell's equation;

Curl $\mathbf{H} = \mathbf{J}$ with $\mathbf{J} = \mathbf{J_c}$ or Curl $\mathbf{B} = \mu_0 \mathbf{J_c}$

Therefore; $$\text{Curl } \mathbf{B} = \Delta \wedge \mathbf{B} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ B_x & B_y & B_z \end{vmatrix} = \mu_0 \mathbf{J_c}$$

Assumptions;

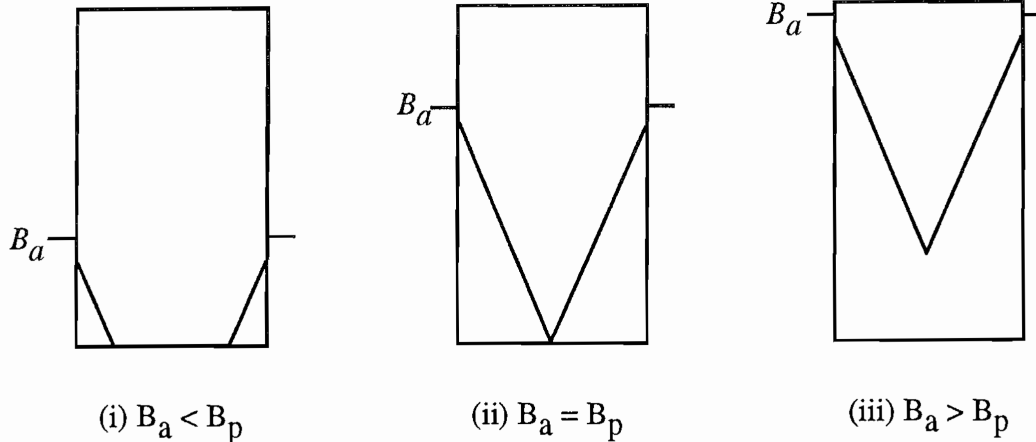
1. $\mathbf{B}$ is independent of J_c
2. $\mathbf{B}$ is constant for constant y and constant z, hence $\frac{\partial}{\partial y} = \frac{\partial}{\partial z} = 0$.
3. $\mathbf{B_x} = \mathbf{B_y} = 0$.

Derivation of equation for slab geometry;

$$\text{Curl } \mathbf{B} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \frac{\partial}{\partial x} & 0 & 0 \\ 0 & 0 & B_z \end{vmatrix} = \mu_0 \mathbf{J_c} \qquad \text{i.e. } \frac{\partial \mathbf{B_z}}{\partial x}\mathbf{j} = \frac{\partial \mathbf{B}}{\partial x}\mathbf{j} = \mu_0 \mathbf{J_c}$$

i.e.; $$\frac{\partial \mathbf{B}}{\partial x} = \mu_0 \mathbf{J_c}$$

Flux profiles;



(i) $B_a < B_p$ (ii) $B_a = B_p$ (iii) $B_a > B_p$

Note that these assume J_c is independent of applied field. [30%]

(c) Nickel has an FCC crystal structure, which has 4 atoms, and hence $4 \times 0.6 = 2.4$ Bohr magnetons, per unit cell.

Unit cell volume = $(0.35 \times 10^{-9})^3 = 4.29 \times 10^{-29}$ m^3

$$\text{Vol. magnetisation} = \frac{\text{number of Bohr magnetons per unit cell} \times \mu_B}{\text{unit cell volume}}$$

$$M = \frac{2.4 \times 9.27 \times 10^{-24}}{(0.35 \times 10^{-9})^3} = 5.19 \times 10^5 \text{ A/m}$$

$B = \mu_0 M = 4\pi \times 5.19 \times 10^5 = \mathbf{0.65\ T}$ [20%]

(d) (i) The field generated at the end of a long, thin rod of nickel is half that generated at its centre. Hence $B_{end} = 0.65/2 = 0.33$ T.

(ii) The field generated at the centre of the YBCO disc is given by;

$$B = \mu_0 \frac{J_c d}{2} = 4\pi \times 10^{-7} \times \frac{10 \times 10^7 \times 0.01}{2} = 0.63 \text{ T}$$

The superconductor generates approximately 2 × the field of the solenoid.

The factors that may limit realising these fields are;

Nickel rod: The field at the centre of the rod is inaccessible, and therefore not practical for use in magnetic devices.

YBCO: Necessary to cool the YBCO cylinder to around 77 K to achieve properties of this magnitude, which limits access to end of cylinder and again makes it difficult to incorporate into devices. [20%]

3 (a)(i) Thermally activated processes are those driven by the thermal energy of atoms or other particles. They can be either rate processes (such as diffusion) or equilibrium concentrations (such as the conductivity of semiconductors). A third example is the vapourisation of liquids or solids (i.e. vapour pressure).

The dominant factor in thermally activated processes is their dependence on the exponential factor;

$$\exp\left(-\frac{U}{kT}\right)$$

where U is the activation energy of the process, k is Boltzman's constant and T is the temperature in K. Thermally activated processed can be identified from an 'Arrhenius plot ' in which the logarithm of the rate (or concentration) is plotted against $\frac{1}{T}$. A thermally activated process will yield a straight line of slope equal to the activation energy. [20%]

(ii) Pressure is a thermally activated process and is proportional to $\exp\left(-\frac{U}{kT}\right)$.

Hence, for any two temperature and pressures; $\ln\left(\frac{p_1}{p_2}\right) = U\left(\frac{1}{k\,T_2} - \frac{1}{k\,T_1}\right)$

Using the values for p pressure and temperature given in the question, and the Data Book values for k and the charge on the electron, e, gives U= 1.67 eV.

Alternatively, U = 1.73 eV if the approximate value of 1/40 eV at 300 K is used (k ≡ 1/12000 eV/K, which yields U in eV without the need to use the electronic charge). [15%]

(iii) Electron volts are used to quantify activation energy because most processes that take place on an atomic scale involve moving an electron over distances comparable to that of an atomic radius. The use of eV avoids the large numbers often involved in expressing results in SI units, and allows different systems to be compared easily. In addition, accelerated particles gain energy (in eV) equal to the applied accelerating voltage, so it is easy to compare values. The fact that expressing physical quantities in eV gives simple numbers is not, of course, a coincidence. It arises from the original definition of the volt as the potential across a simple electrolytic cell so that it reflects naturally the energy of a typical ionic reaction. [15%]

(b)(i) EDAX is used for this application, using the same electron beam as the scattered electron image but detecting emitted X-rays instead. The energy is characteristic of the element and the intensity gives the concentration. Heavy elements require large accelerating voltages (typically around 10 kV). Light elements could use low voltages, but the X-rays produced are absorbed easily. [15%]

(ii) Secondary ion mass spectroscopy (SIMS) is used for this application (Rutherford back scattering may also be used as an alternative, although this technique is expensive and rare). In SIMS, ions are accelerated and knock ions off the thin film. These enter a mass spectrograph where a combination of electric and magnetic fields separates the ions according to their mass (or more strictly, mass to charge ratio). Ions are used as they have the necessary mass to knock-out other atoms. In principle only a few hundred volts are sufficient as atomic bonds are typically less than 10 eV, although the velocity of the sputtered ions also needs to be sufficiently high to enter and traverse the mass spectrometer. [20%]

(iii) Reflection high energy electron diffraction (RHEED) is used for this application (although Auger spectroscopy is an alternative). A high energy electron beam is fired at glancing incidence to the surface of the growing film. The glancing incidence means that only the top few atomic layers are samples, and the high energy is then needed to fulfil the Bragg diffraction condition. The angle of diffraction then gives the atomic layer spacing, which is used to monitor the growing composition. [15%]

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4(a) While the electron mass in free space is a universal constant, in a solid the effective mass m* is a variable. m* is derived from the ratio of the kinetic energy of the electron, and the k vector of the electron, from

$$E = (\hbar k)^2/2m^*$$

A standard band structure plots E versus k, thus m* is proportional to 1/curvature of bands at an extremum. A sharper extremu = lower mass. [25%]

(b) The effective mass or hydrogenic model of dopant energy level notes that the carrier moves in the 1/r Coulombic potential of the ionised dopant. This is equivalent to the potential of the electron in a hydrogen atom, so that the binding energy is given by;

$$E_0 = \frac{e^4 m}{32\pi^2 \varepsilon^2 \hbar^2}$$

As it is in a solid, we replace m with m*, and ε_0 with $\varepsilon_0\varepsilon_r$. Thus

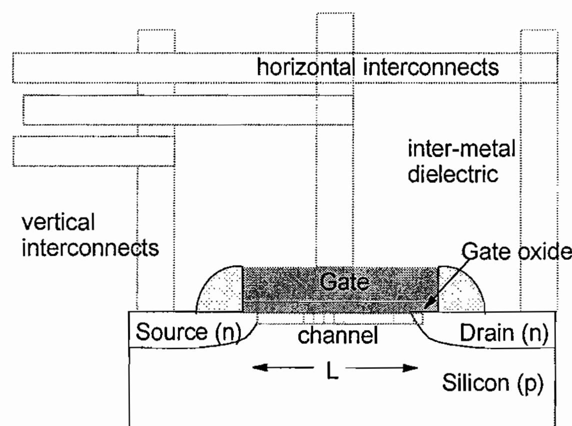
$$E' = E_0 \, m^*/\varepsilon_r^{\ 2}$$

To ionise a dopant, a small E′ is needed. This occurs for small m* and large ε.

From is $\sigma = ne\mu$ and $\mu = e\tau/m^*$, τ tends to be a constant, so that the mobility μ varies as 1/m*. Hence, the conductivity varies as 1/m*. Lower m* = higher conductivity. Higher conductivity per added carrier is desired. [25%]

From (b), it is also advantageous to use a low m* solid, so that dopant levels are easily ionised at room temperature.

(c)



channel = Si

drain, source regions = doped Si
gate electrode = doped poly Si
gate oxide = SiO_2
interconnects = Cu

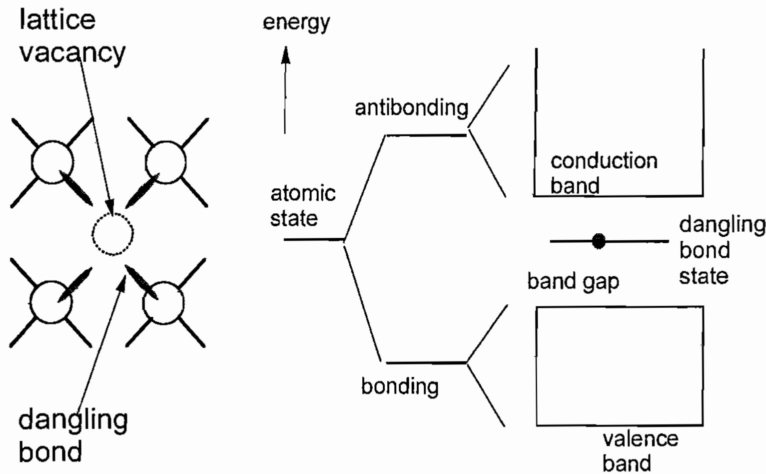
Interconnects were recently Al, changed to Cu for higher conductivity, will change ultimately to carbon nanotubes. Need for higher conductivity

Gate oxide will change from SiO_2 to a high dielectric constant (K) oxide such as HfO_2 this year. Need for higher K so that oxide can be thicker to stop gate leakage.

Channel semiconductor will be changed to a higher mobility substrate like strained Si, or SiGe alloy. Need for high mobility to get higher channel current for a given gate voltage.

[50%]

5(a)

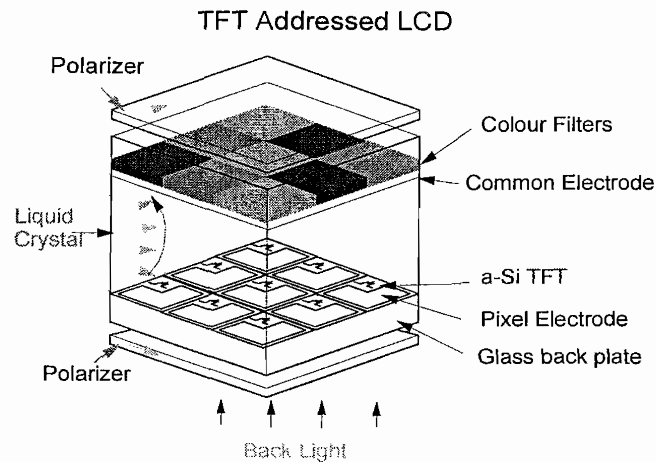


As defect states (dangling bonds) are not forming a bond, their states form energy levels which lie at the energy of the unbonded state. These lie between bonding and antibonding levels. Hence they lie in the middle of the band gap.
[25%]

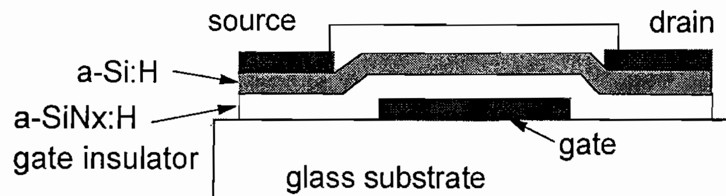
(b) Defect states due to dangling bonds are monovalent. They are passivated by monovalent elements like hydrogen or F. They form Si-H bonds, whose states lie well outside the band gap.

Surface states come from the dangling /broken bonds on the surface. They are usually passivated by oxidation. This turns the DBs into Si-O bonds. The states of the Si-O bonds lie well away from the band gap, so it passivates them. [20%]

(c)

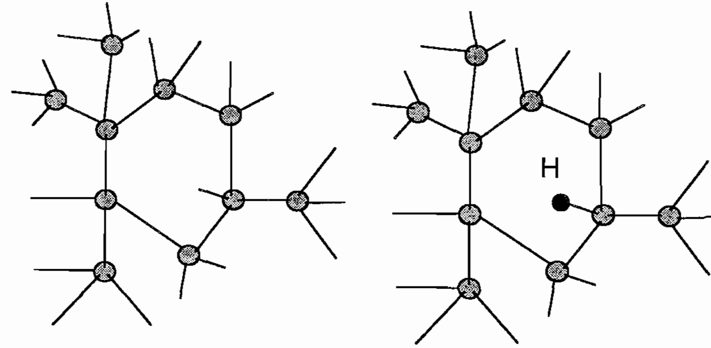


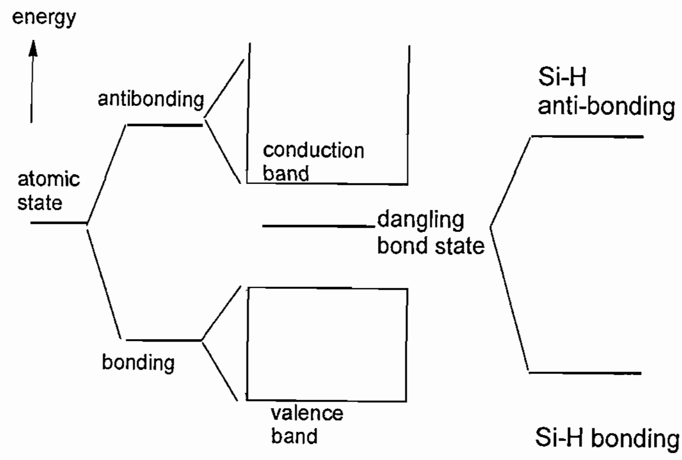
Light from back light passes through a polariser. It then passes through the liquid crystal which can rotate the plane of polarisation, depending on the voltage across it. The light then passes through a crossed polariser. Only if light is rotated does light come through. Hence this behaves as a voltage controlled light valve.



TFT = gate electrode a bottom, gate insulator (silicon nitride not SiO_2), conductive a-Si layer (instead of c-Si), followed by source and drain electrodes (Cr). [25%]

(d) Defect passivation in a-Si:H by hydrogen passivating Si dangling bonds.





[30%]

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