

# Protokoll: X-Ray Photoelectron Spectroscopy

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## 1 Motivation

The phenomena of the photoelectric effect is known since the beginning of the 20th century and lead to many methodes to examine surfaces of solid state bodies. One particual methode is the X-ray photoelectron spectroscopy or short **XPS**. It can give a good understanding of the composition of an solid state and furthermore it yields information about the chemical bounds between the different elements of the sample, effectively taking a fingerprint that can easily compared with similar samples.

## 2 Fundamentals

To analyze the chemical and physical structure of a surface one can use photoelectron spectroscopy (PES). For this high energetic electromagnetic radiation is applied to the surface. Due to this radiation the electrons bound to the atoms become excited and will be removed from the surface. In order to leave the solid body they have to overcome the binding energy  $E_{\text{bin}}$  and the work function  $\phi$  and they will have a kinetic energy of

$$E_{\text{kin}} = h\nu - E_{\text{bin}} - \phi, \quad (1)$$

where  $h\nu$  is the energy of the incident photon. In order to release the electrons the photon energy has to be higher than the binding energy and the work function. Therefore high energetic X-Rays ( $h\nu > 1000 \text{ eV}$ ) will be used for the excitation. This method is named X-Ray photoelectron spectroscopy (**XPS**). Due to the different types of binding and the corresponding difference in binding energy, the released electrons have distinct kinetic energy, which makes it possible to determine the target material composition and also the types of binding. A closer look at the processes after the absorption of a photon by an electron shows three stages in the progress of the particle:

1. The absorption of the photon and the excitation of the electron,
2. The transport of the electron to the surface and
3. The release of the electron followed by the detection.

On the second stage the electrons can scatter and lose some of their momentum and therefore result in a background noise for the measurement. Additionally to the specific peaks of the unscattered electron and the background one will notice peaks beneath the main peaks of one electronic state caused by small shifts in the binding energy due to the superposition of electronic and atomic states. This phenomenon is called chemical shift and for this experiment, is mainly a result of oxidation of the surface. In summary the intensity of measured electrons one yields from the radiated sample can be expressed as

$$I(E_i, X_i) = I_{h\nu} T(E_A) A_{\vartheta} \int_{\Omega=0}^{\Omega_0} \frac{\delta\sigma_X}{\delta\Omega} d\Omega \int_0^d D_X(z) \exp\left(-\frac{z}{\lambda_{\text{mfp}} \sin(\vartheta)}\right) dz. \quad (2)$$

$T(E_A)$  : function of transmission of the apparatus

$A_{\vartheta}$  : adjusted surface of the sample towards the detector, at an solid angle  $\Omega$ ,  $\vartheta$

$E_i$  : energy level  $i$

$D_X(z)$  : density of electrons at the depth of the sample  $z$

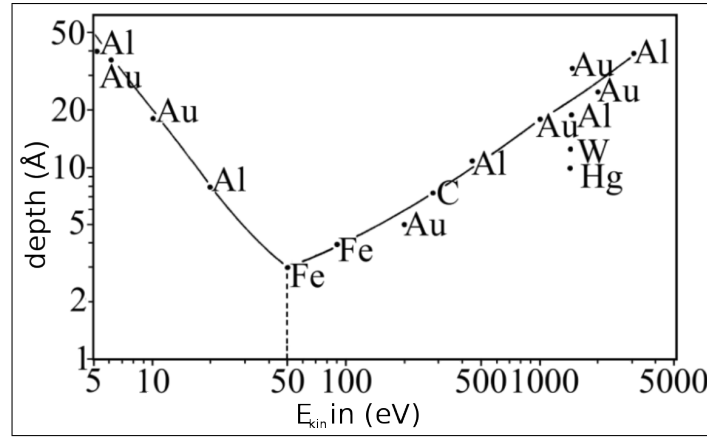
$\sigma_X$  : cross section of interaction between an electron at  $E_i$ ,  $h\nu$

Furthermore one has to consider, that the photons or more specifically the electrons that add to the detected yield, can vary strongly with the depth of the absorption of the photon or respectively the depth of the origin of the electron. X-ray-photons can penetrate the surface of a solid body by up to a few  $\mu\text{m}$ , while the usual mean free path of an electron is not more than a couple of  $\times$ . That means that the deeper the electrons originate, the less unscattered

electrons will be detected. The statistical relation according to Lamber-Beer can be expressed as

$$I_e(\lambda_{\text{mfp}}) \propto \exp\left(-\frac{z}{\lambda_{\text{mfp}}}\right). \quad (3)$$

In conclusion to that, a penetration depth  $d \sim 3\lambda_{\text{mfp}}$  can be defined, while the mean free path of the electron is dependent on its energy, its surroundings and the traveling direction. Experimental results for some metals and their penetration depth are shown in fig.1



**Figure 1:** Exit depths of different metals over kinetic energy.[1]

The mean free path can be expressed as

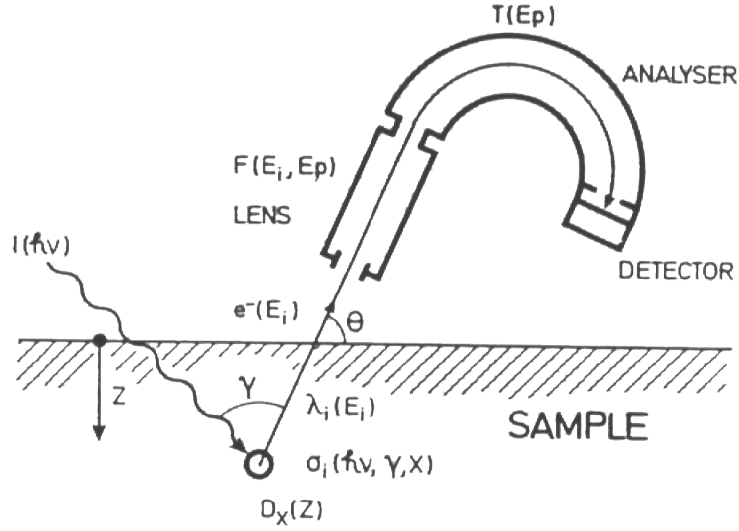
$$\lambda_{\text{mfp}} = \frac{538 \cdot a[\text{nm}]}{(E_{\text{kin}}[\text{eV}])^2} + 0,41 \cdot a^{3/2}[\text{nm}^{3/2}] \sqrt{E_{\text{kin}}[\text{eV}]} . \quad (4)$$

Quantitative expressions about the composition can be achieved by the comparison of the peak areas  $A_i$ . One also has to consider different atomic sensitivity factors  $ASF_i$  for the different elements. In conclusion is the concentration of an element  $i$  in an spectrum with multible elements  $j$  given as followed

$$c_i = \frac{A_i \cdot ASF_i^{-1}}{\sum_j A_j \cdot ASF_j^{-1}} . \quad (5)$$

### 3 Realisation and Execution

This experiment utilizes a vacuum chamber at a pressure of approximately  $10^{-8}$  mbar, which contains the rest of the apparatus, a x-ray tube with Mg as anode material, a fixture for the target with the ability to set the angle of incidence and an energy analysing detector for the secondary electrons. For the general measurement shown in fig.2 one uses the characteristic radiation of Magnesium  $K\alpha$  at a frequency of 1253 eV. The incident radiation excites the bound electrons in the lower orbitals of the atoms. These electrons leave the atom with a distinct lower kinetic energy than the incident photons, since they need to overcome their binding energy. This distinct energy difference can be detected and will show up as peaks in the energy diagram. This type of measurement is done multiple times to compensate the statistical noise and also done with higher resolution for certain peaks in the spectrum (O1s, C1s, Si2p).

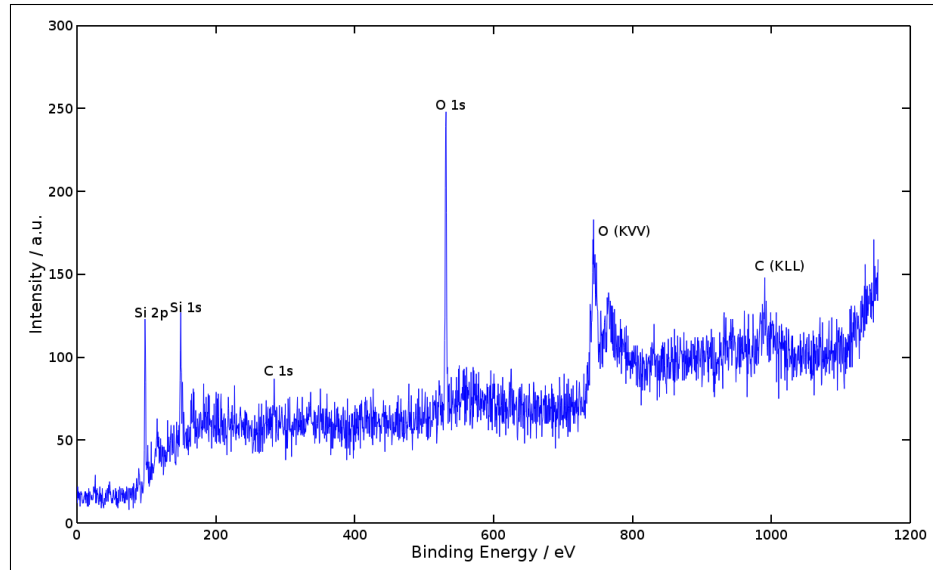


**Figure 2:** Schematic realization of the experiment.

## 4 Analysis

### 4.1 Overview Spectrum

The first measurement consist of the making of a overview spectrum for the target witha an energy intervall of 100 – 1253 eV in steps of 0,5 eV. To minimize the signal to noise ratio the mesurement is iterated over 10 cycles. The spectrum is shown in fig.3



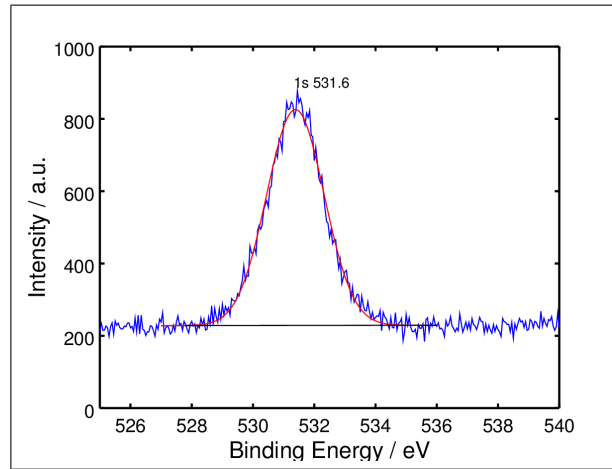
**Figure 3:** Overview spectrum of the Silicon target.

The elements and nuclear niveaus corresponding to the energy peaks in the mesurement are matched with the the given data from the instruction manual. One distinctly notices, that the nuclear nievaus for Oxygen, Silicon and Carbon and the KLL-Auger-Lines and for Carbon and the KVV-Lines for Oxygen are matching the signal. Due to the limitations for the maximum energy given by the  $MgK\alpha$ -radiation higher nuclear levels and the Silicon-Auger-Lines can not observed in this spectrum.

### 4.2 Single peaks

In the following three of the peaks from the overview spectrum shall be examined more closely. For this, new mesurements are made in the respective energy intervalls at a higher resolution with 10 iterations per peak. The first peak is the 1s peak of Oxygen at 531,6 eV peak energy. The mesurement with a noise fit and gaussian fit is shown in fig.4. The mesurement confirms the expectations for the position of the peak.

The second peak is the 1s peak of Carbon. This peak is expected at an energy of 284,6 eV for polyethylene. The fig.5 shows the mesured data with the background noise fit and the gaussian fit. In contrast to the Oxygen peak, this



**Figure 4:** Intensity of the photoelectron in an energyinterval near the O 1s binding energy. The blue line represents the measured data, the black line represents a fit for the background noise and the the drawn line red line represents a gaussian fit for the datapoints.

measurement has a noticeably worse signal to noise ratio due to the relatively low yield for this peak.

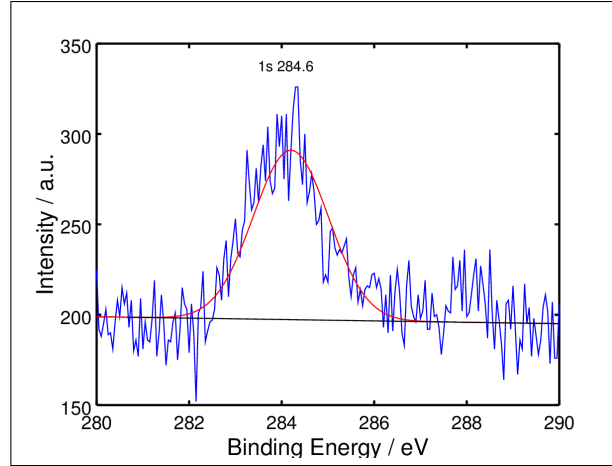
The third peak is the 2p peak of Silicon. The peak is expected at an energy of 99,15 eV with a secondary peak at 103,4 eV due to a chemical shift of Silicon bound in SiO<sub>2</sub>. The Measurement is shown in fig.6 with a background fit, two gaussian fit for the respective peaks and the combined value of the gaussian fits. The measured data matches the expected position of the peaks.

### 4.3 Concentration of the Elements

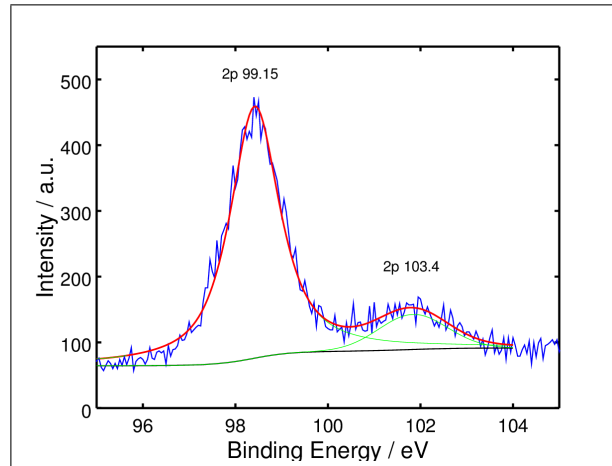
To determine the concentration of the mesured elements, once can use (5) and insert the area under the gaussian fit for  $A$ . The  $ASF$  is taken from the instruction manual. The calculated concentrations are shown in tab.1. The calculations impy, that the target consist of 42% Silicon, where 6% of that occurs in a bound with 2 Oxygen. Thus, one can assume, that 12% of the Oxygen yield is bound to Silicon, where the remaining 27% will be bound to the Carbon or other soiling.

**Table 1:** Comparison of the different elements and their concentrations.

Element	Bondingstate	$A / \text{a.u.}$	$ASF$	$c$
O	1s	1384,83	0,711	0,39
C	1s	191,35	0,296	0,13
Si	2p	719,35	0,339	0,42
SiO <sub>2</sub>	2p	98 95	0 339	0,06



**Figure 5:** Intensity of the photoelectron in an energyinterval near the C 1s binding energy. The blue line represents the measured data, the black line represents a fit for the background noise and the the drawn line red line represents a gaussian fit for the datapoints.



**Figure 6:** Intensity of the photoelectron in an energyinterval near the C 1s binding energy. The blue line represents the measured data, the black line represents a fit for the background noise and the the drawn line red line represents a gaussian fit for the datapoints.



## 5 Apendix

### References

- [1] L. E. Davis J. F. Moulder C. D. Wanger, W. M. Riggs and G. E. Muilenberg.  
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