Time allowed - Two (2) hours.
Total number of questions - Six (6).
Answer ALL Six (6) questions.
Allow 20 minutes for each question.
All questions are worth 20 marks.
Answer each question in a separate book.
This paper may be retained by the candidate.

Answers must be written clearly in ink. Except where expressly required, pencils may be used only for drawing, sketching or graphical work.
SECTION A

QUESTION 1

(i) The unit cell of copper is shown below; X-ray data measured at $\lambda_i = 1.5406$ Å and $T = 298$ K has a (111) peak at a scattering angle of 43.317°. When the sample was heated to 469°C, the same peak shifted to 42.980°.

(a) What is the density of copper at 25°C?
(b) Calculate the coefficient of thermal expansion of copper based upon a linear rate of expansion and expressed as a % °C⁻¹.

[10 marks]

(ii) The lattice dimension in NaCl is 5.64 Å, calculate the packing efficiency and the density.

[5 marks]

(iii) How does the resistance of the following materials change with temperature:
(a) a metal?
(b) an intrinsic semiconductor?
(c) an extrinsic semiconductor?

Provide an example of each of these materials.

[5 marks]

*Question 2 follows on the next page*
QUESTION 2 [Parts (i) and (iii) are worth 7.5 marks, part (ii) is worth 5 marks]

(i) A metal organic framework (MOF) material has a formula mass of 467 amu and is found to uptake nitrogen gas at 77 K, to the extent that 1 mol. of MOF adsorbs the equivalent of 1.66 l of N\(_2\) at STP.

What is the specific surface area of the MOF (in units of m\(^2\)g\(^{-1}\)) if one assumes a close-packed Langmuir-type adsorption of hard spheres in which each N\(_2\) molecule has a surface area of 13.5 Å\(^2\)?

If one assumes that both the specific surface area and the adsorption characteristics are the same for H\(_2\), what would be the wt % uptake of H\(_2\) if the distance between the centres of neighbouring H\(_2\) molecules is determined by diffraction methods to be 3.5 Å?

(ii) How does a Bloch wall differ from a grain boundary?

(iii) Draw the hysteresis curves of the following materials, each on a separate, fully-labelled figure:
(a) a simple paramagnet.
(b) a soft ferromagnet.
(c) a magnetic material suitable for magnetic storage media.
(d) a superparamagnet in an increasingly viscous medium.

Sections B and C follow on the next page
SECTION B

QUESTION 3

A) Scanning Probe Microscopy

To obtain a topography as shown in Figure 1 requires a scanning probe microscope (STM or AFM) to fulfil four criteria. The first of these is a strong distance dependent interaction between the surface and the probe.

Figure 1

i) Explain the operational principles which allow this criterion to be satisfied with both scanning tunneling microscopy (STM) and atomic force microscopy (AFM).

ii) List the remaining three criteria that will need to be satisfied.

iii) With STM, electrons must tunnel between a probe which terminates at a single atom and a surface. Determine, using the equation which relates tunneling current to distance, the ratio of the tunneling current that will come from an atom 2 Å further from the surface than the terminating atom.

Assume the barrier factor is constant with distance and is 4 eV, and A is $1.025 \text{ eV}^{-1/2} \text{ Å}^{-1}$.

[10 marks]

Question 3b follows on the next page
B) X-ray Photoelectron Spectroscopy

The surface chemistry in the following scheme has been developed for molecular electronic applications so one end can be connected to silicon and the thiol on the distal end can be used to connect to another electrode. The thiol however must be protected to ensure it does not react with the silicon surface.

The narrow scan of the C1s region for the middle surface looks like

a) Explain why XPS is so sensitive to surface species and discuss how you could alter the surface sensitivity of an XPS measurement (you may want to use an equation in your answer).
b) XPS detects changes in the core level electronic states. Why can it be used to determine chemical states?
c) Explain why you think the three peaks at 286, 289 and 293 eV appear in those positions. That is, explain the order of the three peaks.
d) Draw what you think the C1s narrow scan would look like once the protecting group is removed.

[10 marks]
QUESTION 4

You are given a research project related to the detection of cancer cells in cell cultures via the binding of quantum dots (luminescent nanoparticles) to the cancer cells. To ensure the interaction between the quantum dots and the cancer cells is a specific interaction, antibodies specific to surface features found only on the cancer cells are immobilised onto the quantum dots. For the purposes of this question assume the quantum dots have an outer gold layer. Your job is to come up with a strategy to immobilise the antibodies onto the quantum dots so they will binding specifically to the cancer cells but not other cells. Discuss a strategy in detail to achieve this. Your answer should address some or all of the following issues and explain your decisions.

(i) The requirements the surface modification must achieve.

(ii) Other things in the sample that might also bind to the quantum dots and how you might limit them.

(iii) How the surface of the quantum dot will be modified, that is with a presynthesized self-assembled monolayer forming molecule containing the antibody or using a stepwise approach where a base self-assembled monolayer is formed and then the antibody is attached.

(iv) In the latter case of the stepwise formation of the modifying layer on the quantum dot how would the ligand be attached to the base monolayer?

(v) How you will know the surface modification process has been achieved as you desired. Specifically what sort of information you could derive using XPS and STM.

(vi) How you might ascertain that the system will give you a specific interaction between the quantum dots and the cells.

[20 marks]
SECTION C

QUESTION 5

A) For each of the systems listed below, indicate which technique/s should be used to characterise the structure of the nanoscale thin-film or interface: (X-ray reflectometry, neutron reflectometry, or both). Clearly explain the reasons behind your choice and the advantages of using that technique.

(i) Nanoscale water adsorption on a –COOH terminated self-assembled monolayer on a polished silicon wafer.

(ii) A thermally annealed, 50 nm thick, polystyrene/polyethylene oxide diblock copolymer film that has been spin-coated onto a polished silicon wafer.

(iii) Studies of antimicrobial peptides on supported phospholipid bilayers

(iv) Correlation between structure and magnetism on a magnetic thin film on a polished silicon wafer.

[10 Marks]
B) Figure 1 shows neutron reflectivity data from the Platypus neutron reflectometer for a Bragg Mirror composed of alternating layers of Ti and Ni.

![Neutron Reflectivity Data](image)

**Figure 1.** Neutron Reflectivity data from a multilayer Ti/Ni Bragg Mirror

Using the above neutron reflectivity data, calculate:

- The thickness of each Ti/Ni bilayer in the Bragg Mirror stack.
- The total number of bilayers in the Bragg Mirror

Use a sketch to describe the neutron reflectivity profile of a 200 Å thick nickel metal film on a polished silicon wafer.

[10 marks]

*Question 6 follows on the next page*
QUESTION 6

Aromatic heterocyclic molecules such as those shown in Figure 2 below are used in thin-film organic light emitting devices (OLEDs). Chemical deuteration is used in such studies to improve contrast between molecular layers in morphological studies of such devices.

A) Calculate the X-ray and neutron scattering length densities for TCTA and CBP

![Molecular structures of TCTA and CBP](image)

**Figure 2.** Molecular structures of TCTA and CBP

**Mass Densities:**
- TCTA: 1.23 g/cm³
- CBP: 1.19 g/cm³

**Useful Equations:**

\[
\text{SLD}_x = r_e N_A \rho Z / M \\
\text{SLD}_n = N_A \rho b / M
\]

- \(r_e\): the classical electron radius = 2.818 \times 10^{-15} \text{ m}
- \(N_A\): Avogadro’s constant = 6.022 \times 10^{23}
- \(\rho\): the mass density of the film
- \(Z\): the total number of electrons per molecule in the film
- \(b\): the sum of neutron scattering lengths per molecule in the film
- \(M\): the molecular mass per molecule in the film

(Nota 1 \text{ fm} = 1 \text{ femtometre} = 10^{-15} \text{ m})

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[12 Marks]

*Question 6 continues on the next page*
B) The critical angle ($\theta_c$) below which total external reflection occurs is given by:

$$\theta_c = \lambda \times \sqrt{\frac{\text{SLD}}{\pi}} \quad \text{(in radians)}$$

Calculate the critical $Q$ value ($Q_c$) for a set of neutron reflectivity data measured from a 50 nm thick fully deuterated CBP film on a Si wafer.

(For small angles $\sin \theta_c \sim \theta_c$ )

[8 Marks]