Surface and Interface Science
Physics 627 / Chemistry 541
Homework 2
Due Monday 1-November 2010

1) Recall that in lecture we argued that the surface energy is related to the cohesive energy of the bulk crystal. In this problem, we will estimate the cohesive energy of a simple metal that is modeled as an array of positive ions of charge e, imbedded in a “free electron gas.” The electron gas it typically parameterized by a dimensionless length parameter r_s where $r_s = r_o / a_o$, where r_o is the radius of the spherical volume associated with one electron (i.e. the volume per electron is $\frac{4}{3}\pi r_0^3$) and a_o is the Bohr radius ($a_o = \frac{\hbar^2}{e^2 m}$).

(a) First we must account for the kinetic energy of the electrons. The maximum kinetic energy of an electron in free electron gas is called the Fermi energy, E_F, which is given by

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

where V is the total volume and N is the total number of electrons in the solid. The density of states (number of electrons per unit energy per unit volume) is given by

$$D(E) = \left(\frac{V}{N}\right)\left(\frac{1}{2\pi^2}\right)\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

The average kinetic energy of and electron is therefore given by

$$\langle E \rangle = \int_0^{E_F} E D(E) dE$$

Show that $\langle E \rangle = \frac{2.21}{r_s^2}$ where $\langle E \rangle$ is measured in Rydbergs (1 Ryd $= \frac{me^4}{2\hbar^2}$).

(b) Recall that the coulomb energy required to assemble a charge distribution is given by $U_C = \int V d\rho$ where V is the electrostatic potential and $d\rho$ is an element of charge. From this, calculate the coulomb energy of a charge distribution consisting of a positive point charge e, surrounded by a uniform sphere of charge with total charge $-e$. Show that this energy can be written as $U = -\frac{3e^2}{2r_o}$ or $-\frac{3}{r_s}$ in Ryd.

(c) Now, using the same approach as in part (b), calculate the coulomb “self-energy” of the electrons by determining the energy associated with assembling a uniform sphere of charge with net charge $-e$. To do this, imagine you have assembled a sphere of radius r ($< r_o$) with uniform charge density $\rho = \frac{e}{\frac{4}{3}\pi r_0^3}$ and consider the incremental energy dU_S associated with adding a spherical shell of charge $\rho 4\pi r^2 dr$. Then integrate from $r = 0$ to $r = r_o$ to find this “self-energy” U_S. Show that this energy can be written as $U_S = \frac{3e^2}{5r_o}$ or $\frac{6}{5r_s}$ in Ryd.

(d) Sum the results of parts (a) , (b), and (c) to find an expression of the total energy in terms of r_S. Minimize the energy with respect to r_s and show that the equilibrium value of r_s is 2.45.

2) A beam of 2 MeV $^4He^{++}$ ions is incident on a silver foil 10^{-6} cm thick and undergoes Coulomb scattering in accordance with the Rutherford formula.
   (a) What is the distance of closest approach?
   (b) Find the impact parameter for He ions scattered through 90°.
   (c) What fraction of the incident 2 MeV He ions will be backscattered (i.e., $\theta > 90°$)?
   [The density of silver is 10.50 g/cm^3 and its atomic weight is 107.88 g/mol. Also, note that the integrated cross section for scattering through angles 0° to 90° is $\int_0^{\pi} d\sigma$.]

3) An α particle, $^4He^{++}$, makes a head-on collision with (a) a gold nucleus, (b) a carbon nucleus, (c) an α particle, and (d) an electron, each initially at rest. What fraction of the α particle's initial kinetic energy is transferred to the struck particle in each instance?

4) Starting with the boxed equation on P. 16 of the notes for Lecture 5 (Tues, Sept 16) derive the relationships between XPS intensity and relative concentration (χ_A/χ_B), overlayer coverage Θ, and film thickness, *d*, found on pages 18, 19, and 20, respectively, of those lecture notes.

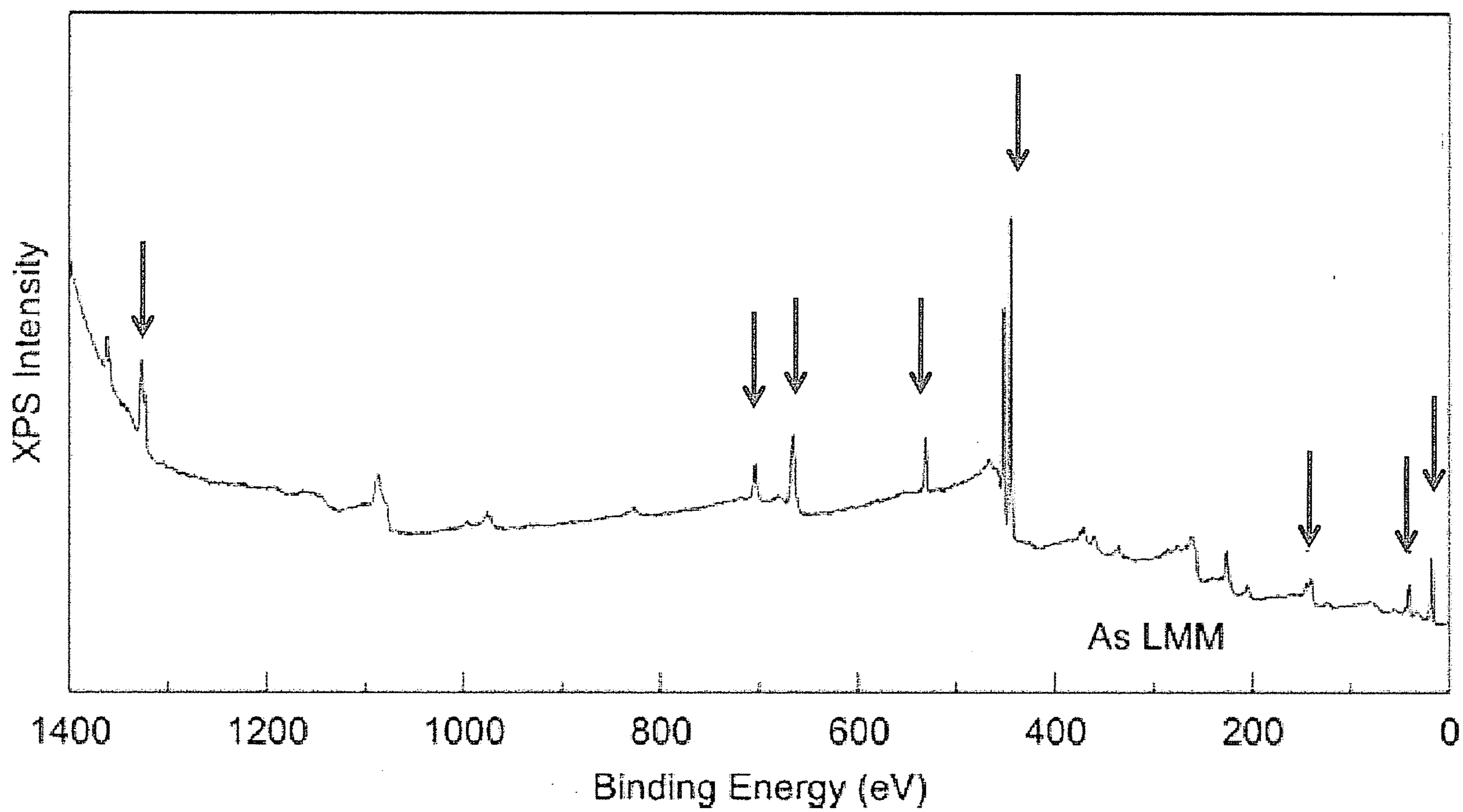
5) XPS is highly surface sensitive owing to the short electron attenuation length, λ(E). At a given energy, E, for normal emission ($\theta = 0°$) what fraction of the total signal from a planar elemental solid comes from the top layer of thickness λ? [Consider the z-dependence of the boxed equation on P. 15 of the Lecture 5 notes.] Calculate the fraction of the total signal for layers of thickness 2λ, 3λ, ... and plot this fraction as a function of depth <u>normal</u> to the surface. Compare the results at $\theta = 0°$ (normal emission) to those with $\theta = 80°$ (glancing emission).

   If you had access to a synchrotron radiation source (where the photon energy is not fixed, but could be varied from ~ 100 eV to ~ 3,000 eV) how would you optimize surface sensitivity in photoelectron spectroscopy? You may wish to choose a particular XPS peak from an element to make your case.

6) The Si $2p_{3/2}$ binding energy is 99.0 eV in elemental Si. When Si is oxidized to SiO_2, a chemical shift [ΔE_B = E(SiO_2) – E(Si)] of 4.0 eV is observed. What is the sign of the chemical shift and why? Using a simple ionic model, calculate the magnitude of the Si $2p_{3/2}$ chemical shift between a free Si atom and a free SiO_2 molecule (use r_{Si} = 1.0 Å). Why is this different from 4.0 eV? If you were able to measure the binding energy of the Si 1*s* level, would you expect the chemical shift to be the same, larger, or smaller than 4.0 eV? Why?

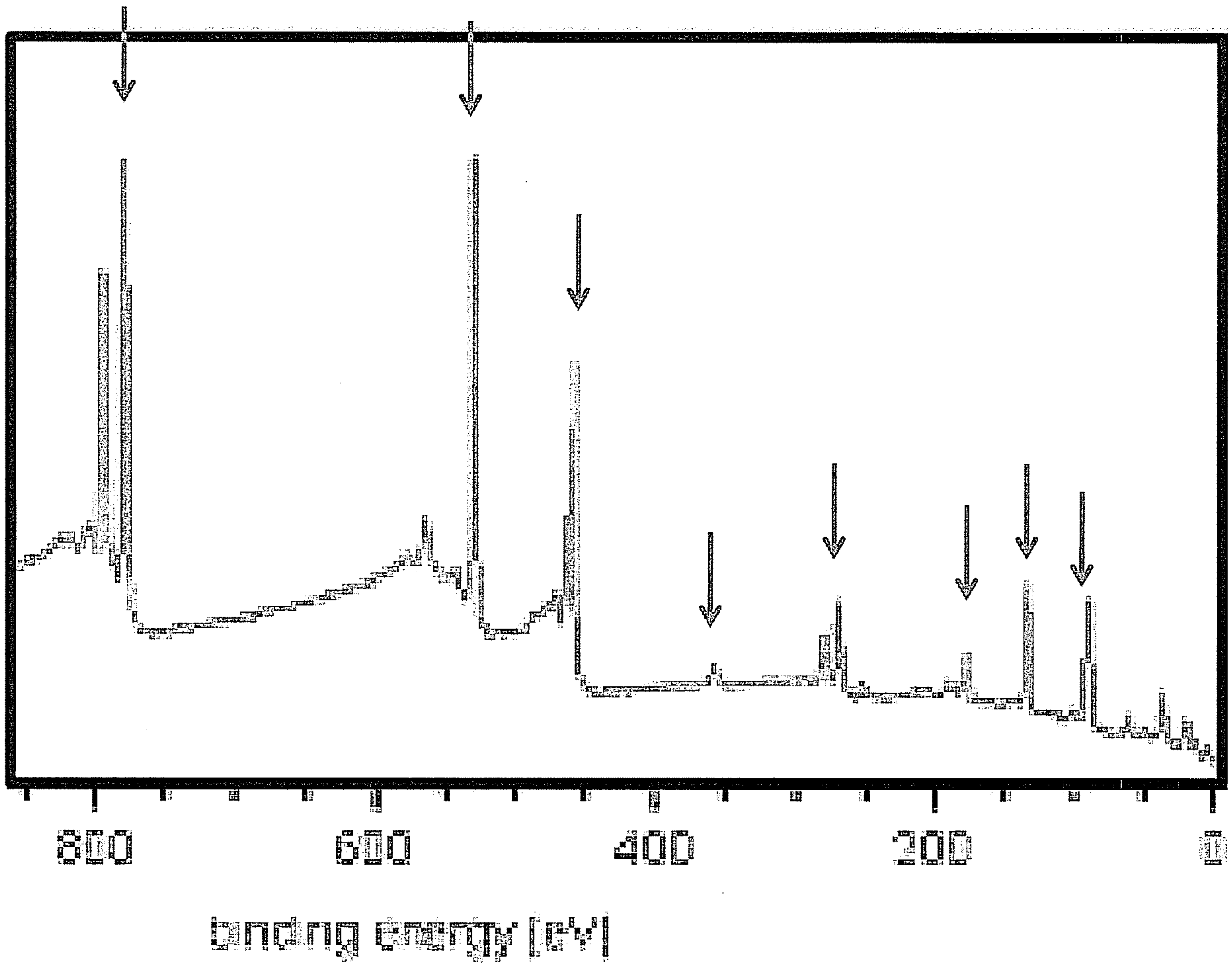
7) Figures (a), (b), and (c) show XPS spectra. In each case, identify (element and core level) all of the major spectral features indicated by the arrows [Note: some are doublets].
   (a) This is a compound semiconductor. Identify the compound. One of the indicated peaks is from contamination. Identify the contaminant. From the relative intensities of the compound peaks and their XPS cross sections, what is the (approx) stoichiometry? [Be sure to remove an appropriate background before considering peak intensities.]
   (b) This is a perovskite compound. Identify the major elements in this complex oxide.
   (c) Transition metal oxide coated semiconductor. Identify the major contaminant.

(a)



XPS Intensity
As LMM
1400
1200
1000
800
600
400
200
0
Binding Energy (eV)

(b)



(c)