X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), or Electron Spectroscopy for Chemical Analysis (ESCA) is a quantitative method to determine the elemental composition of surfaces and surface layers. In addition, XPS provides information on molecular bonding states and layer thickness.

For the analysis a sample is irradiated by mono-chromatic X-rays[1], which leads to the emission of photoelectrons from the excited atoms (see figure 1). Only electrons from the top 5-10 nm are able to leave the sample surface without further energy loss (→ information depth). The kinetic energy, E_{kin}, of these photoelectrons is a function of the binding energy (BE), and, hence, element-specific (→ quantitative determination of the surface composition). On top of that, the binding state of the element leads to shifts in the binding energies. With these "chemical shifts" quantitative information about molecular bonds (e.g. oxidation state) of the elements can be obtained.

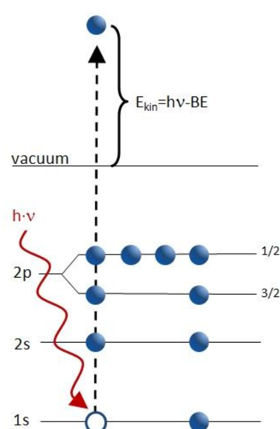

Figure 1: Excitation of photoelectrons in XPS (photoelectric effect)

[1] e.g. Al K_α; energy: hν = 1486.6 eV

Properties of XPS:

- qualitative and quantitative element composition:
  detection limit: about 0.1 atomic%
- molecular information by chemical shift
- information depth: 5 - 10 nm
- suitable samples: all solid materials

Operational Modes of Measurements:

- spectra (overview & detail)
- line scans (series of spectra)
- chemical images
  (spatial resolution ≥ 8 µm)
- thickness analysis by model-based analyses or angle-resolved XPS
- depth profiles (sputtering)

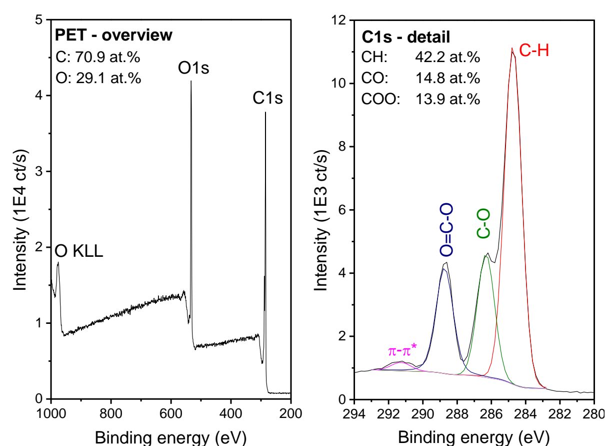

Figure 2: XPS overview and detail spectrum of PET

Figure 2 shows an example of an overview and detail spectrum of a polyethylene terephthalate (PET) reference sample. Based on the overview, the existing elements can be identified and quantified (see the concentration information in figure 2). More detailed, quantitative information about molecular bonds can be derived from the detailed spectra. The (fitted) C detailed spectrum shows the contributions of chemical bonds that are typical for PET. In addition, a

satellite signal (π-π *, → aromatic hydrocarbons) can be recognized.

Due to the outlined characteristics, XPS belongs to the commonly used standard methods of surface analysis. In addition to spectroscopy on selected surfaces (e.g. good-bad comparisons), line scans are used as the acquisition mode in the characterization of discontinuities or material transitions. In this case XPS spectra are recorded along a predetermined line. The combination of chemical and lateral information makes it possible to draw conclusions about the distribution of chemical substances over the surface.

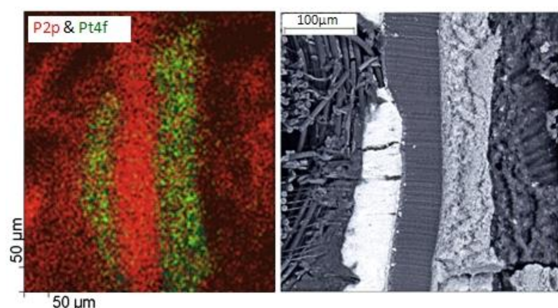

Figure 3: Cross section of a fuel cell membrane (left XPS-Overlay; right: SEM image)

Modern XPS devices also offer the possibility to depict the chemical composition of surfaces by imaging. Figure 3 shows an XPS correlation analysis of the cross-section of a fuel cell membrane. For convenience it is compared to an SEM image. The polymer-based membrane in the centre of the image is surrounded by platinum containing coatings. This layer system is stabilized by a phosphor containing support. The structure of the membrane system is clarified in the XPS overlay of P (red) and Pt (green). Based on these data, the exact composition of the Pt coatings can be determined quantitatively.

In addition to the spectroscopy of the surface and the imaging of lateral distributions XPS can be used to determine the layer structure as a function of depth. Already from a single XPS spectrum, in layers with a thickness below the XPS information depth, a model-based calculation of the average outer layer thickness can be made (e.g. to determine the oxide layer thickness in Al_2O_3 on Al). Apart from that the angle between the sample and analyser can be varied to alter the information depth. This angle-resolved XPS (AR-XPS)) can lead directly to conclusions on the layer structure. For thicker layers, the "classic" XPS spectroscopy is combined with a removal of sample layers by sputtering with Ar^+ ions. The crater floor that is formed by the sample erosion is then analysed quantitatively by XPS with respect to its chemical and molecular composition. Figure 4 shows such an XPS depth profile of an oxide layer at the interface of an Al contact to an organic light emitting diode (OLED). The data clearly show an accumulation of magnesium and oxygen at the interface between contact and organic electronics.

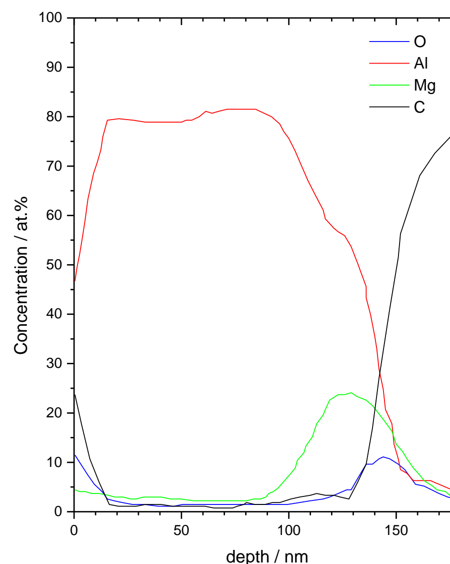

Figure 4: XPS depth profile of an Al contact for an organic light emitting diode (OLED)