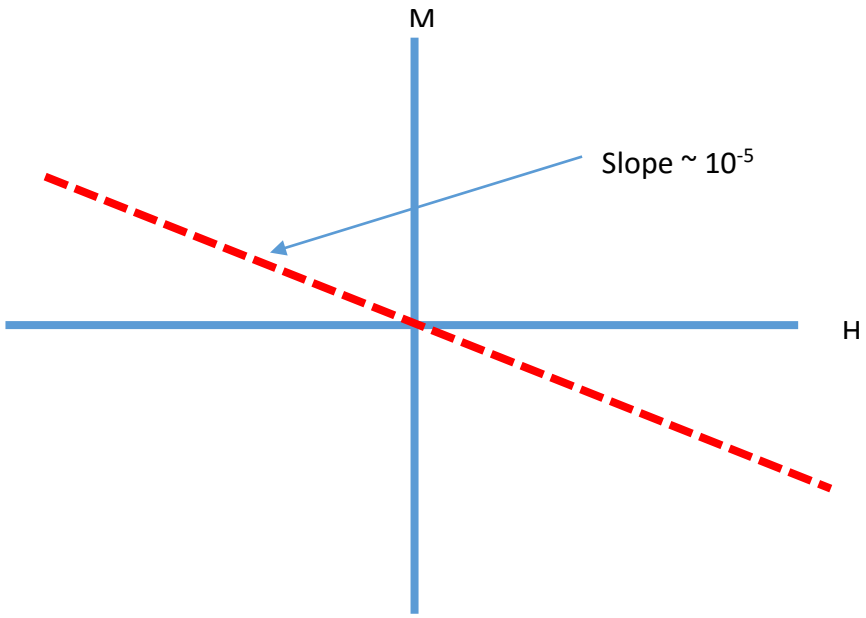
ENGINEERING TRIPOS PART IIB
Tuesday 26 April 2016, 2 to 3.30

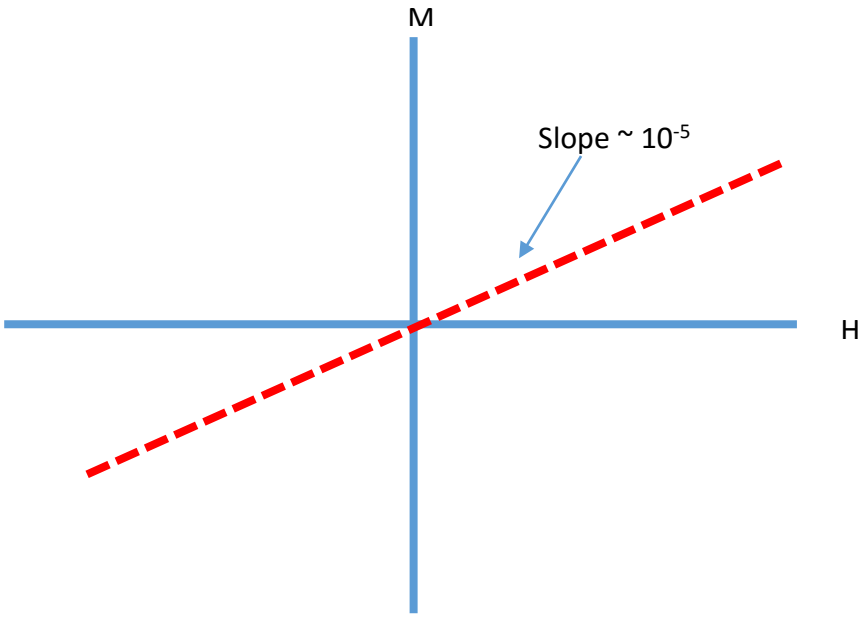
Module 4C3 - ELECTRICAL AND NANO MATERIALS

Crib

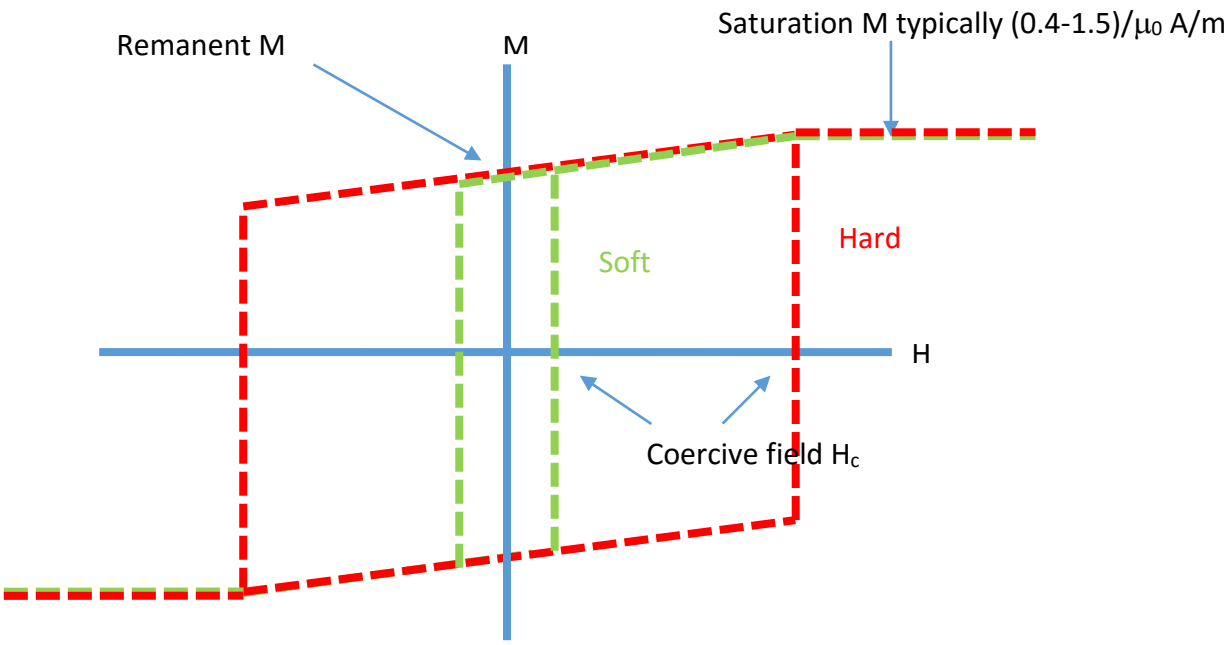
Q1 a) $M=\chi H$, for a diamagnetic material χ is negative so a plot with a negative slope is required. Students should recall that χ is of the order of 10^{-5}.



$M=\chi H$ for a paramagnetic material χ is positive so a plot with a positive slope is required. Students should recall that χ is of the order of 10^{-5}.



Soft and hard ferromagnetic materials exhibit a loop in their M-H characteristic but Hc is larger for a hard material. Sketches should also indicate remanent magnetisation and saturation magnetisation .



Only hard and soft ferromagnetic materials find significant applications. Soft materials are useful where we do not want a big loop dissipating energy or where the application is essentially where we are after a material that behaves like a paramagnet but with orders of magnitude better χ . Transformers, inductors, electromagnets etc.

Hard materials are used in permanent magnets, in high coercivity magnetic storage (e.g. bank card) etc.

b) i) In a hard magnetic material the remanent field arises from aligning the spins associated with each atom/ion in the lattice. Due to the exchange interaction there is a tendency for the spins to align with each other to give an overall net magnetisation even when the magnetising field is removed. For the material to remain magnetised a hard material needs a large coercive field which requires strong domain wall pinning possible coupled with a large magneto crystalline anisotropy. The remanent field is essentially an intrinsic function of the material used to make the ferromagnetic material and is not greatly changed by processing. The Coercive field depends on magneto-crystalline anisotropy so processing to align easy directions is helpful. It also depends on the pinning of domain walls by defects, a small grain structure is found in hard materials as grain boundaries are potent domain wall pinning centres.

The Coercive field needs to be large enough so that when fabricated into a particular shape the sample does not self-demagnetise. In a permanent magnet the materials properties are fixed and do not change with sample size.

ii) In a superconducting material the application and removal of an externally applied field induces a current flowing in the sample. The resultant magnetic properties entirely derive from the magnitude of this current. The size of the current that can be set up depends on the critical current of the superconductor which in turn depends on how well magnetic flux vortices are pinned. The temperature at which the material becomes superconducting is a fixed property of the material. The strength of flux pinning, however, is controllable by processing to introduce additional defects. The trapped field in a superconductor increases linearly with the size of the sample, this is in contrast to the behaviour of a conventional ferromagnet.

c) i) The energy stored in a magnet is proportional to BH. B=(M+H) while in this case H is purely given by the demagnetising field –NM.

So BH $\propto$ (M-NM).NM

Thus

BH $\propto NM^2-N^2M^2$

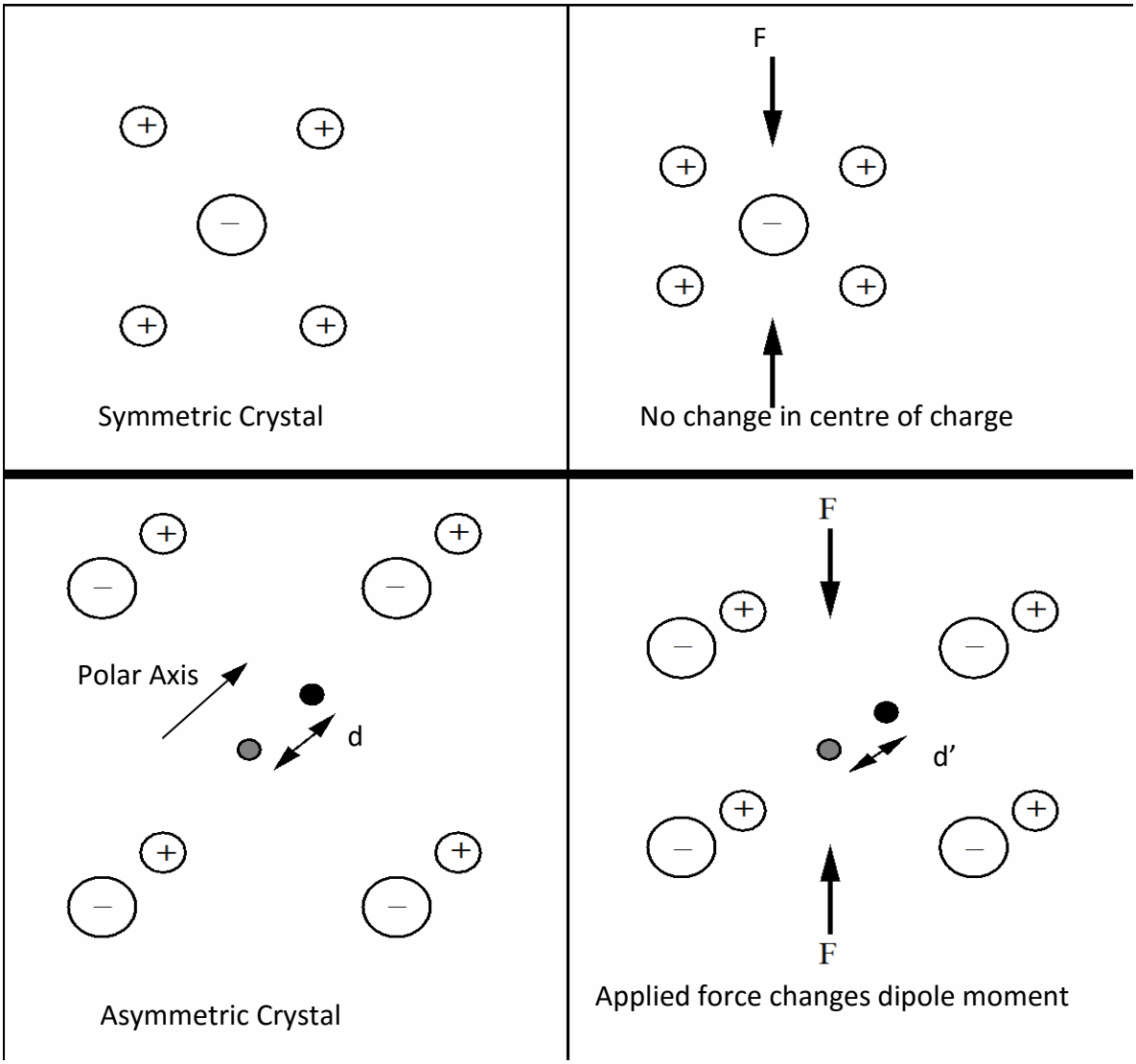
dBH/dN is M^2-2NM^2 or $M^2(1-2N)$ this is zero when N=1/2 so BH is maximised for N=1/2

ii) Pure iron has a relatively small coercive field. If a pure iron magnet is fabricated in a shape with N=1/2 the demagnetising field is going to be much larger than the coercive field and thus the magnet will spontaneously demagnetise.
Ferrite, NdBCO and SmCo are all materials with large coercive fields that can be made into any shape (even one where N=1) without demagnetising. This is why modern magnets do not need keepers.

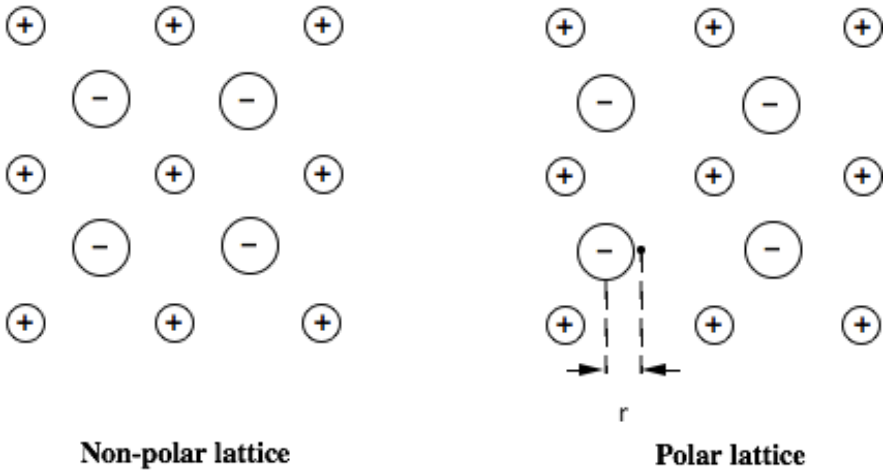
[This question was overall well answered. Part a) was generally well done although marks were lost in some cases by candidates who did not give plausible values on their sketches. Part b) gave candidates the most trouble with many simply writing everything they could remember rather than providing a coherent explanation that related both intrinsic and extrinsic factors to the field generated by the material. Almost all candidates correctly derived c)i), and cii) was very well answered.]

Q2 a) In order piezoelectric materials exhibit a spontaneous electrical polarisation when subject to an externally applied stress (and vice versa) . They are used in transducers, nano positioners, spark generators, sonar and speakers. Of the materials that are piezoelectric some materials are in addition pyroelectric. These materials exhibit a spontaneous polarisation when subjected to a change in temperature. They are used in infra red detectors, typically in alarm systems. Ferroelectric materials exhibit both the above effects and in addition can exhibit a spontaneous polarisation in the absence of an applied field. They exhibit a history dependent behaviour somewhat akin to a ferromagnet. Practically they are often employed where a piezo or pyro electric material is required as they have good properties for both these applications and because they can be poled using a large field to change the preferential direction of polarisation.

b) If a material's crystal structure has the right kind of asymmetry if a stress is applied the material reacts by deforming the vector between the centres of positive and negative charge. This results in piezoelectricity.



In a subset of piezoelectric materials when a change in temperature changes the size of the unit cell this leads to a change in the dipole moment. Pyroelectric materials are a subset of piezoelectric materials.



In both cases the charge separation between +ve and –ve charge can be used to write the vector dipole per unit cell: $q\boldsymbol{r}$ Cm where q is the charge on each ion and $\boldsymbol{r}$ the displacement between positive and negative charge centres.

The total polarisation is simply the sum of all these dipoles divided by the volume of the material considered:

$$\boldsymbol{P_s} = \frac{\sum_{\boldsymbol{all\ cells}} q\boldsymbol{r}}{\boldsymbol{V}}$$

c) i) The simplified equation given does not take into account that the response of the material is not exclusively along the direction that the field is applied. In reality $\boldsymbol{d}$ is a tensor. While technically of rank 4 students have learnt that it simplifies to the following:

$$\boldsymbol{P}_i = d_{ij}\sigma_j$$

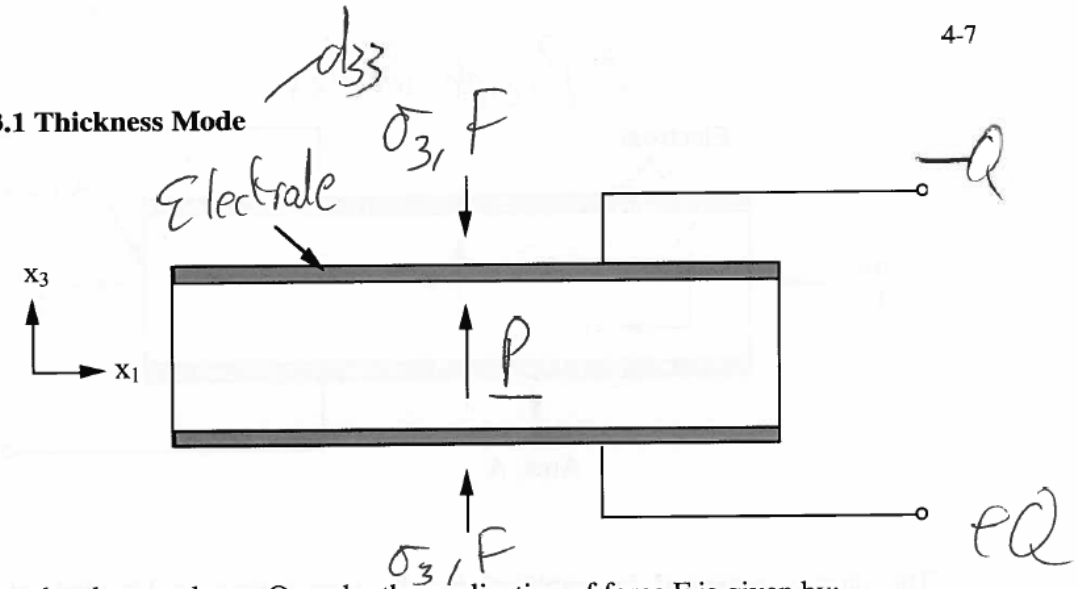
In full (not required) d_{ij} is :

$$\begin{pmatrix} \mathbf{P}_1 \\ \mathbf{P}_2 \\ \mathbf{P}_3 \end{pmatrix} = \begin{pmatrix} \mathbf{d}_{11} & \mathbf{d}_{12} & \mathbf{d}_{13} & \mathbf{d}_{14} & \mathbf{d}_{15} & \mathbf{d}_{16} \\ \mathbf{d}_{21} & \mathbf{d}_{22} & \mathbf{d}_{23} & \mathbf{d}_{24} & \mathbf{d}_{25} & \mathbf{d}_{26} \\ \mathbf{d}_{31} & \mathbf{d}_{32} & \mathbf{d}_{33} & \mathbf{d}_{34} & \mathbf{d}_{35} & \mathbf{d}_{36} \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix}$$

ii) If a thin sheet is used the problem simplifies significantly as then the only non zero coefficients are $d_{31}=d_{23}$, d_{33} and $d_{15}=d_{24}$. Each of these represents a particular mode of operation viz. Longitudinal, thickness and shear respectively.

iii) Accept a labelled sketch of any of the three modes and a sensible potential application.

4.3.1 Thickness Mode



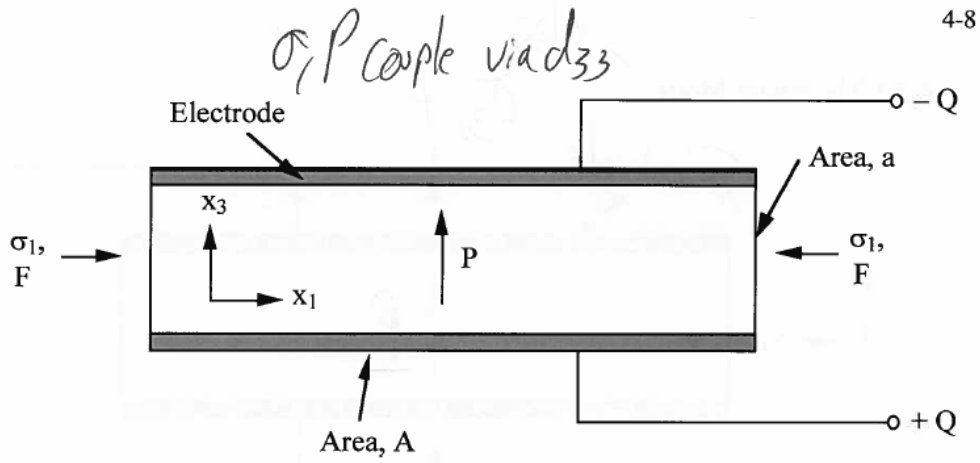
Here the charge release, Q, under the application of force F is given by;

$$P_3 = d_{33}\sigma_3 \Rightarrow Q = d_{33}F \quad (P \text{ in } Cm^{-2},\ \sigma \text{ in } Nm^{-2})$$

Similarly, in active mode the application of an electric field E_3 parallel to x_3 (the polar axis) will lead to a strain along x_3.

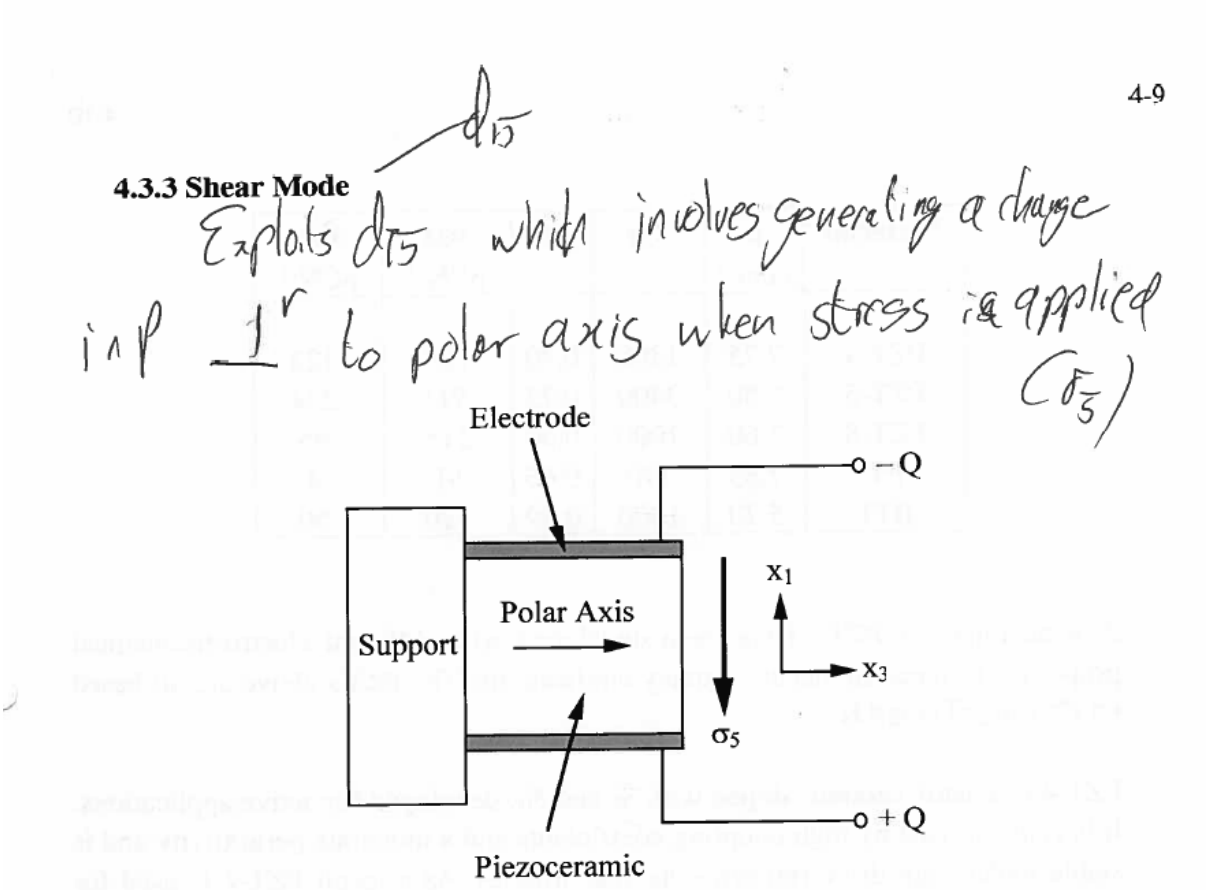
Thickness mode operation is frequently used in passive devices to detect sound underwater.

Longitudinal mode



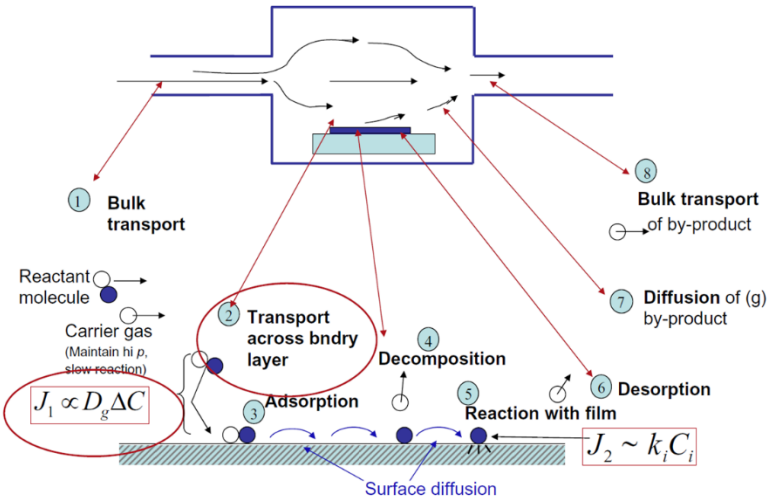
The charge generated is amplified by the aspect ratio in longitudinal mode operation. This is the basis of operation of the piezoelectric microphone, which has been used in telephone handsets;

Shear Mode

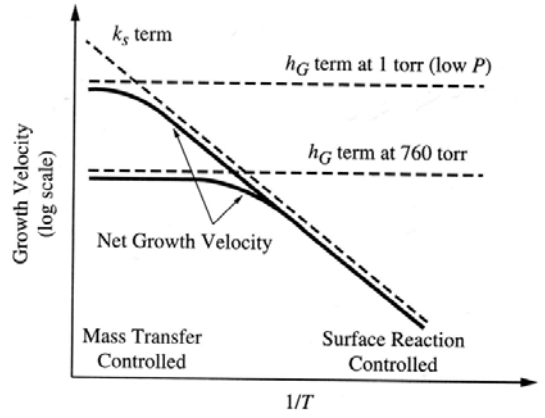


[This question was answered somewhat patchy with some candidates providing confusing sketches and non-coherent arguments. In part a) many candidates lost marks because, while they correctly identified the relationships between the three classes of materials, they did not explain their behaviours. The best candidates identified the utility of ferroelectrics as being due to their ability to be poled. A surprising, and somewhat worrying, number of candidates had clearly confused ferroelectric and ferromagnetic materials. Equally there were very few good answers to part b) which used sketches to clearly explain the origin of the polarisation. In contrast part c) was well answered albeit that some candidates argued that the simplification in ci) was that the E field was neglected in spite of the first line of the question specifying that it was to be neglected.]

Q3 (a) In CVD the substrate is exposed to gaseous precursors at elevated temperatures. The gas species adsorb and decompose on the substrate to produce the desired growth species and film growth. Key steps are thereby the transport of gas species to the substrate (step 2 in Fig. below) and the surface reactions of the various species (steps 3-6): (see lecture notes)



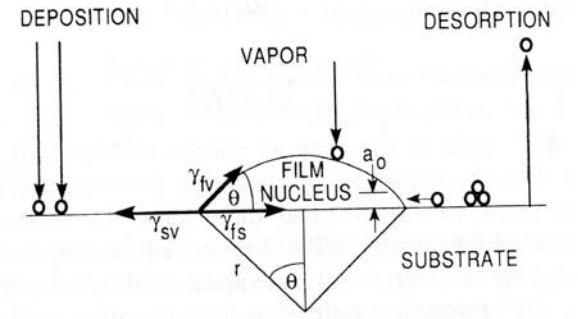
The overall CVD growth rate can be either limited by step 2, ie diffusion of gas species through boundary layer, or the surface reactions, commonly simplified as one overall first order reaction. For the latter case, which is referred to surface reaction control, the rate constant is exponentially dependent on temperature. In comparison, the gas diffusion in the so-called mass-transfer controlled regime only weakly depends on temperature. Hence the overall CVD growth rate has the following characteristic temperature behaviour



(b) For lower pressures the range of the surface reaction controlled regime can be extended (see Fig. above). The CVD growth rate in this regime critically depends on temperature, which can typically be well controlled, but importantly does not depend on gas transport, which is often harder to control. Hence low pressure CVD offers more process control, more uniformity, better step coverage, greater control over stoichiometry and contamination problems.

(c) (i) For atomic layer thickness control the CVD process can be broken down into two half-reactions, with each of the respective surface reactions being self-limited. This is referred to as atomic layer deposition (ALD). For alumina film deposition the two gaseous ALD precursors could be Trimethylaluminium (TMA) and water. The graphene substrate is exposed to TMA and water not simultaneously but in individual pulses in cyclic fashion.

(ii) Film nucleation can be described in terms of classical thermodynamics, where the surface and interface energies define the expected nucleation mode (akin to wetting for water droplets, see lecture notes):



Graphene can be expected to have low surface energy, ie is hard to wet with new film, hence a so-called Volmer-Weber growth mode is likely to prevail, where alumina islands will form during ALD rather than initially continuous film.

(d) In XPS X-ray absorption results in the creation of photo-electrons, the energy of which is characteristic of the elements in the sample and their chemical state. However the mean free path of these photoelectrons within a sample is in the order of nano-metres (see so-called universal curve, lecture notes). Hence XPS is extremely surface sensitive, and only the top layers of the alumina film can be probed. XPS can thereby confirm the presence of Al and O and their oxidation state. Also the relative abundances can be extrapolated, allowing confirmation of film stoichiometry. If film was transferred in air or kept in low vacuum, surface contamination has to be taken into account.

(e) (i) The electrons will interact elastically and inelastically with the polymer. The dominant elastic interaction is Rutherford scattering, the differential scattering cross section of which strongly depends on the atomic number Z of the polymer and the energy E of the electrons:

$$\frac{d\sigma_{elastic}}{d\Omega} \propto \left(\frac{Ze^2}{4E}\right)^2$$

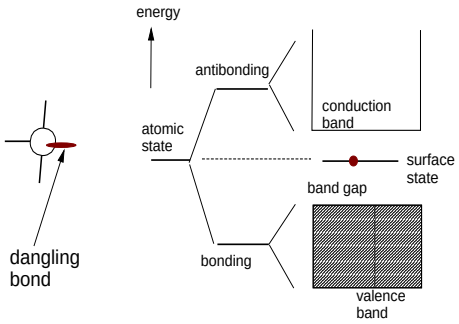
Inelastic interactions are those that excite the sample and the incident electron is slowed as a consequence. For electron microscopy, this energy exchange is limited to atomic electrons and there is a multitude of different inelastic scattering processes, incl. phonons, plasmons, catholuminescence.
When the well-focussed e-beam hits the polymer surface, the elastic scattering is initially weak and the electron penetrate the polymer. As the electrons steadily loose energy, the elastic cross-section strengthens and electrons start to scatter strongly. The beam starts to spread laterally, resulting in a characteristic pear shape.

(ii) For higher Z the elastic scattering cross-section is larger and the electrons scatter more frequently and with greater angles. Hence the interaction volume becomes more hemispherical about the point of entry of the electron beam.

[*This question was generally well answered. All candidates did well in the basic descriptive parts, such as for CVD (part a), ALD (part c) and XPS (part d). I was pleased to see that a large number of candidates also showed a solid understanding and gave good answers to the more challenging parts of the question. In part (a)/(b) the correct temperature dependence of the CVD deposition rate and clear arguments based on extending the surface reaction limited regime was only given by the top students. Similar for part (e) were the quality of answers ranged from superficial, inconsistent lists of possible e-beam interactions*

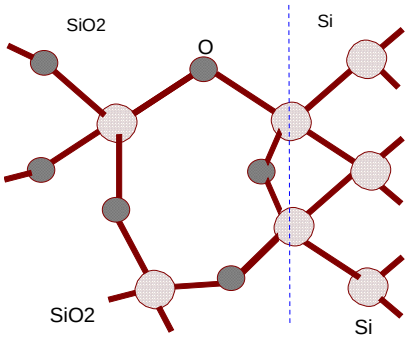
to very concise and well-argued correct answers on the interplay between inelastic and elastic scattering mechanisms.]

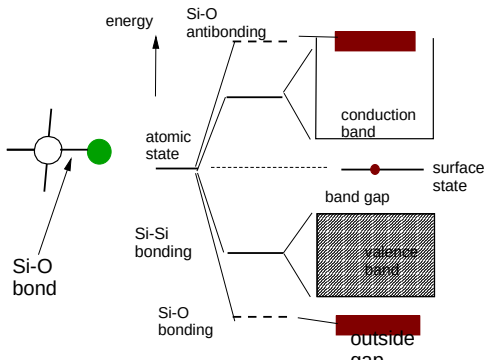
Q4 a. Surfaces of covalent semiconductors end in broken (dangling) bonds. These give rise to surface states that lie in the band gap.



They cause recombination of electrons and holes. They trap charges when in FETs.

b. In a planar FET, the Si surface has a SiO2 layer. The Si-O bonds of the interface remove the Si DBs. So no longer surface states in the gap. The states due to Si-O are well into bands, away from gap.





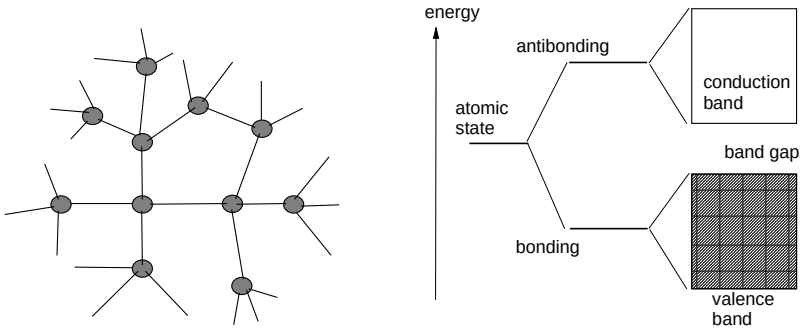
c.

Gauss' law: $Ne.d = \varepsilon E$,

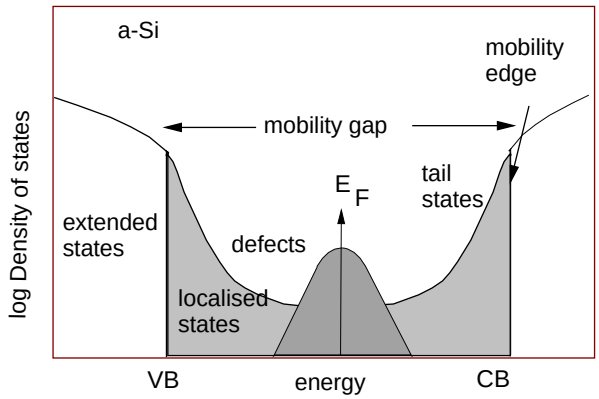
$E = Ne.d/\varepsilon$ hence $V = Ne.d^2/2\varepsilon$

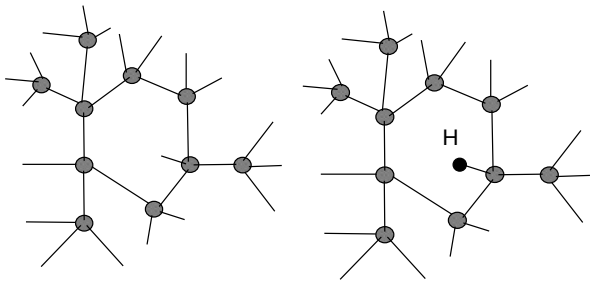
V = 5e24 x 1.6e-19 . (5e-9)^2 /(2 x 5 x 8.8e-12.) = 0.22 V

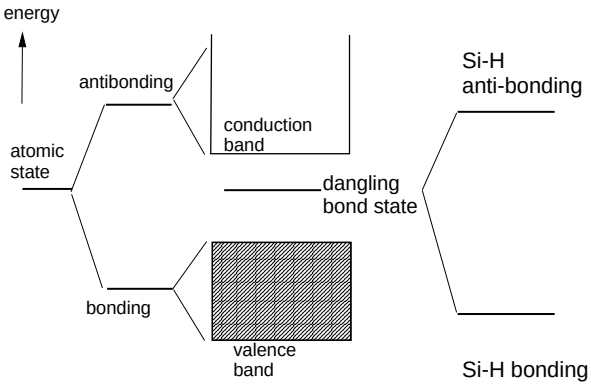
d. Si forms four sp3 hybrid orbitals. Each sp3 forms bond with a sp3 of an adjacent atom. These bonds give rise to bonding and antibonding states, the VB and CB of the solid. This does not depend on periodicity.



e. 2 types of gap states, tail states and deep defect states. Tail state due to angular disorder, cannot be removed. Defect states are passivated by hydrogen, removing gap states, and pushing the states into VB or CB.







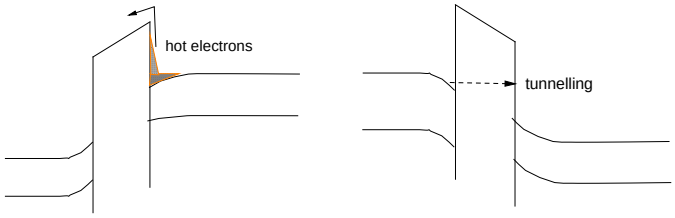
[*Most students got the right idea, and differed mainly in how complete their answers were. Most challenging proved the numerical estimate of threshold voltage shift in part (c), which required a clear understanding of the topic.*]

Q5 a. In 1965 – 2000 Moore's Law followed pure dimensional scaling, with no change in materials, Si and SiO2 only. Thus FET dimensions scaled downwards by a factor k, so speeds increased by factor k. Assuming voltage also scaled by factor k, then power density is unchanged, current densities increased by $1/k^2$, etc.

From 2000, Cu replaces Al in wires, HfO2 replaces SiO2 as gate insulator, SiOF, SiCHO replaces SiO2 as interlayer dielectric, CoSi2 replaces Al as contacts, metal gates replace highly doped poly-Si as gate electrode.

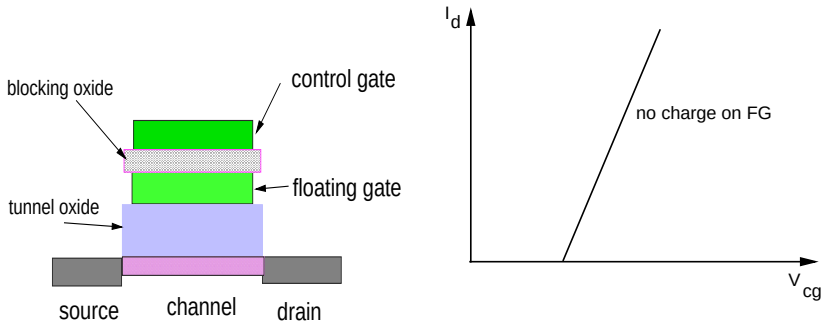
b. Poole-Frenkel hopping, Fowler-Nordheim tunnelling (see lecture notes).

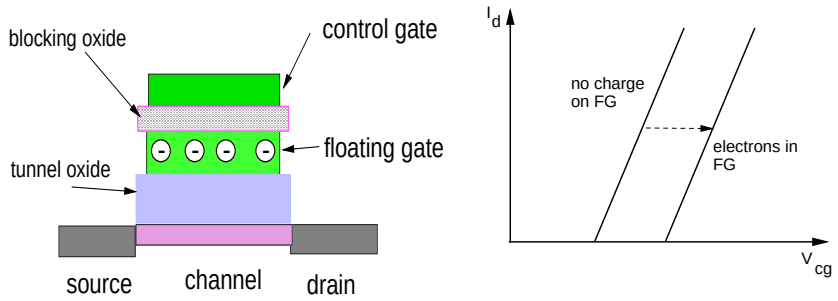
c. channel, floating gate, control gate, SiO2 layer on either side of floating gate.
Write process. Hot electron injection of electrons into floating gate. Tunneling for erase.



SiO2 must be good insulator to retain charge in floating gate for 10 years if necessary. But is also must pass erase/write current under high voltage for these processes. But must not breakdown during these currents.

d. charge in floating gate by Gauss give extra field at top gate. This means that the gate threshold voltage at which current switches on is shifted (read).





[*This question was generally answered well, with less or more detail on part (a). Most students provided good answers to parts (b) and (c). Many also got the full answer to part d, using the correct diagram of shifted gate threshold voltage.*]