Surface XPS Simulator

May 8, 2015

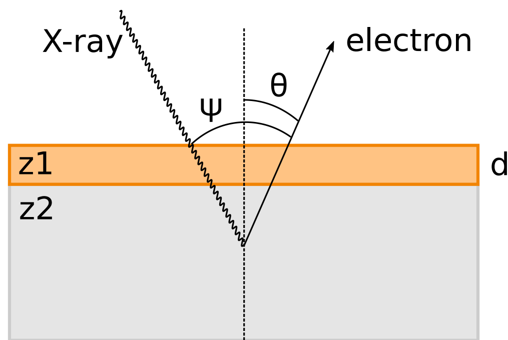


Figure 1: Schematic of photo-emission for a sample of bulk element z2 with an overlayer of element z1 with thickness d.

This document contains basic documentation of the Surface XPS Simulator. Material related to basic XPS theory has been obtained from [1] and [2].

1 List of files

```
README.pdf

RUN:
COMMAND.m
GUI.fig
GUI.m

examples:
instructions_si_example.m
instructions_si_example_roughness_final.m
si_ex_plot.m
si_example_plot_peaks.m
silicon_example.m

plotting:
ddf1_with_roughness.m
ddf2_with_roughness.m
depth_plot.m
depth_plot_with_roughness.m
imfp_plot.m
make_description.m
make_peak_names.m
schematic_plot.m
schematic_plot_with_roughness.m
surface_xps_simulatorv6.m
xps_lineshape.m
xps_plot.m

spectrum:
calculate_energies.m
calculate_intensity_bulk.m
calculate_intensity_bulk_with_roughness.m
calculate_intensity_layer.m
calculate_intensity_layer_with_roughness.m
calculate_spectrum.m
integrated_ddf2_with_roughness.m
mean_free_path.m
relative_sensitivity_factor.m

support:
binding_energies.csv
clear_peaks.m
cross_sections.csv
read_be_database.m

tracking:
track_peak_theta.m
track_peaks_alpha.m
track_peaks_depth.m
track_peaks_energy.m
track_peaks_theta.m
user_peaks.m
```

2 XPS line intensities under normal assumptions

Typically, XPS intensities for a surface normal geometry are modeled as [1]:

$$I = F_x \left(\frac{d\sigma_x}{d\Omega} \right) \lambda M x f A_0 T D \Delta\Omega \tag{1}$$

where the relevant parameters are:

I	Photoelectron signal intensity
F_x	X-ray beam flux
$\frac{d\sigma_x}{d\Omega}$	photoionization cross section of the atoms in the sample
λ	$1/e$ attenuation length for electrons traveling within the sample. The Surface XPS Simulator uses the inelastic mean free path.
M	Density of the sample in atoms per unit volume
x	Fraction of atoms in the sample that are emitting electrons
f	Fraction of photoelectrons contributing to the main spectrum peak
A_0	Area of the sample irradiated and viewed by the electron analyzer
T	Electron analyzer's transmission function
D	Detection efficiency
$\Delta\Omega$	Solid angle of the electron analyzer

3 Line intensities for sample with a surface layer

In the surface XPS simulator, we consider a sample composed of a bulk material covered by an overlayer of a different composition (fig. 1). For simplicity, we restrict ourselves to the pure elements from hydrogen to gold (typically hydrogen and helium are not detectable in XPS due to their low cross sections [2]). We model how the line intensities are changed from the case of a homogeneous bulk sample. Specifically, the mock spectrum is calculated as (*calculate_spectrum.m*):

$$I(E) = \sum_{i,n} A_{n,i} g(E - E_{n,i}), \tag{2}$$

where g is the lineshape function, and $A_{n,i}$ is the area of the ith peak for element n, with binding energy $E_{n,i}$. The sum is over all of the binding energies for each of the elements, as tabulated in [3]. The peak areas are calculated in the Matlab functions *calculate_intensity_bulk.m* and *calculate_intensity_layer.m* as

$$A_{1,i} = I^{\circ}_{1,i} \exp\left(-\frac{d}{\lambda_2(h\nu - E_{1,i})\cos\theta} \right) \tag{3}$$

$$A_{2,i} = I^{\circ}_{2,i} \left[1 - \exp\left(-\frac{d}{\lambda_2(h\nu - E_{1,i})\cos\theta} \right) \right] \tag{4}$$

Line-shape *xps_lineshape.m* Gaussian lineshape with fixed width of $\sigma_E = 0.25$ eV.

$$g(E) = \frac{1}{\sigma_E \sqrt{2\pi}} \exp\left(\frac{-E^2}{2\sigma_E^2} \right) \tag{5}$$

Electron kinetic energy cutoff *calculate_spectrum.m* Ignore electron kinetic energies below 10 eV. This can be changed by changing `Ecut`. In reality, electrons with kinetic energies lower than the work-function (combined XPS spectrometer and material work function) will not make it out of the sample.

Electron trajectory and interactions We use the straight line approximation, ignoring elastic interactions, and assume an exponential dependence of the escape probability on the electron path length (l) within the sample ($P(l) = \exp(-l/\lambda)$).

Inelastic mean free path *mean_free_path.m* Use a "universal curve" model of the inelastic mean free path for the pure elements as a function of electron energy [4]:

$$\lambda_n(E) = r_n \left(\frac{538}{E^2} + 0.41\sqrt{r_n E} \right), \tag{6}$$

where n indexes the element, r_n is the monolayer thickness, and E is the electron energy. We use the Van der Waals atomic radius for r_n as an approximation to the monolayer thickness, as these values are conveniently tabulated in the CRC Handbook [5].

Relative sensitivity factor *relative_sensitivity_factor.m* Use a simple theoretical model implemented on some commercial instrument systems to account for energy-dependent attenuation factors and analyzer response functions. [6] The intensity of each line is referenced to the intensity of the C 1s line through:

$$I^{\circ}_{n,i} = \frac{I_{n,i}}{I_{C1s}} = \sigma_{n,i} \left(\frac{E_{k,i} - E_{C1s}}{E_{C1s}} \right)^{p+q} \tag{7}$$

where $I^{\circ}_{n,i}$ is the intensity of the line i for element n, I_{C1s} is the intensity of the C1s peak under the same conditions, $\sigma_{n,i}$ is the photoionization cross-section, and energies are the kinetic energies for the lines. Exponents p and q account for the energy dependence of the IMFP and electron analyzer response, and are approximated as -0.5 and 0.75, respectively. Detailed calculations exist for how this model deviates from empirical data.

Photoionization cross-section Scoffield photoionization cross sections for Al K_α X-rays are used [7]. The cross sections are therefore inaccurate for photon energies significantly different from 1487 eV. These values are stored in the file *cross_sections.csv*. Cross-sections are only included for the more intense lines for each element; the remaining values are treated as zero.

Electron depth distribution *depth_plot.m* For a bulk material (n), the depth distribution of electrons with energy E_k is [1]

$$\phi^{(\infty)}(E_k, z) = \exp\left(-\frac{z}{\lambda_n(E_k)\cos\theta} \right) \tag{8}$$

For the layer system that we consider, the finite thickness of the overlayer and the attenuation of bulk electrons by the overlayer have to be included to satisfy the normalization condition $A_{n,i} = \int dz \phi_{n,i}(z)$:

$$\phi_{1,i}(z) = \frac{A_{1,i}}{\lambda_1(E_{k,i})\cos\theta} \exp\left(\frac{-(z-d)}{\lambda_1(E_{k,i})\cos\theta} \right) \tag{9}$$

$$\phi_{2,i}(z) = \frac{A_{2,i}}{\lambda_2(E_{k,i})\cos\theta} \left[1 - \exp\left(\frac{-d}{\lambda_2(E_{k,i})\cos\theta} \right) \right]^{-1} \exp\left(\frac{-z}{\lambda_2(E_{k,i})\cos\theta} \right) \tag{10}$$

where z is the depth. To account for the fact that we have multiple peaks, we normalize by the sum of all peak areas, and we add up the contributions from all of the lines.

4 Roughness

The simulator models roughness of the overlayer with a triangular prism model (refer to the schematic produced in the simulator), with roughening angle α (`alpha`), and `depth` referring to the height of the triangle apex with respect to the interface.
Peak intensities are calculated under the same approximations as in the smooth case. Shadowing is assumed to be complete and electrons are assumed to travel with a straight-line trajectory. For further details, refer to the comments in the files: *calculate_intensity_layer_with_roughness.m*, *calculate_intensity_bulk_with_roughness.m*, *ddf1_with_roughness* and *ddf2_with_roughness*.

5 Basic instructions

First, make sure that all of the files are in Matlab's search path.

Start up Users have the option to use a command line or graphical user interface.

Graphical Interface

```
>>GUI
```

Select atomic composition for the bulk and overlayer, photon energy, detector angle (0-90 degrees), thickness of the sample, and roughness (1-90 degrees). Note that the graphical user interface only calls `with_roughness.m` functions and therefore roughness angle must be greater than zero.
Click on "Simulate XPS!" to generate XPS spectrum with an auxiliary diagrams of electron depth distribution, mean free path, and geometry of selected parameters.
Tracking functions may be invoked by clicking on the checkbox next to each parameter and referring to instructions in the command line (see below).

Command Line Interface

```
>> COMMAND % Enter spectrum parameters and calculate the XPS spectrum
```

Enter `z1`, `z2`, `depth`, `Ep` and `theta`, as prompted.

```
>> surface_xps_simulatorv6 % Plot the XPS spectrum
```

All of the values specifying the sample and the spectrum are stored in the workspace.

`z1`	atomic number of the bulk element
`z2`	atomic number of the overlayer element
`Ep`	photon energy (eV)
`depth`	thickness of the overlayer (nm)
`theta`	θ (radians)
`Eb1, Eb2`	binding energies for the bulk and overlayers, respectively
`intensities1, intensities2`	intensities of the peaks for bulk and overlayer, respectively
`xps_spectrum`	2-row array of the spectrum: energy bin value in row 1, intensity in row 2
`pk_intensity`	peak intensities from tracking functions: parameter bin value (θ, $h\nu$, d or α), remaining rows are intensities of the peaks being tracked

Adjust values by changing them in the workspace. You can also modify the data in the `binding_energies` database, and it will not be overwritten on subsequent calls to `COMMAND` and `surface_xps_simulatorv6`. Always rerun `COMMAND` and `surface_xps_simulatorv6` after modifying a parameter to re-calculate the spectrum and to refresh the plots.

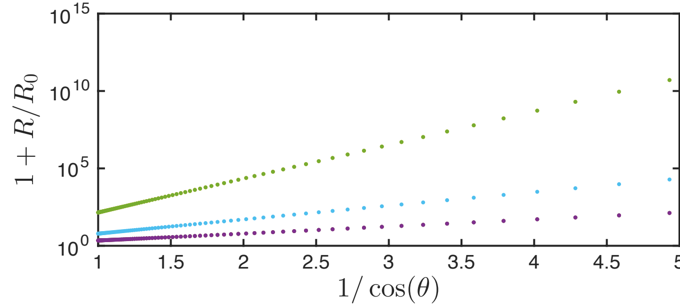
Example: angle-resolved XPS

```
>> COMMAND % Start up the simulator
Surface XPS simulator

Atomic number of the bulk material:  14
Atomic number of the overlayer element:  8
Bulk Si with an overlayer of O
Depth of overlayer in nm:  1
Detection angle in degrees:  20
Photon energy in eV: 1487
Do you want to include roughness? (y/n) n
```

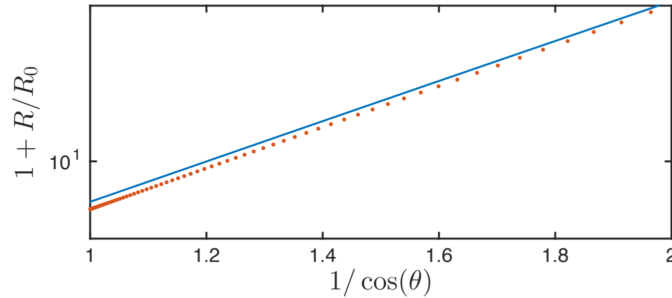
```
>> surface_xps_simulatorv6 % Create the spectrum plot


>> theta = 60*pi/180   % Reset theta to 60deg.  Value must be entered in rad.

theta =

    1.0472

>> COMMAND % Recalculate the spectrum
Surface XPS simulator

Bulk Si with an overlayer of O
Do you want to include roughness? (y/n) n

>> surface_xps_simulatorv6 % Refresh the plots.


>> theta = 70*pi/180 % Reset theta to 70deg.

theta =

    1.2217

>> COMMAND % Recalculate the spectrum
Surface XPS simulator

Bulk Si with an overlayer of O
Do you want to include roughness? (y/n) n
>> surface_xps_simulatorv6 % Refresh the plot.
```

Track peak intensities with angle, photon energy, layer thickness or roughening angle Call the appropriate script `track_peaks_theta`, `track_peaks_energy`, `track_peaks_depth` or `track_peaks_alpha`. Specify the peaks to track and the range of the parameter value to vary, as prompted. See the example plot shown in figure **??**.
Example usage:

```
>> track_peaks_theta
Track a peak for Si or SiO2? (1 / 2) 1
Which peak? (Peaks are counted from high to low energy)3
Enter another peak? (y/n) n
Start angle (deg): 0
Final angle (deg): 90
Number of steps 100
```



(a) Demonstration of the relationship $d = L\cos\theta\ln(1 + R/R_0)$ used to measure film thicknesses via XPS. R is the ratio of the Si2p peak intensity in pure Si to that in SiO_2, and R_0 is the calibration ratio, using the values from bulk Si and SiO_2. Green, blue and purple points correspond to depths of 5 nm, 2 nm ans 1 nm, respectively.



(b) Comparison of using the Si2p peak (points) or the O1s peak (line) for film thickness measurement. The comparison demonstrates that equation 11 is an approximation, relying on the overlayer and bulk peaks being similar in energy.

Figure 2: Example exercise: Film thickness measurement for SiO_2/Si, using angle-resolved XPS.

6 SiO_2/Si example

We provide examples of simulating angle-resolved XPS experiments. The comparison to experiments is primarily limited by the IMFP model.

Film thickness measurement Film thickness measurement commonly uses the relationship [8]:

$$d = L\cos\theta\ln\left(1 + \frac{R}{R_0}\right), \tag{11}$$

to extract the film thickness d from angle resolved XPS measurements, where in this case R is the ratio of the Si2$p_{1/2}$ peak intensity in pure Si to that in SiO_2, R_0 is the calibration ratio, using the values from bulk Si and SiO_2, and L is the effective attenuation length (EAL) of the Si2p electrons in the oxide layer.

Guided exercise The file *instructions_si_example.m* is a guided exercise in film thickness measurement for SiO_2/Si. Copy paste the instructions line by line into the Matlab command line. Figure 2 shows some of the results generated in the exercise.

References

[1] C.J. Powell, A. Jablonski, Journal of Electron Spectroscopy and Related Phenomena **178-179**, 331 (2010)

[2] P. Van der Heide, *X-ray photoelectron spectroscopy: an introduction to principles and practices* (Wiley, Hoboken, N.J., 2012)

[3] G.P. Williams, *Electron Binding Energies* (Lawrence Berkeley National Laboratory, Berkeley, California, 2009), 3rd edn., chap. 1.1. URL `http://xdb.lbl.gov`

[4] M.P. Seah, W.A. Dench, Surface and Interface Analysis **1**, 2 (1979)

[5] M. Mantina, R. Valero, C.J. Cramer, D.G. Truhlar, in *CRC Handbook of Chemistry and Physics*, 95th edn. (CRCnetBASE, 2014). URL `http://www.hbcpnetbase.com/`

[6] G.C. Smith, *Compositional analysis by Auger electron and X-ray photoelectron spectroscopy* (CRC Press, 1998), pp. 189–195

[7] J.H. Scofield, Journal of Electron Spectroscopy and Related Phenomena **8**, 129 (1976)

[8] M.P. Seah, S.J. Spencer, F. Bensebaa, I. Vickridge, H. Danzebrink, M. Krumrey, T. Gross, W. Oesterle, E. Wendler, B. Rheinländer, Y. Azuma, I. Kojima, N. Suzuki, M. Suzuki, S. Tanuma, D.W. Moon, H.J. Lee, H.M. Cho, H.Y. Chen, A.T.S. Wee, T. Osipowicz, J.S. Pan, W.A. Jordaan, R. Hauert, U. Klotz, C. van der Marel, M. Verheijen, Y. Tamminga, C. Jeynes, P. Bailey, S. Biswas, U. Falke, N.V. Nguyen, D. Chandler-Horowitz, J.R. Ehrstein, D. Muller, J.A. Dura, Surface and Interface Analysis **36**, 1269 (2004)