

# X-Ray Photoelectron Spectroscopy (XPS/ESCA)

- surface analysis
- chemical composition
- air sensitive samples
- information depth  
1 nm – 2  $\mu$ m

XPS (X-ray Photoelectron Spectroscopy) or ESCA (Electron Spectroscopy for Chemical Analysis) is based on the principle that X-rays hitting atoms generate photoelectrons. It is a typical example of a surface-sensitive technique. Only electrons that are generated in the top few atomic layers are detected. In this way quantitative information can be obtained about the elemental composition of the surface of all kinds of solid material (insulators, conductors, polymers). An important strength of XPS is that it provides both elemental and chemical information.

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**PHILIPS**

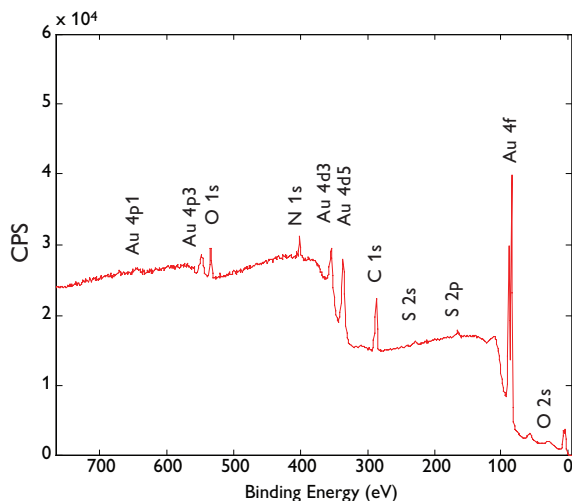


Fig. 1: XPS spectrum of a self-assembled monolayer (SAM-layer) of biotinylated alkyl thiol (see figure 2) on gold. XPS peaks of C, N, O, S and Au, can be observed. The appendix to the element symbol, e.g. 1s or 2p, denotes the atomic orbital from which the electrons originate.

### Basic principle

Bombarding a sample in vacuum with X-rays gives rise to the emission of electrons. If monochromatic X-rays are used with a photon energy  $h\nu$ , the kinetic energy of the emitted electrons  $K_e$  is given by:

$$K_e = h\nu - B_e - \phi$$

where  $B_e$  is the binding energy of the atomic orbital from which the electron originates and  $\phi$  is the work function. The work function is the minimum amount of energy an individual electron needs to escape from the surface.

Each element produces a unique set of electrons with specific energies. By measuring the number of these electrons as a function of kinetic (or binding) energy, an XPS spectrum is obtained. All elements can be detected, except H and He. Figure 1 shows an example of a survey spectrum of a SAM layer (self-assembled monolayer) on gold. XPS peaks of C, O, Au, N and S can be observed.

### Chemical state

Binding energies of photoelectrons depend on the chemical environment of the atoms. Accurate measurement of the exact peak position of the elements present gives information on the chemical state of these elements. Figure 3 shows a more detailed XPS spectrum of the sulphur peak of the SAM layer. A good fit of the signal is obtained using two doublets indicating two different chemical environments of the sulphur atoms.

### Depth profiling

To obtain information at larger depths (1 – 2  $\mu\text{m}$  at most), concentration profiles can be recorded by alternating sputtering with  $\text{Ar}^+$ -ions and spectrum collection. Typical sputter rates are 5 - 10 nm/min. A disadvantage of sputtering is that the chemical state of the elements present may change due to the ion bombardment. In addition, the elemental composition may be influenced by preferential sputtering.

### Inert atmosphere

It is also possible to analyze samples that are sensitive to oxygen, nitrogen and/or water. These samples can be prepared in an argon atmosphere and transported to the XPS instrument without exposure to ambient air.

### Micro XPS

With the aid of a focused X-ray beam it is possible to obtain data from areas as small as 10  $\mu\text{m}$  in diameter. Scanning the beam over the sample allows the acquisition of a two-dimensional element map as shown in figure 4. This map makes accurate positioning of the X-ray beam possible enabling spatially resolved studies.

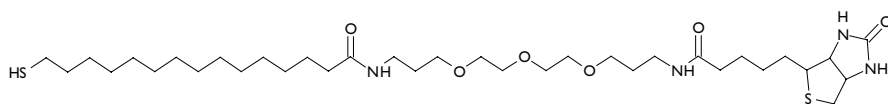
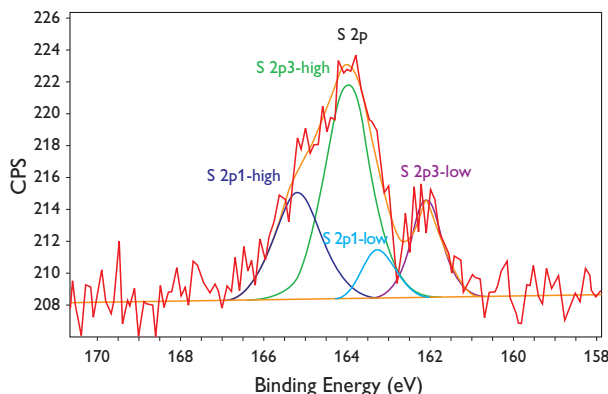


Fig. 2: Molecular structure of biotinylated alkyl thiol (BAT).

Fig. 3: XPS spectrum of S in BAT on gold (see figure 2). Two doublets (high and low) can be fitted to the signal indicating two different chemical states of sulphur: The S 2p-low doublet at 161.9 eV corresponds to the sulphur as Au-thiolate, the S 2p-high doublet at 163.9 eV corresponds to sulphur in the unbound thiophene groups.



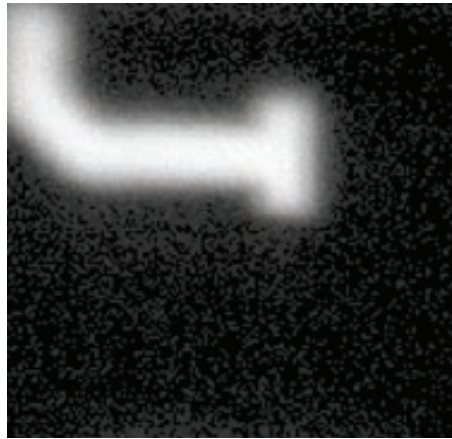
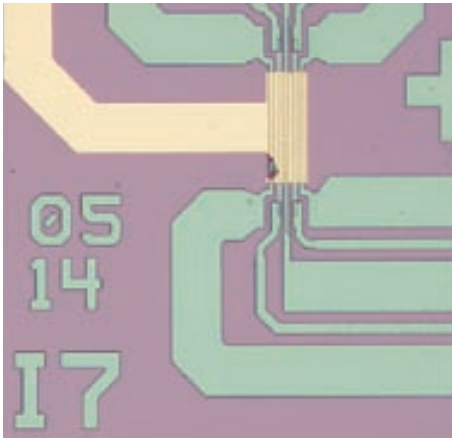


Fig. 4: At the left a photograph of a pattern of gold lines in a biosensor is shown. These gold lines are present at different depths within the device. At the right the Au X-ray image of the same sensor is shown. Only the gold line on the upper surface shows up. This area is covered by a SAM layer.

### Quantitative analyses

The number of detected electrons is a measure for the elemental concentration. In order to obtain quantitative results, peak areas are divided by standard sensitivity factors and normalized to 100% to obtain atomic concentrations. In this way, for bulk materials the surface composition can be determined with a 20% inaccuracy in concentration. However, most materials do not have a homogeneous chemical composition in the upper few nanometers, but rather a composition that varies as a function of depth. In the case of a real multi-layer system the signal of an element in a lower layer will be attenuated more strongly than the signal from an element in the top layer. To obtain quantitative information for non-homogeneous samples, either angle-resolved measurements or model calculations can be performed.

### Angle-resolved measurements

A way to get more insight into the composition of a non-homogeneous sample is to measure a number of spectra at different measuring angles. Variation of the emission angle causes changes in the effective information depth of analysis. At glancing incidence (small angles) only the upper layers of the sample are examined; at high measuring angles deeper layers are detected. With respect to SAM layers angle-resolved measurements give qualitative information about the position of the sulphur in the layer. In figure 6 ratios are shown of the relative concentrations of different elements in a SAM layer, measured at different angles. The lower the concentration ratio the deeper the element is positioned in the sample. Obviously, the sulphur is closest to the Au substrate (see figure 5).

### Model calculation

For the analysis of multilayer systems, a model calculation method has been developed. With the model only one measurement at one measuring angle is needed to determine thickness and composition of each layer on the substrate. SAM layers on gold can be seen as multilayer systems due to their ordered structures. For such layers the model gives insight into the layer composition and allows the coverage of the gold with sulphur to be calculated (figure 7).

Fig. 5: Schematic of a self-assembled alkane-thiol layer on gold. SAM layers play an important role in the development of biosensors. The strong chemical interaction between the thiol (SH) and the gold surface plus the chain-to-chain interaction of the molecules (e.g. van der Waals forces) forces the molecules to align parallel to each other on the gold surface.

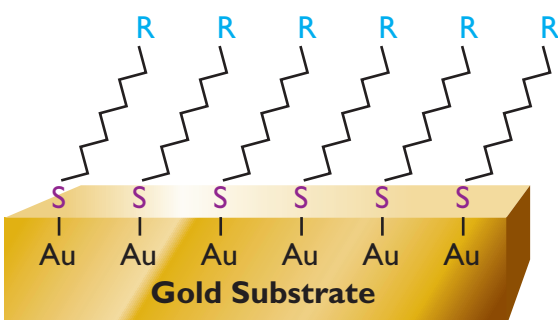


Fig. 6: Concentrations measured at 25 and 45 degrees divided by the concentrations measured at 90 degrees for a SAM layer based on  $\text{CH}_3 - \text{O} - (\text{CH}_2 - \text{CH}_2 - \text{O})_3 - (\text{CH}_2)_6 - \text{SH}$  on gold. The ratios (especially at 25 degrees) give a good idea about the position of the different elements in the sample. C and O are present in the top layer with O at the outer surface. S is closest to the Au substrate.

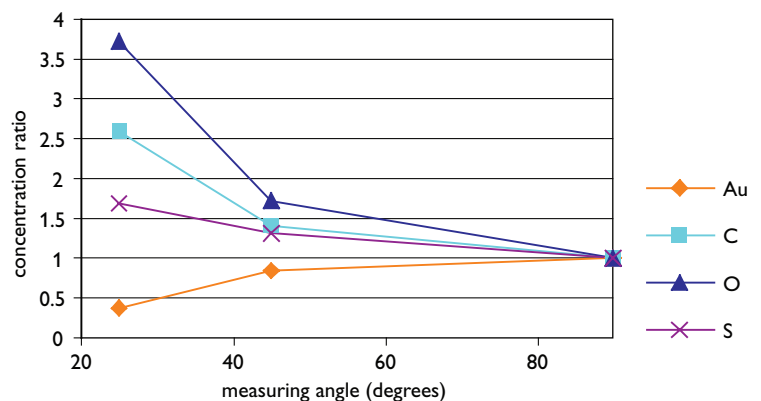




Fig. 7: Multilayer model of BAT on gold (see figure 5). This SAM layer can be seen as two organic layers on top of the gold substrate: a lower layer containing the  $-(CH_2)_x-$  part of the molecules and a top layer containing predominantly CO groups and N, O and S of the thiophene group. The S of the thiol group is present at the gold surface only. One single measurement results in the 'raw' concentration. A subsequent model calculation provides the real layer composition, as shown next to the figure.

### Remote analysis

The available XPS-instruments are part of the Virtual Laboratory of MiPlaza Materials Analysis. The Virtual Lab allows customers to collaborate real-time with the XPS-operator during the analysis of their samples.

The remote customer only needs a PC with Internet-browser and obtains access via a fully protected, encrypted connection. To setup the connection the remote customer only needs a session ID; the session ID is supplied by the operator and is valid for one session only.

More information to be found at <http://s2s.hightechcampus.nl>

### Applications

- **Characterization of thin layers (< 10 nm)**  
Determination of composition and effective layer thickness of multilayer systems (high-k oxide layers on Si, self-assembled monolayers on a gold substrate, monolayers of biological materials such as proteins, antibodies and DNA)
- **Characterization of thick layers by sputtering**  
Determination of the composition of layered-structures like ITO-Cr-SiN systems and of additional (oxide) interface layers herein
- **Contamination**  
of surfaces of wires, glass, leadframes, ribbons, inner surface of lamp bulbs
- **Effect of specific treatments**  
like cleaning, heating, oxidation or gas treatments on the surface composition
- **Cause of bad adherence**  
of e.g. crystals on leadframes, glass-metal interfaces
- **Chemical information**  
Identification of the chemical state in which elements are present, i.e. determination whether a metal is oxidized, if a salt is present, valence of specific elements in glasses

### MiPlaza Materials Analysis

offers a full range of analytical methods and expertise to support both research and manufacturing, serving customers by taking an integral, solution-oriented approach.

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### Technical Note 3

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### Characteristics

#### Sample type

- solid materials (bulk, powders, multi-layers)

#### Sample sizes

- from a few mm<sup>2</sup> up to 70 mm in diameter; the maximum allowable thickness of samples is 25 mm

#### Information depth

- 1 - 10 nm, by sputtering with Ar<sup>+</sup>-ions up to approximately 2 μm

#### Lateral resolution

- ≥ 5 μm for both imaging and spectroscopy

#### Detection limit

- 0.01 atom % for heavy elements and 0.1 atom % for light elements

#### Elemental range

- All elements except H and He

