# XPS

an activity within the
Nanolab Analysis Labs

XPS is a clean, non destructive, Ultra High Vacuum requiring technique to study the chemical nature of a material surface within the probing depth of approximately 10 nm. All elements with a concentration > 0.5 atomic % can be detected, except for H and He.

Principle

When light strikes an atom, an electron may be ejected if the energy of the light is high enough. The energy in the light is determined by its wavelength or frequency (short wavelength = high energy and high frequency = high energy). X-rays have high energy. When X-rays strike a solid, electrons are always ejected from the near-surface region of the solid. XPS measures photoelectrons in an energy dispersive way.

Practice

When electrons generated by a high voltage electron source hit a material, e.g., Al, an X-ray beam is generated. Part of this X-ray beam is mirrored and focused by a mirror / monochromator onto a sample. As a result, photoelectrons are emittted by the sample, and electrons that can escape are partly captured by the analyzer lens, energy filtered and subsequently counted by the detector.
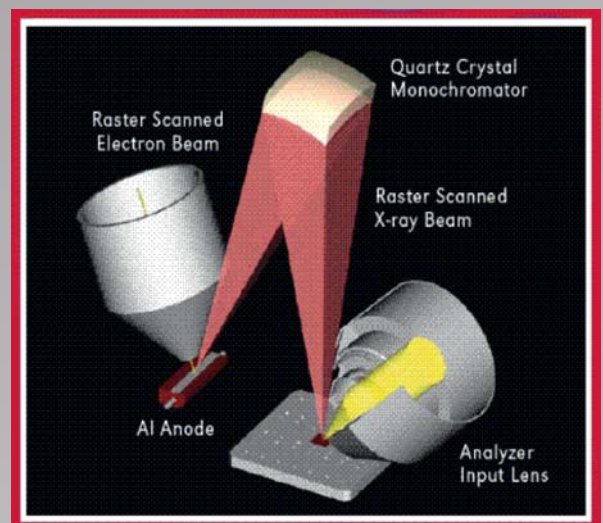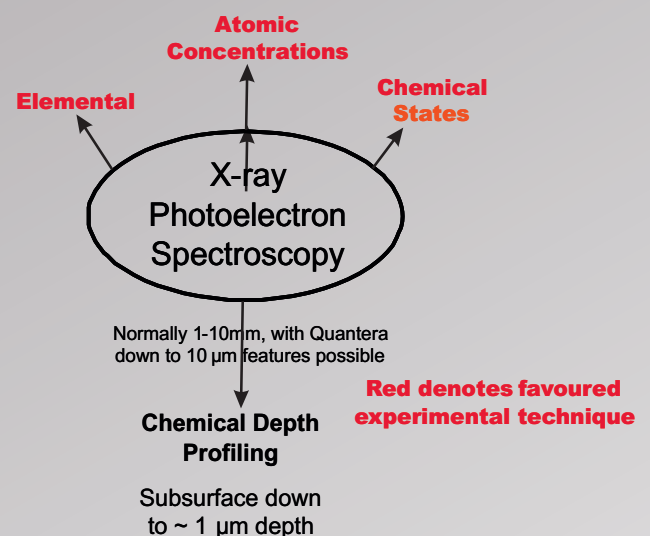
Variations

Dual X-ray source: can generate X-rays with different energies. Some materials can be detected better with a certain X-ray energy. Auger lines, generated also in the photo electron process, lie at different positions relative to the XPS lines. If, e.g., Cd is involved, a Cu-Kα X-ray source would be a better choice than our Al-Kα source.
Monochromatic source: like the one in our XPS system, delivers sharper peaks without satellites. The data interpretation becomes much easier. Only an Ag-source would be compatible with the Al-source as a second source.
Mapping: The narrow X-ray beam or the sample itself can be moved to give a position dependent composition.
Variable angle: together with a narrow detection angle gives information about the depth position of elements with respect to the surface.

Quartz Crystal Monochromator
Raster Scanned Electron Beam
Raster Scanned X-ray Beam
Al Anode
Analyzer Input Lens

Atomic Concentrations
Elemental
Chemical States

X-ray Photoelectron Spectroscopy

Normally 1-10mm, with Quantera down to 10 µm features possible

Chemical Depth Profiling

Subsurface down to ~ 1 µm depth

Red denotes favoured experimental technique

Other instruments

Used for surface characterization; some with a higher lateral resolution and some with less probing depth: SIMS, LEIS, and SAM.

Pricing

XPS, also known as ESCA, is the most widely used surface analysis technique because of its relative simplicity in use and data interpretation. The sample is irradiated with mono-energetic x-rays causing photoelectrons to be emitted from the sample surface. An electron energy analyzer determines the binding energy of the photoelectrons. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of an element can be determined. The information XPS provides about surface layers or thin film structures is of value in many industrial applications including: polymer surface modification, catalysis, corrosion, adhesion, semiconductor and dielectric materials, electronics packaging, magnetic media, and thin film coatings used in a number of industries.

Nanolab Analysis Labs XPS equipment

Physical Electronics Quantera system
- Automated measurements on 2 or 3 platens full of samples.
- Sample volume: 75x75x25 mm^3 samples. 3" wafers will fit.
- Special platen for Angle Resolved XPS
- Special platen for cooling (-135°C) and heating
- Charge neutralization, by electrons as well as low energy Argon ions
- Mapping of elements thanks to scanning X-ray beam with a focused diameter of less then 10 µm.
- Sputter facilities, up to 5 keV Argon ions
  Angle dependent 5° – 85°, i.e., escape depth 0.1x – 1x normal escape depth.
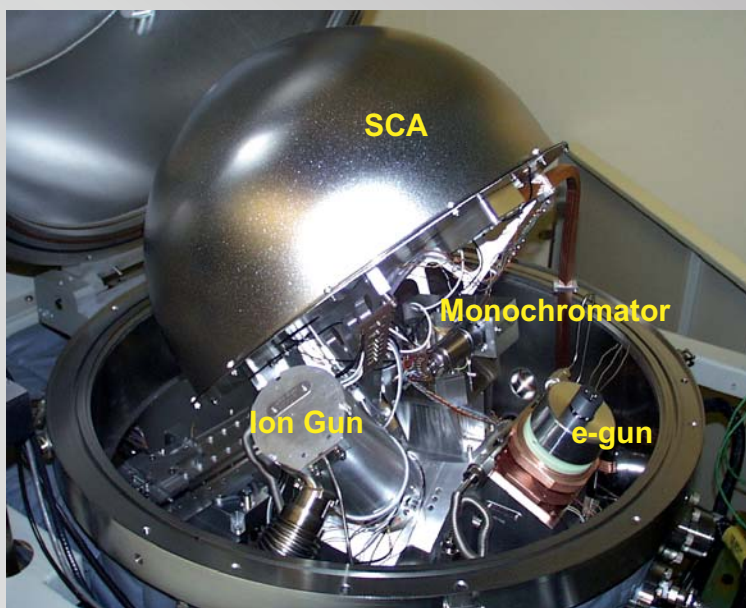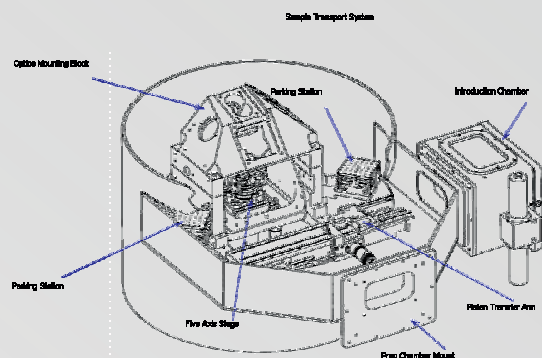
Sample Positioning System
- Microscope assisted
- Computer controlled
- Point of Interest determination

Sample preparation and repository
- Nitrogen store box to keep the samples out of a standard "fatty" atmosphere

Quantera XPS SYSTEM

Examples
Non-Destructive analysis

Charge neutralization

By means of an electron flow gun and a low energy Argon ion beam, non-conducting surfaces can be neutralized without damage. Except for SAM's terminated with Br. In these special cases the ion energy can be decreased to an even less destructive level.

Standard survey scan

Detecting all elements with an abundance > 0.5%. A rather powerful beam is used at a point or over a scanned area, spreading the heat across a reasonable volume, trying to avoid sample degradation by heat or X-ray dose. Typically -5 .. 1345 eV in 0.8 eV steps. 3 cycles to reduce noise, in about 7 minutes.
(Heavy elements, more electrons available, >0.1%)

Survey spectrum

High energy resolution element spectra

These can reveal chemical shifts and from this atomic bonding information can be extracted. Important for carbon in polymers and SAM's. Oxides and valence levels of other materials.
1. In this example to the right we see the two types bonded oxygen. One with a binding energy of 529.8 eV and one with binding energy of 531.8 eV. The ratio of the areas of the two is 1 : 1.66. Taking electron affinity into account and the oxides of strontium and titanium, the 529.8eV oxygen is probably more bound to strontium, and the more abundant 531.8 eV oxygen is more bound to titanium

Oxygen bonds

2. Example of a monolayer on a silicon wafer. The N 1s spectrum of nitrogen in a self assembled monolayer on silicon. The nitrogen should be bound to the alkyl chains all in the same way as can be seen in the sketch of the molecule. There are, however, 2 distinct types of bonds. Is this an indication for bridging, making the bonds of the nitrogen not all equivalent? The carbon C 1s spectrum shows at least 3 different type of bonds, which is expected. The areas do not have the expected ratios. C 1s at 284.8 eV is the alkylic carbon. At 286.3 eV it could be the carbon bound to nitrogen and at 288.2 eV the carbon could be in a carboxyl environment.


Nitrogen

Carbon
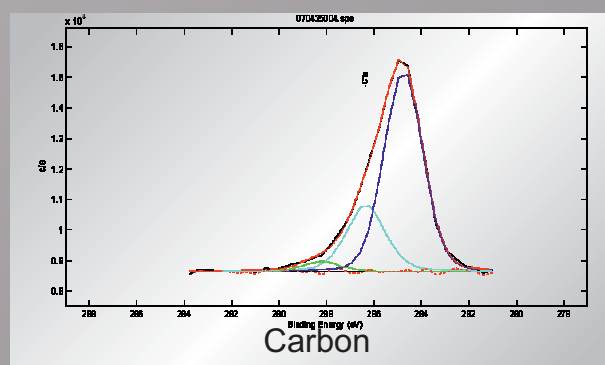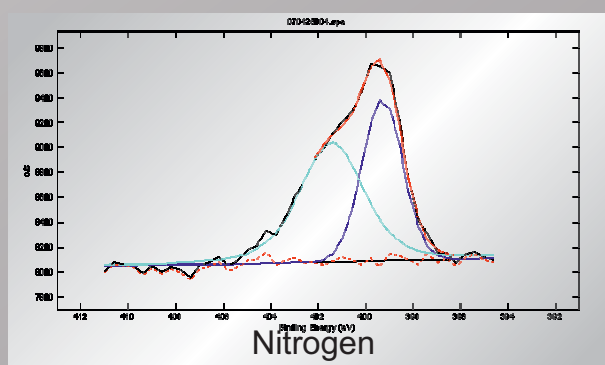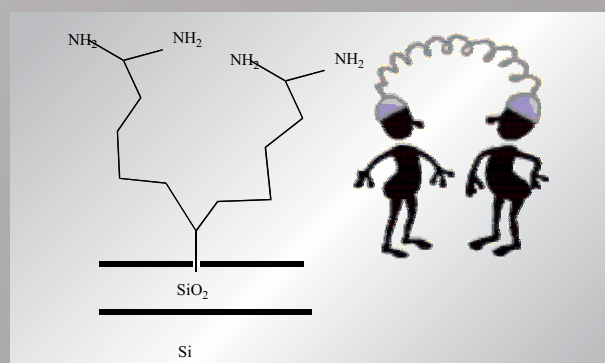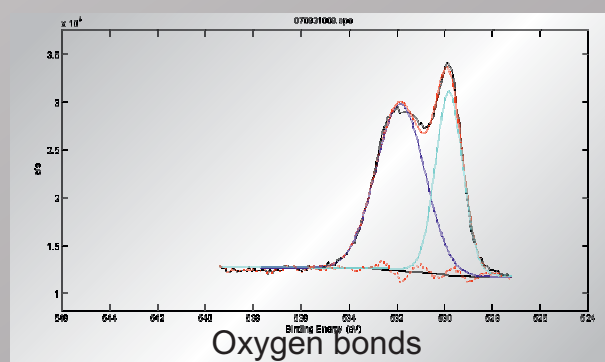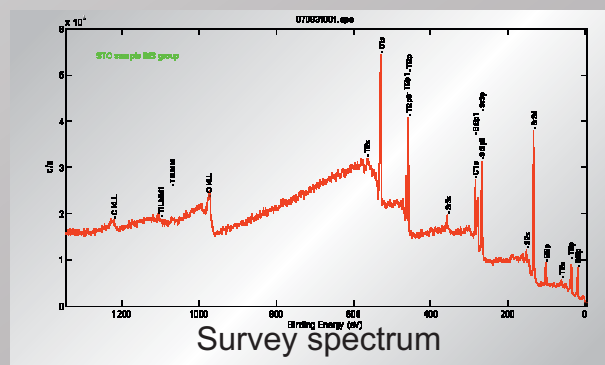
3. The sulphur in a thiol is often used to bind a molecule to a substrate. This could be gold or silicon. In case of silicon, the S 2p peak overlaps with a silicon 2s loss line and we have to measure the sulphur by its 2s line. Less visible, but better calculable.

Sulphur 2p

Sulphur 2s
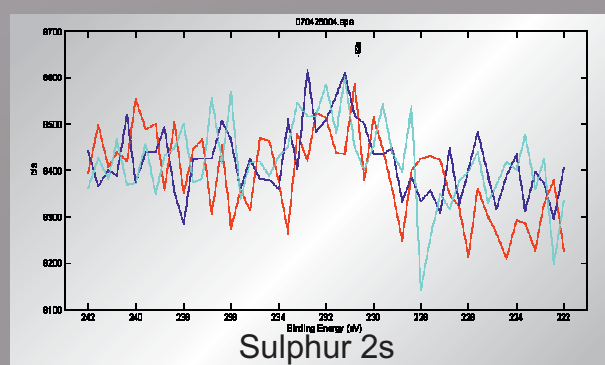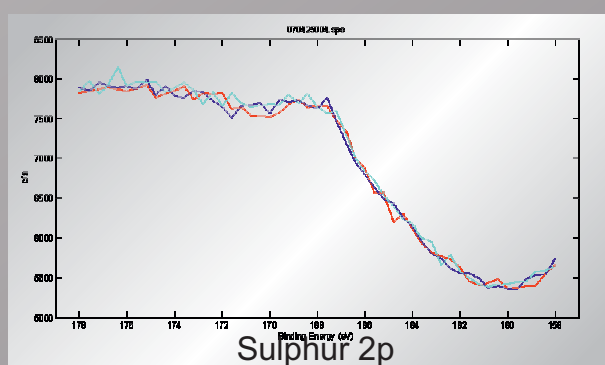
Angle Resolved XPS

Can be used to study thin films on top of substrates or on top of other films if the film thickness is smaller then 0.3x the information depth of the measurement. Optimal measurements if sizes perpendicular to the surface are about the size of the Inelastic Mean Free Path of the XPS electrons. A number of element spectra are taken at several angles. At small angles, the count rate is low and we need more time to sample at these angles.

ARXPS spectra of C, O and P

→ Information depth

Small,   average,   large angle
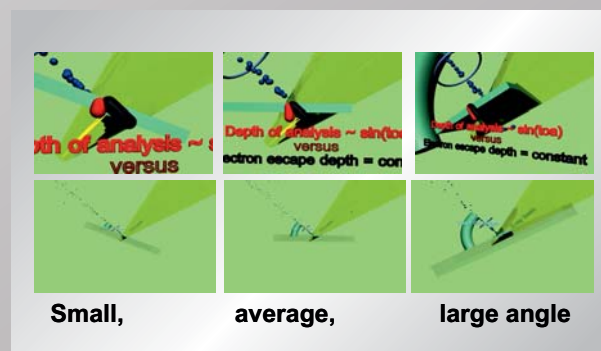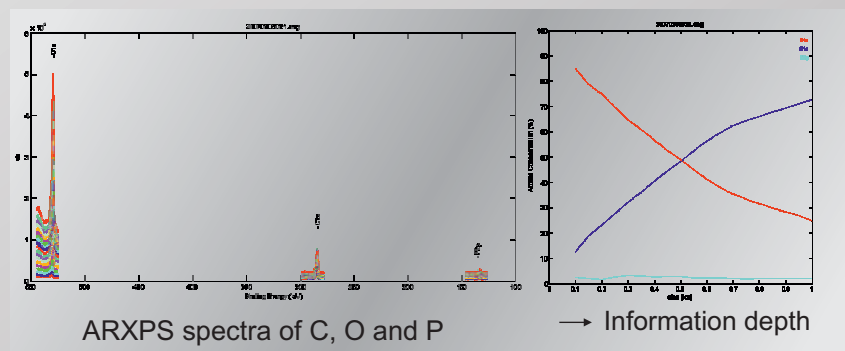
At an angle of 85° the signals become a bit unstable. From the AR spectra, a profile is made that tells us where the elements are in the surface. A special program, Quases, by S. Tougaard, can simulate these profiles for a lot of different models. Comparison between model and experiment can give more insight.

Surface mappings

If the surfaces consist of different materials over different areas, a surface mapping can give lateral compositional information. The lateral resolution is determined by the X-ray beam diameter, which is less then 10 µm

Microscope image   Gold   Oxygen

Chemical information on small scale

Element spectra mappings showing C-F and COOH containing areas

Destructive analysis

Cleaning of surfaces

A sample that is oxidized can be cleaned with a sputter process of "high" energy Argon ions, 100 – 5000 eV. Ambient air gives a constant rate of "carbon black"-like material sticking at all surfaces. By sputtering this contamination away we can study the surface composition better.

Depth profile of SiO2 on top of

SiO2/Si depth profile, Si2p spectra is shown in "3D", oxide in front

Sputter profiling

Opposed to the otherwise non destructive methods described, the Quantera facilitates a Argon ion sputter source. The sputter source can give a rate of 150 nm/min at 5 keV ions over an area of 1x1 mm^2. Slower rates are readily available, down to 0.1 nm/min with an energy of about 250 eV.

Depth profile of a Cr / Ni / Ni$_2$O$_3$ / Cr / Ni / Si standard reference

Destroyed sample, with several sputtered areas

Cr/Cr2O3 multilayers

The Cr spectrum measured during the sputter experiment above, showing the binding energy shift for CrO3. In "3D" and 2D