THE UNIVERSITY OF NEW SOUTH WALES

SUPPLEMENTARY EXAMINATION
S1 2010

NANO3410
Chemistry of Surfaces

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 \( \lambda = 1.5406 \) 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°.

![Copper unit cell diagram]

(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) Calculate the packing efficiency of a face-centered-cubic cell and show how this differs from that of a body-centered cubic cell.

[5 marks]

(iii) How does the conductivity 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) to (iii) are worth 5 marks, part (iv) is worth 10 marks)

(i) How would the working of a metal such as beating or peening affect the microstructure? Why may this be desirable?

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

(iii) What is a superparamagnet? What kind of real materials tend to display such behaviour?

(iv) 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.

Section B and Question 3 follows on the next page
QUESTION 3

(a) Discuss the relative strengths and weaknesses of X-ray reflectometry (XRR) and neutron reflectometry (NR) in the characterisation of nanoscale thin films and surfaces.

[10 marks]

(b) Polarized neutron reflectometry can be used to probe both the nuclear structure and the magnetization with a magnetic thin film.

Consider a 200 Å thick film of metallic iron on a silicon wafer, contained in a saturating magnetic field (i.e. the saturated magnetic moment is perpendicular to the direction of the neutron travel).

The nuclear only and spin-polarized values of scattering length density are shown for this film in the figure below. The magnetic moment within the iron film is such as to add $5 \times 10^{-6} \, \text{Å}^{-2}$ to the nuclear SLD when interacting with spin-up neutrons, and subtract $5 \times 10^{-6} \, \text{Å}^{-2}$ from the nuclear SLD when interacting with spin-down neutrons.

Based on the film thickness and the above scattering length density values, sketch on the same graph the neutron reflectometry profiles for spin-up polarized and spin-down polarized neutrons.

Draw the graph over the $Q$-range 0 - 0.25 Å$^{-1}$.

[10 marks]

Useful Equations:

Position of the critical edge: $Q_c \sim 4 \sqrt{\pi \text{ SLD}}$

Spacing between fringes: $\Delta Q \sim 2\pi / \text{(film thickness)}$

Question 4 follows on the next page
Poly (N-vinylpyrrolidone) (PNVP) is a neutral, water soluble polymer that can be thermally cross-linked to form insoluble thin-film coatings with antifouling properties.

Prior to thermal annealing PNVP has the structure shown below, with a formula $C_6H_9NO$ and a mass density of 0.80 g/cm$^3$.

![Chemical structure of PNVP](image)

Neutron reflectivity data are shown below for an as-prepared PNVP film (red data), and that for the same film after annealing at 200°C for 3 hours (blue data, offset by a factor of $1/10$ for clarity).

(a) From the above reflectivity data, calculate the thickness of the as-prepared film and the annealed film, and hence the percent shrinkage following annealing.

[5 marks]

Question 4b follows on the next page
(b) As a result of thermal cross-linking, the PNVP film becomes more dense and the composition changes, with the most noticeable change being a loss of H from the film.

X-ray photoelectron spectroscopy (XPS) indicates the C:N:O ratio within the film, but is not able to provide values for the H content. The formula of the polymer in the annealed film according to XPS is: \( C_{73}N_{11}O_{16}H_{???} \).

Refinement of X-ray reflectivity data for this film gives a \( \text{SLD}_x = 10.4 \times 10^{-6} \text{ Å}^{-2} \)

Refinement of neutron reflectivity data for this film gives a \( \text{SLD}_n = 1.98 \times 10^{-6} \text{ Å}^{-2} \)

Using the XPS results and the Scattering Length Density values determined from the X-ray and neutron reflectivity measurements, calculate the mass density \( r \) and hydrogen content of the annealed film.

<table>
<thead>
<tr>
<th>Composition from XPS</th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>1</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>( b ) (fm)</td>
<td>-3.739</td>
<td>6.646</td>
<td>9.36</td>
<td>5.803</td>
</tr>
<tr>
<td>( M ) (g/mol)</td>
<td>1.008</td>
<td>12.011</td>
<td>14.01</td>
<td>16.00</td>
</tr>
</tbody>
</table>

(Note 1 fm = 1 femtometre = \( 10^{-15} \text{ m} = 10^{-5} \text{ Å} \))

[15 marks]

Useful Equations:
\[
\begin{align*}
\text{SLD}_x &= r_e N_A r Z / M \\
\text{SLD}_n &= N_A r b / M
\end{align*}
\]

\( r_e \): the classical electron radius = \( 2.818 \times 10^{-5} \text{ (units: Å)} \)
\( N_A \): Avogadro’s constant = \( 6.022 \times 10^{23} \text{ (units: } /\text{mol}) \)
\( r \): the mass density of the film (units: \( \text{g/Å}^3 \))
\( Z \): the total number of electrons per polymer molecule in the film
\( b \): the sum of neutron scattering lengths per polymer molecule in the film (units: \( \text{fm} \))
\( M \): the molecular
SECTION C

QUESTION 5

(a) Scanning Probe Microscopy

To obtain topographical information on an atomic scale requires a scanning probe microscope to fulfil four criteria. 1) Strong distance dependent interactions, 2) close proximity of the probe to the object, 3) an exceedingly sharp probe and 4) stable positioning of the probe relative to the surface with an accuracy better than the resolution.

i) Explain the operational principles which allow the first criteria to be satisfied with both scanning tunnelling microscopy and atomic force microscopy.

ii) With STM, electrons must tunnel between a probe which terminates at a single atom and a surface. Show, using the equation which relates tunnelling current to distance, what ratio of the tunnelling current 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 $1.025 \text{ eV}^{3/2} \text{Å}^{-1}$.

iii) Draw a typical force curve with cartoons of the cantilever deflection at crucial points in the force curve. What forces are involved in determining the shape of the force curve. Explain how force curves can be used to determine acidity constants of surfaces.

[10 marks]
(b) X-ray Photoelectron Spectroscopy

The XPS high resolution Carbon 1s spectrum of milk (Water 87.5%, Lactose 4.8%, Fat 3.9%, Proteins 3.4% and minerals 0.8%). is shown below

a. What special sample preparation is required to achieve the spectrum above?
b. XPS essentially detects changes in the core level electronic states. Why can it be used to determine chemical states?
c. How would you quantify the spectrum?
d. What other XPS information would you need in order to compare it with the known composition noted above?

[10 marks]
QUESTION 6

You are given a research project related to develop molecular memory based on the changes in oxidation state of a ferrocene molecule that is attached to the distal end of self-assembled monolayers attached to a silicon surface. That is ferrocene would be the 0 state and the ferricinium ion would be the 1 state. The reading of the state of each ferrocene/ferricinium molecule would be performed using electrochemical STM which can differentiate between ferrocene and ferrocinium by a difference in the tunnelling current. You need to ensure every ferrocene molecule is isolated from all other ferrocene molecules and that each is in a similar environment. Your job is to come up with a strategy to immobilise the ferrocene molecules on the silicon surface. Discuss a strategy in detail to achieve this. You answer should address some or all of the following issues and explain your decisions.

(i) What are the important features for ensuring good packing of self-assembled monolayers
(ii) What sorts of self-assembled monolayer system you might use for silicon
(iii) The requirements the surface modification must achieve.
(iv) How the surface will be modified with ferrocene, that is with a presynthesized ligand or in using a stepwise approach, and the merits of each strategy.
(v) How you will modify the surface to get individual isolated ferrocene molecules on the surface.
(vi) 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.

[20 marks]