X-ray Photoelectron Spectroscopy (XPS)

Principle of photoelectron spectroscopy

Photoelectron spectroscopy is a method for measuring energy distribution of photoelectrons excited by monochromatic photons. If the applied excitation is an ultraviolet photon source then it is called UPS (Ultraviolet Photoelectron Spectroscopy), if x-ray potons are used as the exciting photon source it is called XPS (X-ray photoelectron spectroscopy. *XPS* is also known as *ESCA* (*Electron Spectroscopy for Chemical Analysis*).

XPS method is based on photoionization. The surface of the examined sample is excited by monoenergetic x-ray photons in the range of 150-1500 eV and the emitted photoelectrons are detected separated according to their energy. The primary photon energy is large enough to extract electrons even from the inner atomic electronshells thus ionizing the atoms of the surface. The penetration depth of photons is between 1-10 μm, but electrons - due to their large inelastic scattering cross section causing multiple scattering process - can leave the surface only from the few topmost atomic layers. X-ray photons can excite electrons from the valence band in the range of 0-25 eV and also from atomic core levels with binding energy in the range of 25-1500eV. In this way XPS is suitable for characterizing electron structure of the surface.

The x-ray photon excitation gives rise to photoelectron emission according to the equation:

$$h\nu = E_i^F + E_k + \Psi_{sp}$$

where $h\nu$ is the energy of the exciting radiation, E_i^F the ionization energy of electrons referenced to Fermi level, E_k the kinetic energy of photoelectrons and Ψ_{sp} is the work function of spectrometer must be taken into account because the sample and the detector of the spectrometer are in metallic contact with each other and the equalization of Fermi levels causes contact potential.

In the above equation the energy of exciting radiation is known, Ψ_{sp} can be calibrated to the energy of a well known photoelectron peak of a precious metal standard, and the value of E_k is measured. Thus E_i^F - what is usually called as the binding energy of the electron - can be calculated. This characteristic energy enables identification of the surface element, and in this way the composition of the sample surface can be determined. Insulating samples may be charged during measurement which can be taken into account by a Ψ_t charging potential energy in the above equation.

XPS is a surface sensitive, nondestructive measuring technique for analyzing the surface chemistry of a sample. The quantitative elemental composition and the chemical state of the elements can also be determined within a sample surface.

Main parts of an XPS equipment

XPS measurements need ultrahigh vacuum (UHV) conditions. The two main part of an XPS equipment is the x-ray source and the electron energy analyser with the detector, which are located in the UHV analytical chamber.

X-ray source

Soft X-ray emission spectrum consists of a continuous background called Bremsstralung extending up to the incident electron energy on which the characteristic lines are situated. X-rays are generated in a material by bombardment with electrons of 10-15 keV energy. Bombarding electrons are thermal electrons emerging from a glowing tungsten fiber (cathode). These electrons are electrostatically accelerated through a potential to the copper anode face which is coated by evaporation with a properly chosen metal layer. In XPS two materials are used most often as anodes in soft X-ray sources: magnesium and aluminium. The MgKα and AlKα lines have sufficiently narrow width (0,7 eV and 0,8 eV respectively) so good resolution can be achieved, and the line energies (1253,6 eV and 1486,6 eV) are also high enough for the detection of all elements. The large intensity of the MgKα and AlKα lines provides high sensitivity measurements.

The resolution can be increased by monochromator. Better energy resolution can be achieved using synchrotron radiation.

Electron Energy analyser

The heart of the technique is the measurement of an electron energy spectrum. Such an analysis is performed by an electron energy analyser. Due to the electrostatic field in the analyser the electrons - according to their kinetic energy - are moving on different trajectories and in this way they become separated by energy. The energy resolution (this means the smallest energy difference of electrons at which they can be separated) is determined by the analyser type and it's technical parameters (e.g. size).

In XPS concentric hemispherical analyser (CHA) are often used because of good energy resolution. But it should be noted that the achievable maximum intensity is lower than in case of cylindrical analysers.

Cylindrical mirror analysers (CMA) are primarily used in Auger Electron Spectroscopy. The electrons are separated by a logarythmic electrostatic field between two coaxial cylinder. The intensities are high but the energy resolution is worser than in the case of CHA. Optimal sample position is determined by strict geometric constrains.

Tipically $<10^6$ electron per second passes through the analyser. To detect so small ($<10^{-13}$A) current, electronmultiplyers (nowadays so called channeltrons) should be used. In this way $\sim10^7$ times a gain can be achieved.

Spectral interpretation

During XPS measurements firstly the wide scan spectrum (or survey spectrum) (Figure 1) is recorded in the range of 1-1100 eV to detect the signal of all the element present in the sample surface (in the total energy range provided by the Mg anode). The electron intensity is usually plotted as a function of binding energy in XPS studies. (The software converts the kinetic energy values according to the applied photon energy.)

When recording such a wide range of spectra, the aim is to maximize the sensitivity, high energy resolution is not important. Therefore, the energy resolution of the spectrometer can be taken to a smaller value, and the step size on the energy scale and dwell time can be increased. The peaks (intensity maxima) visible in the spectrum can be identified using the SpecsLab Prodigy data acquisition software or the database of the CasaXPS evaluation program.

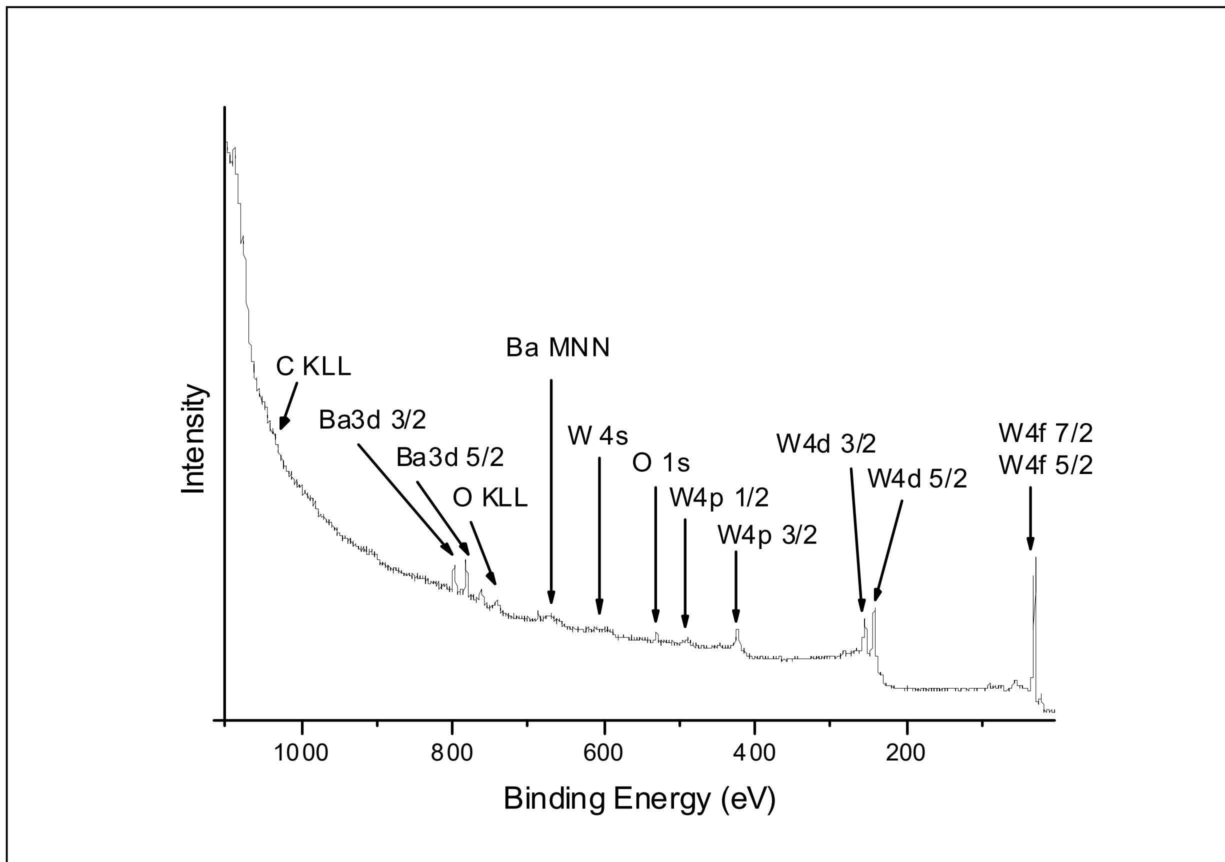

Figure 1.: Survey spectrum measured on a tungsten plate coated with a Ba-containing material

In the spectrum shown in Figure 1, photoelectron peaks from different shells of W, Ba and O can be observed. In addition, peaks from O (KLL) and Ba (MNN) X-ray excited Auger transitions are also detected. By recording such survey spectra, we can detect contaminants present in the sample up to a concentration limit of 0.1%.

Quantitative analysis

From the areas below the measured photoelectron peaks the quantitative composition of the sample can be determined. The number of photoelectrons for a given peak, if the volume of the sample analyzed is homogeneous:

$$I = n\, f\, \sigma\, \lambda\, A\, T,$$

where n is the number of atoms of the given element per unit volume, f is the X-ray flux, σ is the photoionization cross section of the given atomic orbit, λ is the free path length of the photoelectrons in the sample, A is the examined area of the sample and T is the transmission factor of the equipment. From the above equation the atomic density of the given element can be expressed:

$$n = \frac{1}{f \cdot \sigma \cdot \lambda \cdot A \cdot T}$$

The product of the amounts in the denominator is denoted by S and is called the atomic sensitivity factor. Using this, the concentration ratio of two elements:

$$\frac{n_1}{n_2} = \frac{I_1 \cdot S_2}{I_2 \cdot S_1}$$

The quotient S_1/S_2 can be taken as matrix independent with good approximation. In some cases, the value of σ or λ varies from material to material, but their ratio to two elements is practically constant. Thus, the relative sensitivity factors (RFS) for a given equipment can be measured for each element (usually relative to C or F), and the concentration of the xth element in the test sample can be determined from the areas under the peaks (I_x):

$$c_x = \frac{n_x}{\sum_i n_i} = \frac{I_x / S_x}{\sum_i I_i / S_i}$$

The relative sensitivity factors (S) can be found in the database of the CasaXPS evaluation program.

Determination of chemical-bonding state

The change in chemical bonds not only affects the outer electron shell, but also causes a change in the binding energy of the core levels of up to a few eV, which is also reflected in the shift of the photoelectron peaks in the XPS spectra. Thus, from the exact position of the photoelectron peak, the chemical-bonding state of the atoms in the studied sample can be deduced. To determine the chemical-bonding state, good energy resolution is needed, so the resolution of the spectrometer should be chosen to a high value and spectra should be recorded with small step size on the energy scale and in the necessary narrowest energy window in the region of the given photoelectron peak.

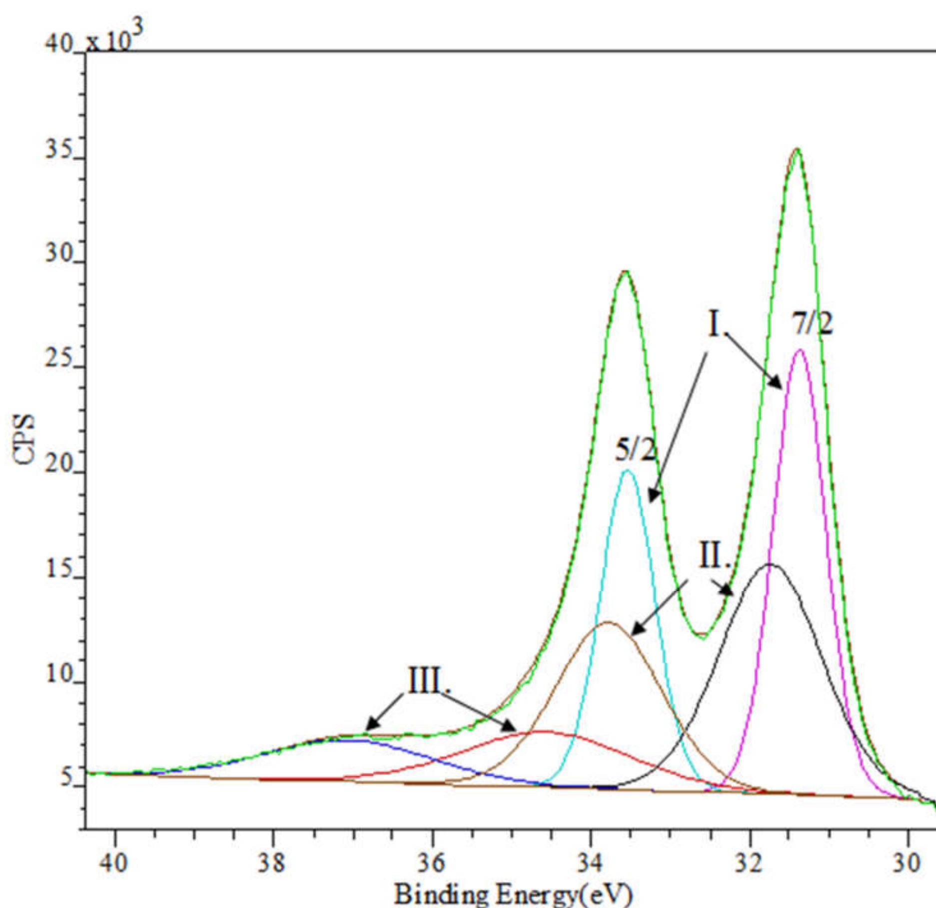

Fig 2.: Peak resolution of the W 4f photoelectron peak according to the different oxidation states

Figure 2 shows the XPS spectrum recorded in the region of the W4f peak (green curve). The measured curve can be synthesized from the sum of Gaussian curves placed at six different energies. The peaks at 31.4eV and 33.5eV (blue and purple) can be identified by the metallic chemical state. (Due to the spin-orbit coupling, the non-spherically symmetric (i.e., with the exception of s, the other p, d, f) atomic orbitals split into energy according to the values of the total j momentum($|\mathbf{j}| = l \pm 1/2$) and appear as doublets.) The doublet at 34.6eV and 37.1eV (red and blue curves) is identified by WO_3 chemical state, while the peak at 31.7eV and 33.7eV (black and brown curves) corresponds to a lower oxidation state. CasaXPS was used to resolve the peaks. Databases are available to identify the bonding states (see recommended literature).

Applications

Applications of photoelectron spectroscopy range from analytical chemistry to solid state physics. In all areas where the interface plays an important role, XPS is an effective method. Adsorption-desorption phenomena can be studied in situ in some cases, because in addition to heating the sample, it is also possible to introduce gas into the vacuum chamber through a fine gas inlet valve. An industrially important area related to such phenomena is the development of gas detection sensors.

In microelectronics, semiconductor technology, it is necessary to separate and modify very thin layers. XPS is also a frequently used method for controlling these processes and exploring new possibilities, for example at solid electrolyte capacitor, production or solar cell production. During the development of coatings or emission materials, the formation of compounds and transport processes as a result of heat treatments can be examined with XPS.

Recommended literature:

D. Briggs, M.P. Seah: Practical Surface Analysis, Vol 1. Auger and X-ray Photoelectron Spectroscopy, John Wiley & Sons, New York, 1992.

D. Briggs Surface analysis of polymers by XPS and static SIMS. Cambridge University Press 1998.