

Fundamentals of Electrochemistry
 CHEM*7234 CHEM 720
 Assignment #5

Question 1: In some recently reported work, a group of researchers in Germany used a synchrotron light source to study the electrochemical oxidation of Si by XPS. They performed the electrochemistry in a chamber attached to the beamline, brought it out of solution at different potentials, washed and dried the sample in the controlled environment, and moved it into the analysis chamber, all without exposing it to ambient conditions. They then acquired the XPS spectrum for Si(2p), O(1s) and F(1s) for different preparation conditions. As is standard practice, the experimental spectra were deconvoluted by computer analysis to determine the collection of signals that made up the overall experimental signal. From this they can measure peak shifts and peak areas.

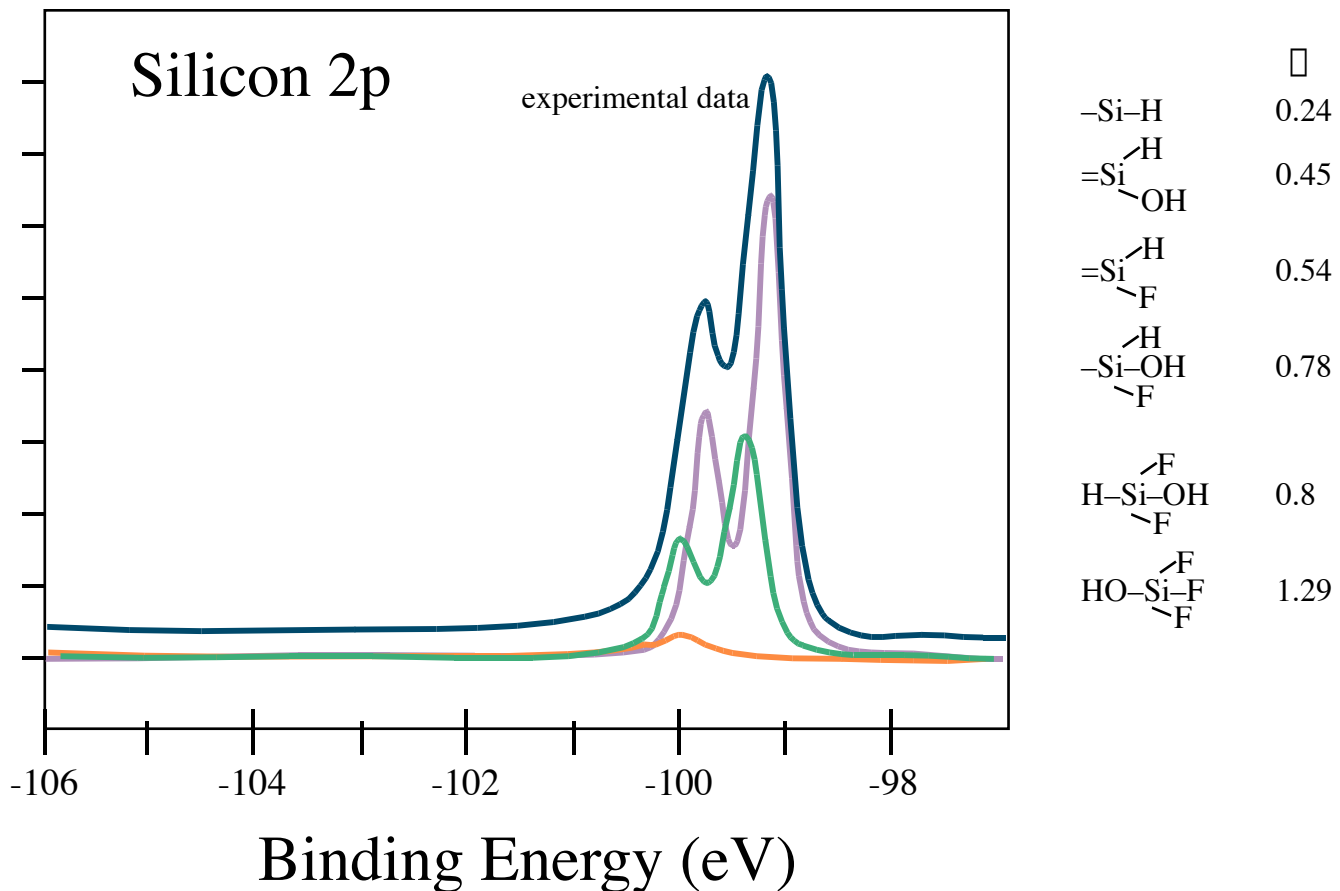
Below is their Si(2p) spectrum for the electrochemically formed H-terminated Si surface. The largest signal is the experimental data while the three small curves are the deconvolution signals of that experimental data. The largest deconvolution peak (in purple) is that arising from bulk Si – it is the unshifted reference peak for Si(2p). The other two peaks arise from some surface species which are to be identified in the experiment.

As part of this study, they performed DFT (density functional theory) calculations on many molecular configurations that might possibly be involved in the reaction at the surface. From these calculations, they determined the fractional charge that resides on the Si atom in each case. It is this variable charge that leads to a shift in the XPS spectrum. In the accompanying table, the fractional Si charge, q , is given for six molecular species (in units of elementary charge e). The first four are still bound to the surface (suggested by the single or double bonds shown on the Si) while the last two are molecular species that could be free. They may still be adsorbed and so need to be considered.

One conclusion of their work was that there was a simple relationship between the fractional charge on Si and the peak shift ΔE (in eV). That relationship was determined to be

$$\Delta E = 2q$$

- (1) Graph this function for $q = 0$ to 2 (yes, this is as easy as it seems).
- (2) Locate the candidate species on the graph and estimate their expected peaks shifts.
- (3) Measure the peak shifts of the two unknown species.
- (4) Identify the two unknowns which are on the surface.
- (5) What is their concentration (peak area) relative to each other? Be creative in estimating this value and explain how you did it.



Question 2: The STM started in 1982 with a publication by Binnig and Rohrer which demonstrated their ability to control electron tunneling through a vacuum gap. Some representative data is found in the accompanying file titled “tunneling_data.txt”. It is a file which reports tip position (gap distance) in Ångstroms vs. tunneling current in amps. The tip position is a relative measure and not absolute gap distance.

In the lecture, we indicated that the relation which predicted the tunneling current as a function of distance z was given by the following expression:

$$I = V \sigma_S \exp(-2\kappa z) \quad \text{where } \kappa = \frac{\sqrt{2m\phi}}{\hbar}$$

Note the dependence upon the square root of the local barrier height, called ϕ . This is something like the work function.

(1) By the use of known constants and unit conversion factors show that the expression for κ can be written as

$$\kappa = 0.512 \sqrt{\phi}$$

when ϕ is expressed in units of eV and κ has units of Å⁻¹.

(2) Download the file tunneling_data.txt, graph the data in the file appropriately, and determine the value of the local barrier height in eV.