NANO 3410 Assignment

X-Ray Photoelectron Spectroscopy and Scanning Tunnelling Microscopy

This assignment is out of 100 marks, divided unequally into 5 questions

Due Tuesday March 27th 2012
Question 1

a) What is the basic principle behind XPS? (1 mark)

b) What does UHV mean? (1 mark)

c) XPS samples that are studied are typically 1 cm$^2$ in size. A gas particle has a radius of 5 Angstroms. How many gas particles can adsorb to form a monolayer on our samples? If we consider that all the molecules in the analysis chamber (more than enough to form a monolayer) collide and adsorb $10^{12}$ times per second with our sample, how long does it take to form that monolayer? This figure goes up to $10^{29}$ times per second in the atmosphere, how long does it take then? What are your thoughts on this? (4 marks)

d) What is considered to be the thickest surface that XPS can reliably be performed on? (2 marks)

e) Why does XPS have these thickness limitations? (3 marks)

f) Are flat surfaces the only materials that XPS can be performed on? If not, what other materials can XPS be performed on? (2 marks)

g) How does XPS have an impact on the surface being measured? (2 marks)

h) How can the signal to noise ratio be improved in XPS? (2 marks)

i) What does it mean if the baseline on the wide scan is staggered? (2 marks)
Question 2

a) What is the most important requirement for the surface in order to perform XPS? (2 marks)

b) Why does the fluorine peak occur at a higher binding energy than the carbon peak? (2 marks)

c) Label the two peaks in the scan below. Why does this narrow scan have two peaks in it? (3 marks)

![C1s Scan](image1)

![Si2p Scan](image2)

d) Label the two peaks in the scan below? Why does this narrow scan have two peaks? (3 marks)
e) How can XPS be used to determine the elemental composition of a surface? (4 marks)

f) Which of the following elements would you use as an XPS marker and why? (2 marks)

<table>
<thead>
<tr>
<th>Element</th>
<th>Orbital</th>
<th>Binding energy</th>
<th>Sensitivity factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>sulfur</td>
<td>2p3</td>
<td>165.5</td>
<td>1.11</td>
</tr>
<tr>
<td>phosphorus</td>
<td>2p3</td>
<td>133</td>
<td>0.789</td>
</tr>
<tr>
<td>iron</td>
<td>2p3</td>
<td>710</td>
<td>10.82</td>
</tr>
<tr>
<td>fluorine</td>
<td>1s</td>
<td>686</td>
<td>4.43</td>
</tr>
</tbody>
</table>
Question 3

a) A researcher wishes to check whether their silicon surface has phosphorus on it. What phosphorus peak should they perform a narrow scan on and why? (5 marks)

b) Below (right) is an Au4f narrow scan of the surface below (left). Why are each of the gold peaks resolved into 2 peaks? (5 marks)

c) Which one of these nitrogen narrow scans below is evidence for a successful ‘click’ reaction and why? (5 marks)
Question 4

A student needs to do a surface modification experiment:

Formation of a self-assembled monolayer of 1,8-nonadiyne on Si (100), followed by a ‘click’ reaction with 11-Azido-3,6,9-trioxaundecanol (below).

![Chemical Structure](image)

**Step 1:** The wafer was thoroughly cleaned by immersion for 30 minutes in a solution of 1:3 H_2O_2/H_2SO_4 (commonly known as piranha solution), leaving the surface free of any contaminants.

**Step 2:** The oxide layer was removed by etching in hydrofluoric acid for 90 seconds, leaving the silicon surface hydrogen-terminated.

**Step 3:** The hydrogen-terminated silicon wafer was then quickly dipped in neat, dry (absence of water, air and any other solvents) 1,8-nonadiyne and left to react in an argon atmosphere at 165°C for 3 h. This reaction is known as hydrosilylation.

**Step 4:** Once the hydrosilylation experiment was over, the student then placed the silicon wafer into a glass test tube, previously cleaned with piranha solution, and immersed it in an aqueous solution of 11-Azido-3,6,9-trioxaundecanol with catalytic amounts of copper sulphate and excess amounts of sodium ascorbate.

a) According to the procedure outlined above, draw the sequence of surface constructs expected, that is the surface bound chemical structures, during each step of the surface modification process. (3 marks)

b) For each step in the modification identify the elements that you expect to be present as well as the number of peaks associated with each element you might expect. (3 marks)

c) Unfortunately, after undertaking the experiment, the student carelessly got several wide scans mixed up; he needs help to find the one he is looking for. Which is the one for his surface and why do you think that this is so? (3 marks)
d) Which narrow scans should the student do on this surface? What information can be gained from each narrow scan? (3 marks)

e) Judging by the scan which was done on a sample analogous to the previous, what do you think of the quality of the surface coverage and why? What would the surface have looked like if otherwise? (3 marks)

f) The student fabricates this surface so they can immobilise a biological molecule on the surface. How would they do this and how would they use XPS to confirm that they have immobilised the biological molecule on the surface? (5 marks)
Question 5

a) Define the term “Density of States”. How does this concept relate to the images received from an STM? (3 marks)

b) Draw the 3D structure of carbon graphite, showing at least 2 layers. How many surface atoms have a neighbouring carbon directly below them in the second layer? How many do not? (4 marks)

c) What form of hybridization does each carbon undergo? Are there any orbitals that are not hybridized? If so, what is their orientation with reference to each carbon sheet? (3 marks)

d) Below is an example of a very good STM image of carbon graphite. The hexagon represents the structure of the surface, with a carbon atom located at each corner. Note how three of the atoms in each hexagon yield a much brighter STM image than the other three. This is shown more clearly in Figure 2.2. With your knowledge of the 3D structure of carbon graphite, sp hybridisation and how the density of states affects an STM image, explain why some carbon atoms are shown as brighter spots than others. In your answer, provide a diagram of the top two graphite sheets and show any non-hybridised orbitals. (This will not only get you marks, but may prove a useful tool in illustrating the concept). (4 marks)

![Figure 2.1](http://medb.colorado.edu/courses/3280/images/afm/08%20angstrom%20graphite.gif)

![Figure 2.2](http://medb.colorado.edu/courses/3280/images/afm/08%20angstrom%20graphite.gif)

*e) Why does an STM give such high vertical (z-direction) resolution? Provide a relevant equation to explain your answer and input some appropriate values into the equation to further explain your answer. (4 marks)

f) What are the advantages and disadvantages of both constant current and constant height modes of an STM. What sample conditions would each mode be most suited to? (4 marks)

g) The figure below gives an idealised force curve measured using an AFM.
i. Explain what the different interactions are at each point on this force curve.
ii. Which way the tip and cantilever would deflect at each point on the curve.
iii. How AFM force curves could allow you to determine the strength of bonds between an antibody and an antigen. Explain how you would do this.

(12 marks)