

Training yourself 1

Training yourself 2

Training yourself 3

# Surface phenomena at the micro- and nano- scale

Master's Degree in Materials Science



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**A.A. 2024-2025**

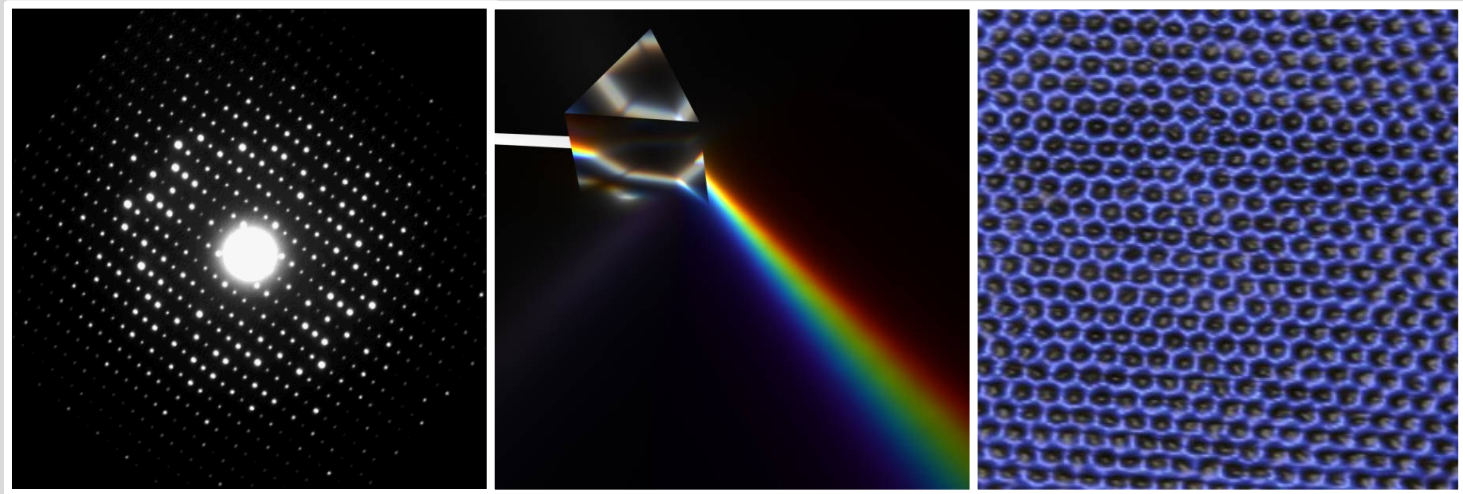
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## 2. Characterization methods in surface science



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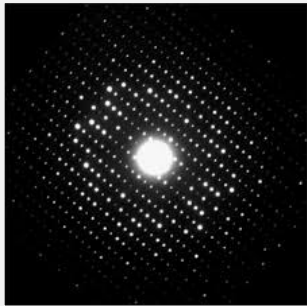
# Questions related to surfaces

Some of the questions to answer when dealing with surface phenomena and high-surface-area materials are:

- Which types of faces do the microcrystals expose (that means, what are their morphology)?
- How flat and regular are the faces defining the morphology of the microcrystals?
- What is the relative fraction of atoms on faces, edges, steps, corners and other surface defects?
- Which is the chemical composition at the surface?
- Which is the surface area?
- Is the material porous and which kind of pores does it have?
- ...

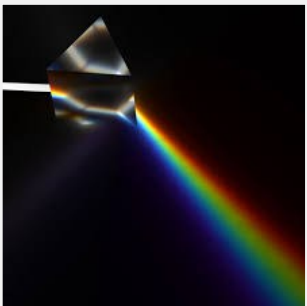
# Which methods?

These questions can be addressed by the combined use of several characterization techniques. Although the number of surface-sensitive techniques is much larger, in the proceeding of this course, we will briefly discuss the basic principles of, and the information obtained by the following two techniques:



## Low Energy Electron Diffraction (LEED)

still commonly regarded as the benchmark technique for quantitative surface structure determination.

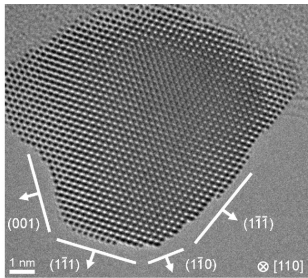


## X-ray Photoemission Spectroscopy (XPS)

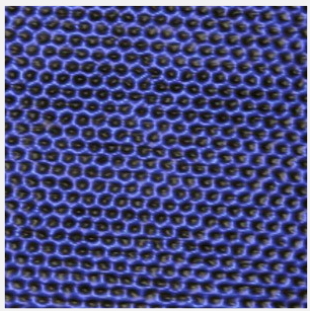
a quantitative technique for measuring the elemental composition of the surface of a material, and to determine the binding states of the element

# Which methods?

We will provide just a few information on imaging techniques (i.e. microscopies), which have been object of previous courses (Bachelor in Scienza e Tecnologia dei Materiali).



**High resolution Transmission Electron Microscopy (HR-TEM)**  
which allows one to image the sample surface at the atomic level.



**Scanning probe microscopies (e.g. STM)**  
which allows one to image the sample surface at the atomic level.

Finally, we will introduce a few concepts about adsorption-desorption techniques, which will be discussed more in details in the following section of the course.

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  - 3b. Scanning probe microscopies (STM)
4. Introduction to adsorption/desorption methods



# How do we investigate surfaces?

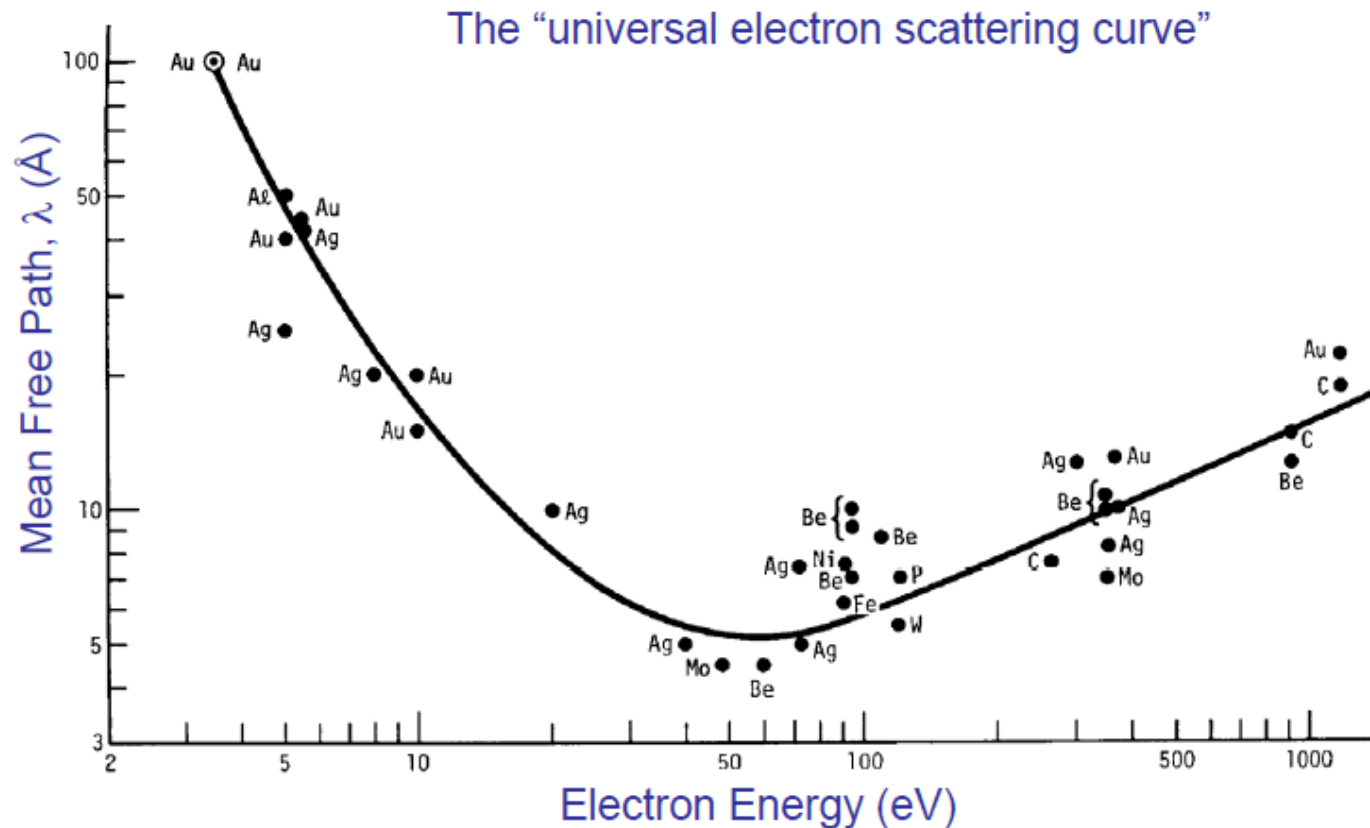
Since we are interested in the structures of (typically) the outermost 1-20 atomic layers, we want surface probes with **sampling depths of about 50 Å or less.**

What determines sampling depth?

Typically, it is the **escape depth of the detected photon/ion/electron**

- Photons: penetration and escape depths are typically 10 nm or more (not good);
- Ions: can be as little as one monolayer, but may present other problems;
- Electrons: escape depth determined by inelastic mean free path (IMFP =  $\lambda$ ).

# Electrons escape depth

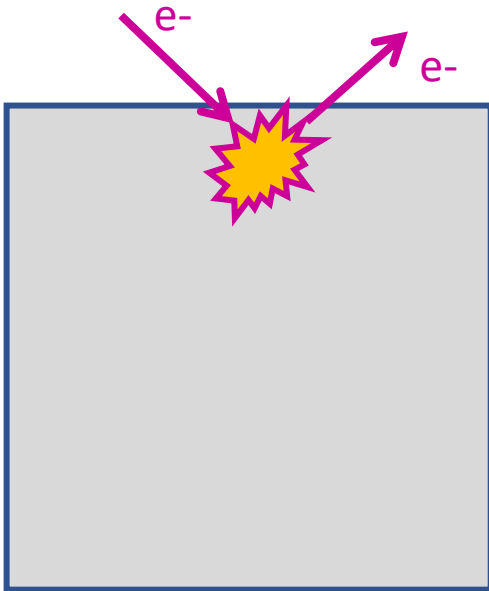


The inelastic mean free path  $\lambda$  for electrons depends on:

- The kinetic energy of the photoelectron
- The specific material

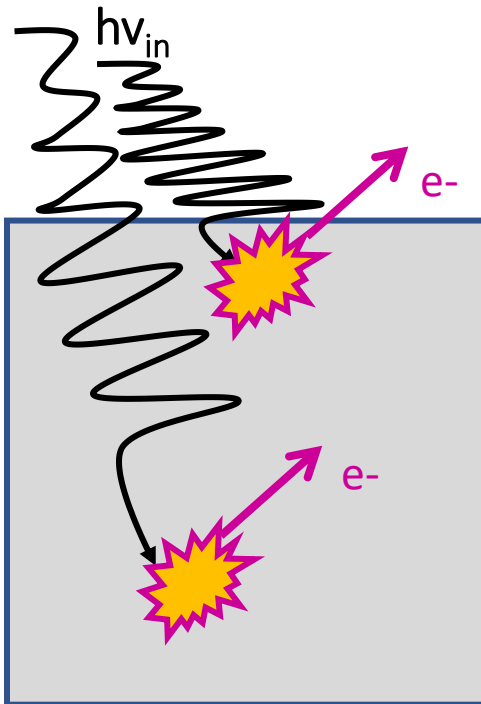
# Surface sensitivity & electrons

Electrons in  
Electrons out



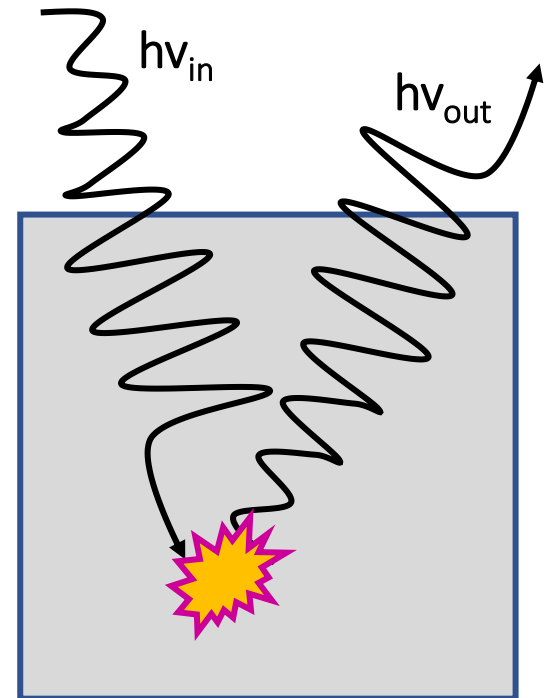
surface sensitive

Photons in  
Electrons out



surface sensitive



Photons in  
Photons out



Not surface sensitive

# Low energy electron-based surface probes

## Development of low energy electron-based surface probes:

1. LEED (low energy electron diffraction) since 1927 (Davisson and Germer) 
  2. AES (Auger electron spectroscopy) 1960's, Palmberg, et al.
  3. XPS (X-ray photoelectron spectroscopy ) 1960's Kai Sigbahn and others at Uppsala University
- 
- atomic geometry
- atomic composition

All the above techniques are linked to technological developments

LEED: Glass-based vacuum systems, fluorescent screens

AES, XPS: Development of accurate electron energy analyzers

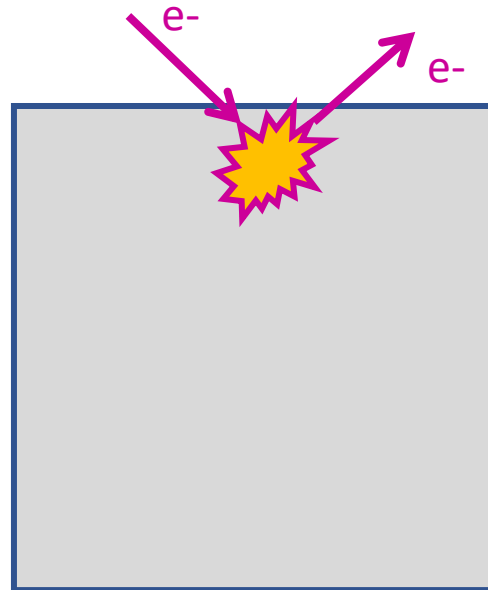
All the above: improved vacuum technology

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# LEED: electrons in/electron out

Electrons in  
Electrons out



surface sensitive

# Relevance of LEED in surface science

LEED is **the oldest of the “modern” techniques of surface science**, not only because its origins lie in the experiment of Davisson and Germer in 1927 which first demonstrated the wave nature of electrons, but also because it was the first such technique for which commercial instrumentation was developed in the early days of stainless steel ultra-high vacuum (UHV) systems in the 1960s.

It remains **the most widely used method of characterizing the long-range order of single crystal surfaces** and is still commonly regarded as the benchmark technique for quantitative surface structure determination.

# LEED: a short history

1897 : J.J. Thomson discovers electron beams

1924: L. de Broglie postulates the energy-momentum relationship

1927: C.J. Davisson / L.H. Germer prove the occurrence of electron diffraction at an atomic lattice

*1937: Nobel Prize to Davisson and Thomson*



**Despite the fast starting, until 1960 no further significant development!**

**In contrast to X-ray diffraction:**

1912: first prove for X-ray diffraction

1913: first quantitative bulk-structure analysis

**Why?**

**LEED is dominated by multiple (=dynamic) scattering**

**XRD is dominated by single (= kinematic) scattering**



# Surface sensitivity and ideal wavelength



An electron ( $m = 9.1093897 \times 10^{-31} \text{ kg}$ ) with a certain energy (KE) is also a wave with wavelength:

$$\lambda = \frac{h}{\sqrt{2m KE}}$$

$$h = 6.626 \times 10^{-34} \text{ m}^2\text{kg s}^{-1}$$

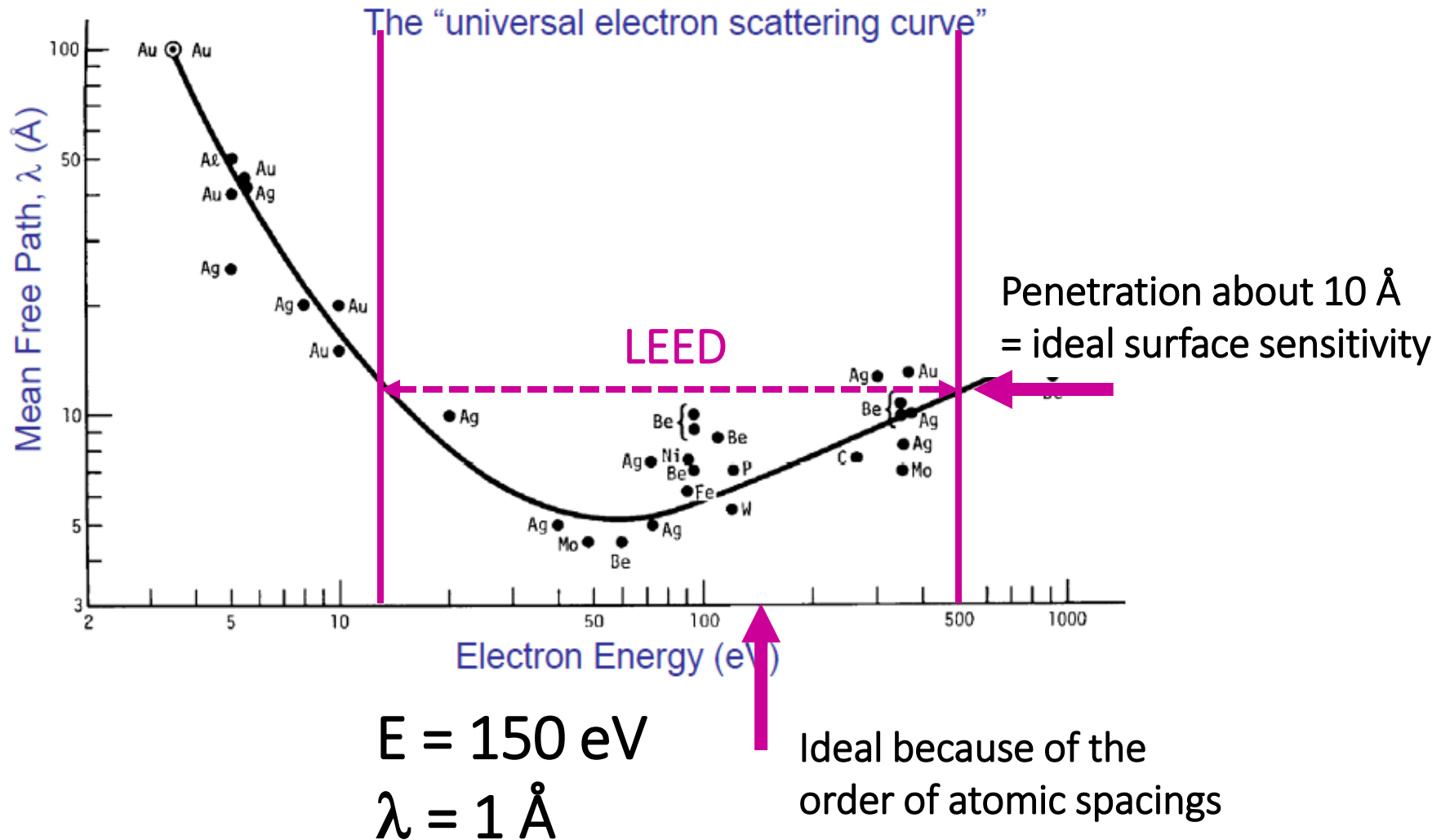
Louis de Broglie  
(1892-1987)

Premio Nobel 1929

## A small exercise

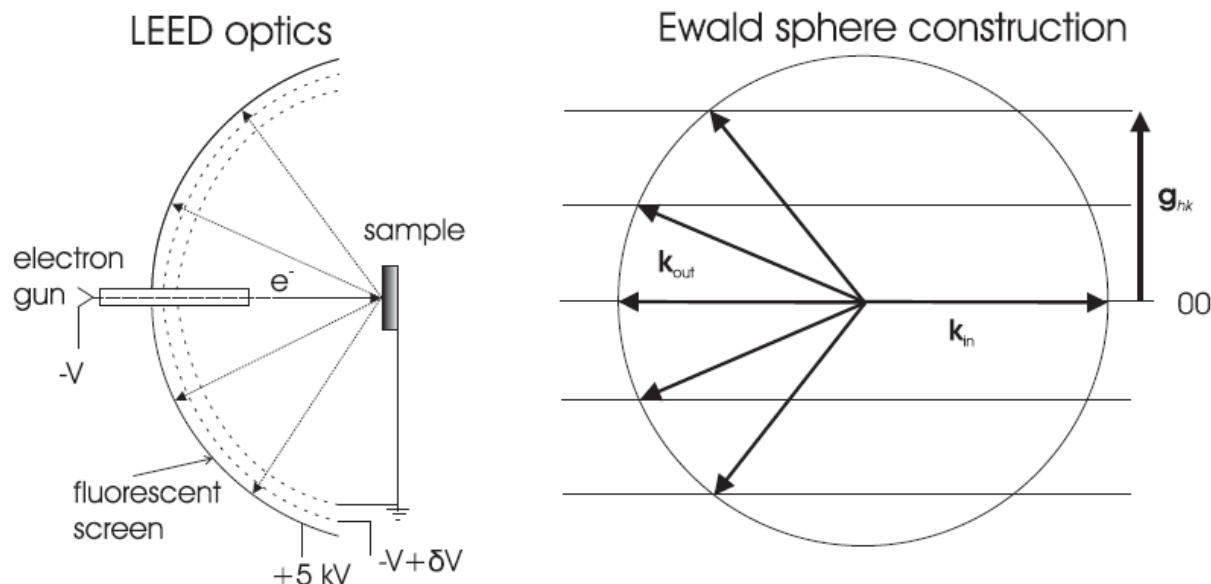
If  $KE = 150 \text{ eV}$ , which is the wavelength?

# Surface sensitivity and ideal wavelength (cont.)



# Experimental details

A beam of electrons of a well-defined low energy (typically in the range 20 - 200 eV) is incident normally on the sample. The diffracted electrons can be observed by a fluorescent screen after energy-filtering grids, which selects only the electrons with the same kinetic energy as the primary electrons.

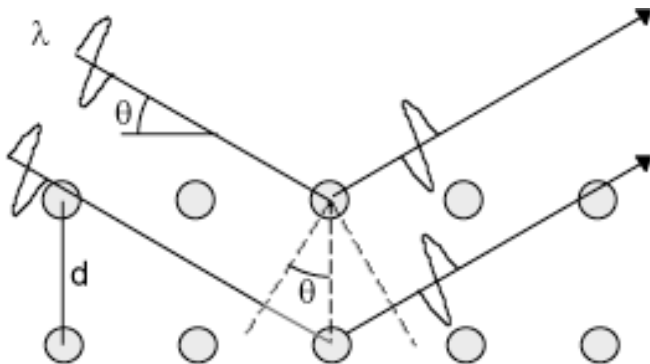


**Figure 1** Schematic diagram (left) of the basic experimental arrangement used in a low energy electron diffraction (LEED) experiment, showing a standard LEED 'display optics' compared to the Ewald sphere construction representing the consequences of the conservation of energy and electron momentum parallel to the surface for a two-dimensionally periodic surface. The horizontal lines shown in the construction are the 'reciprocal lattice rods.'

# Real space considerations

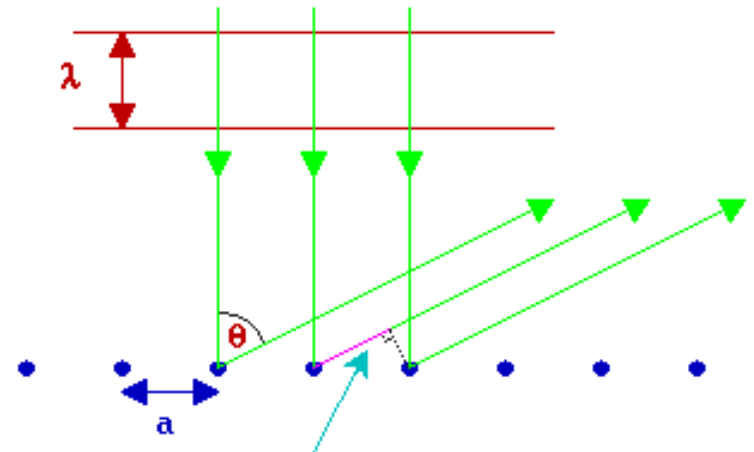
The underlying physical principles of LEED are essentially the same as in other forms of crystalline diffraction except that, because of the high degree of surface specificity, the diffracting object comprises only the outer most few atomic layers of the solid.

For 3D case



Bragg equation  
$$2d \sin \theta = n\lambda$$

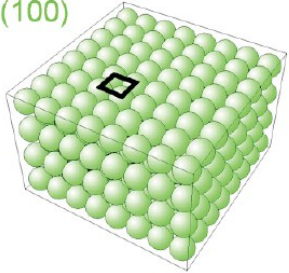
For 2D case



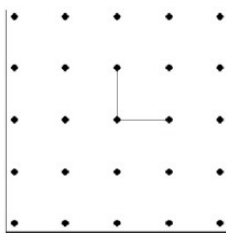
$$a \sin \theta = n\lambda$$

# Examples of LEED patterns

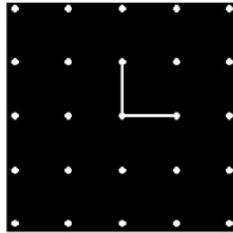
surface structure  
Ni(100)



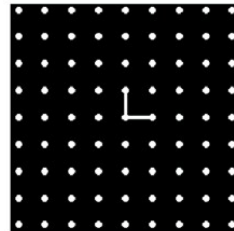
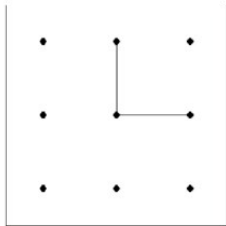
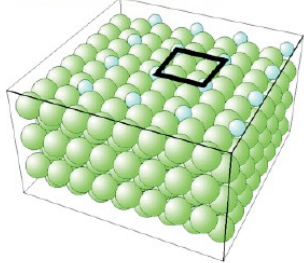
point lattice



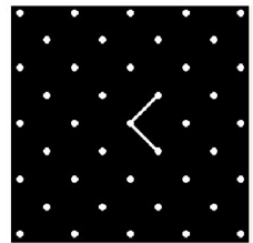
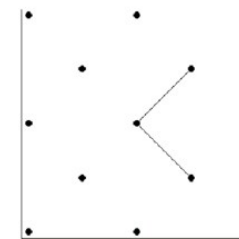
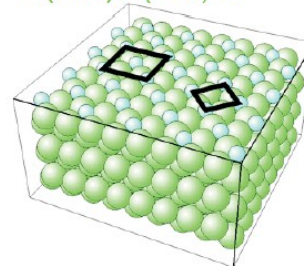
LEED pattern



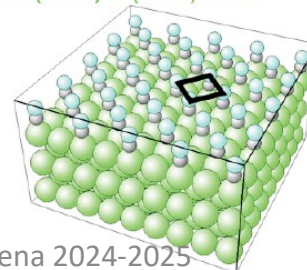
Ni(100)-(2x2)-O



Ni(100)-c(2x2)-O



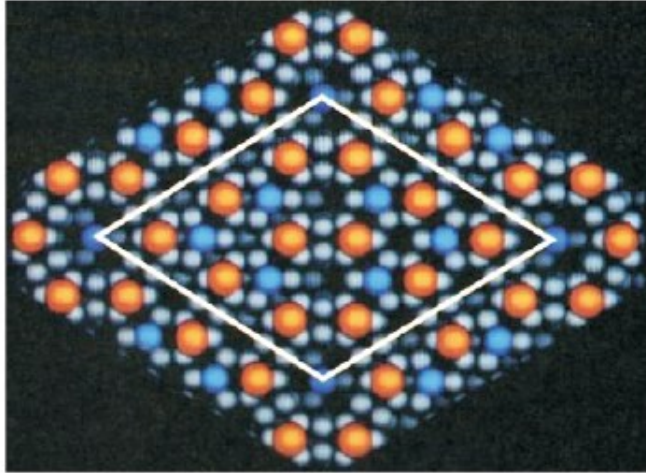
Ni(100)-c(2x2)-CO



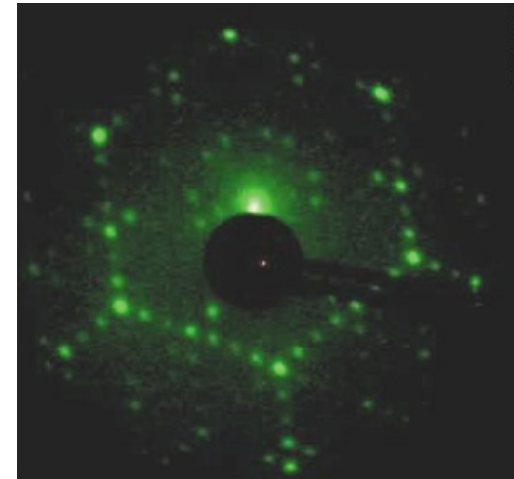
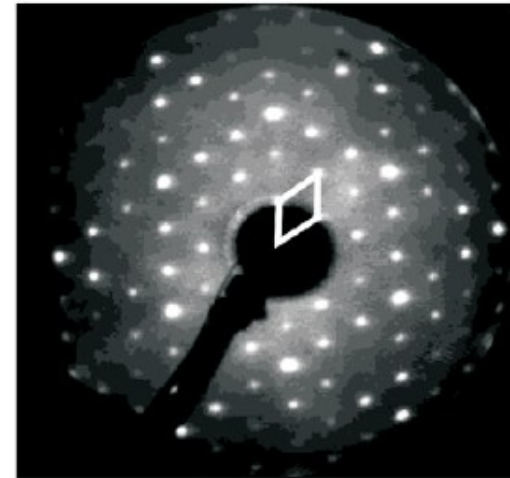
Same,  
but different spot  
intensities

# Examples of LEED patterns (cont.)

Even clean surface can have large/complex unit cells



Si(111)-7x7



# Information from LEED patterns

1. Qualitative analysis: analysis of the **spot positions** yields information on the size, symmetry and rotational alignment of the adsorbate unit cell with respect to the substrate unit cell.
2. Quantitative analysis: the **intensities** of the various diffracted beams are recorded as a function of the incident electron beam energy to generate so-called I-V curves which, by comparison with theoretical curves, may provide accurate information on atomic positions.

# LEED vs. XRD

## LEED

### Advantages

- Relatively simple and cheap experimental set-up (ca. 100 kEuro)
- High surface sensitivity
- Easy information on symmetry and shape of surface unit cell
- Atomic structure can be retrieved with high accuracy

## XRD

- Easy data analysis (no multiple scattering)
- No problems with surface charging (Access to insulators)
- High structural accuracy
- Access to buried interfaces

### Disadvantages

- Demanding data analysis (strong multiple scattering)
- UHV essential
- No insulators accessible
- Electron stimulated processes may take place
- Rather demanding experimental setup
- Surface sensitivity by grazing incidence – high accuracy needed



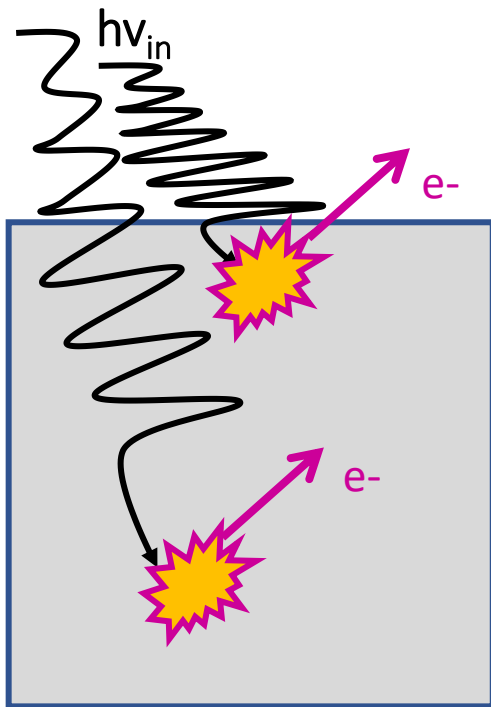
# Ultra-fast electron diffraction

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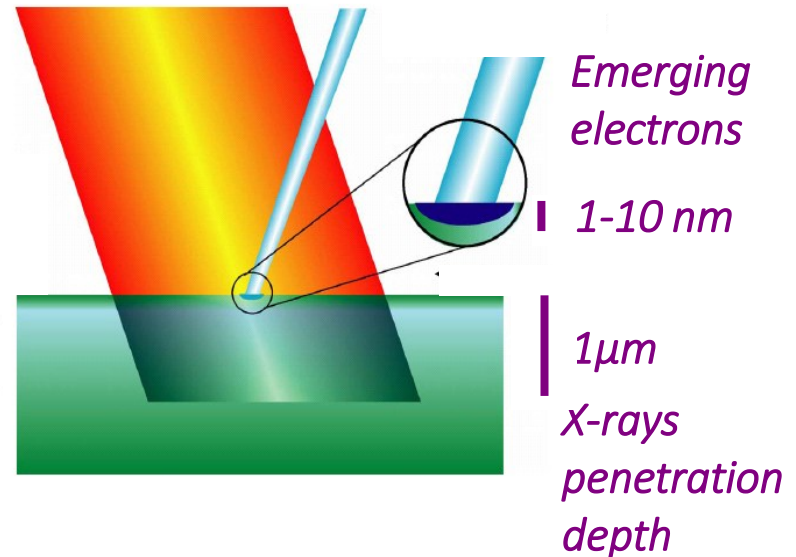
# XPS: photons in/electron out

Photons in  
Electrons out



surface sensitive

Photoelectrons are generated into the whole volume samples by the X-rays, but can escape only from a very thin surface layer.



# XPS: a short history



*Kai M. Siegbahn  
(1918-2007)  
Nobel Prize 1981*

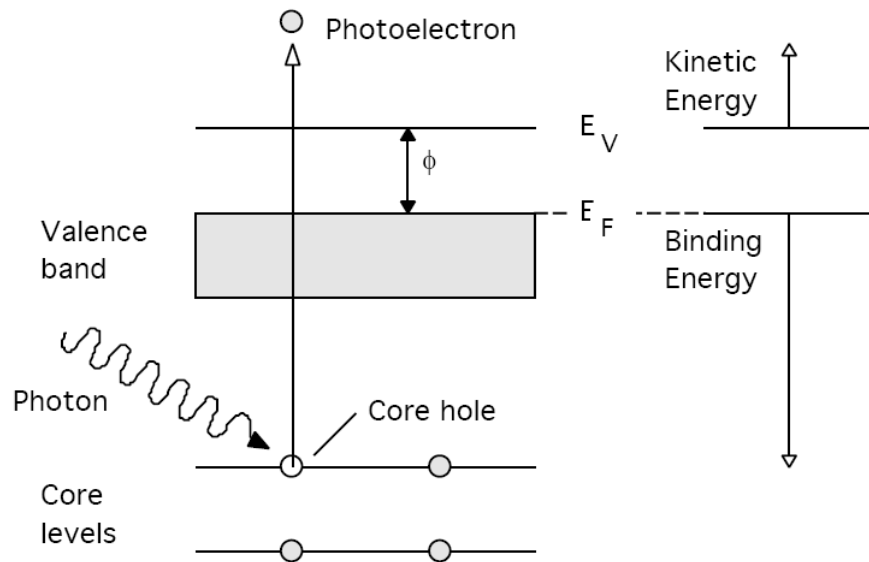
XPS spectroscopy was developed in the 1960s by K. M. Siegbahn and his research group (Uppsala University, Sweden).

Siegbahn received the Nobel Prize in Physics in 1981 *“for his contribution to the development of high-resolution electron spectroscopy”*.

## 50 years of XPS

# Photoelectric effect

The basic of XPS is the **photoelectric effect**, i.e. the emission of electrons when electromagnetic radiation hits a material. Electrons emitted in this manner are called photoelectrons.



The experimental quantity which is evaluated in a XPS experiment is the **kinetic energy of photoelectrons ( $E_k$ )**, which depends on the energy of the incident X-rays and on the binding energy ( $E_b$ ):

$$E_k = h\nu - E_b(-\phi)$$

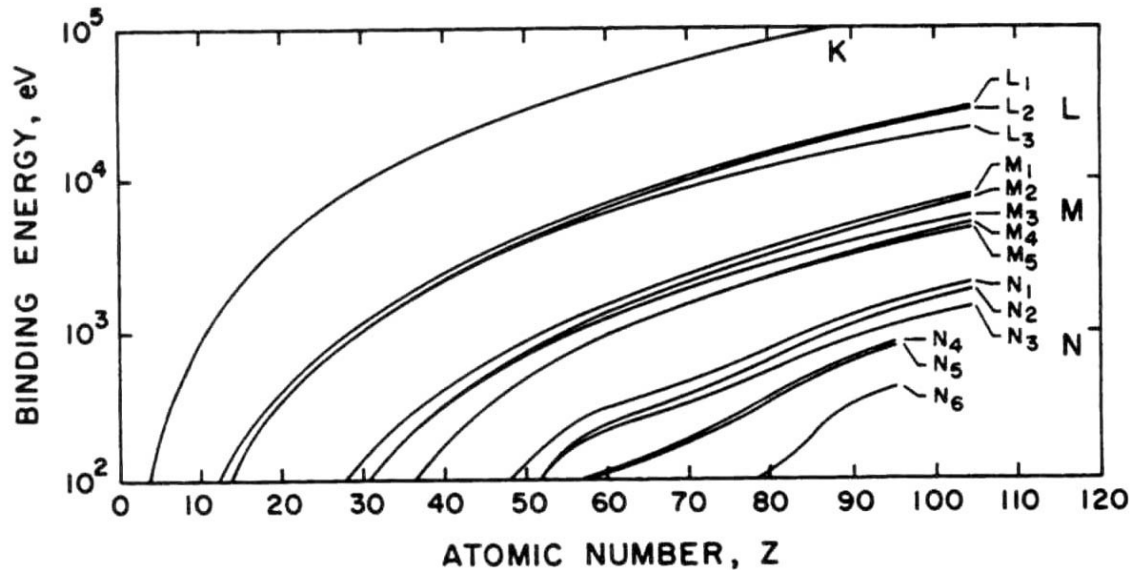
The work function  $\phi$  is a correction factor for the instrument and correlates to the minimum energy required to eject an electron from an atom.

The XPS spectra are reported as **a function of the BE**, to allow comparing data collected on different instruments (different energy of the X-ray beam).

$$E_b = h\nu - E_k$$

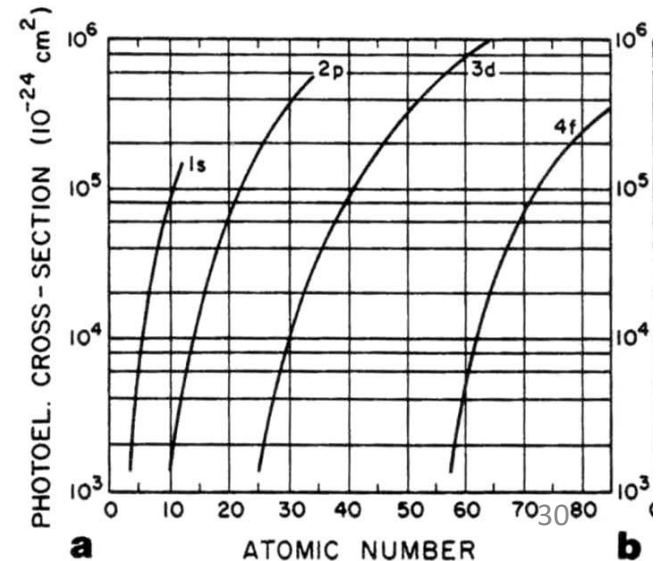
# Atomic sensitivity

Since each element has a characteristic electronic structure, the XPS spectrum is specific for each element.



The binding energy (BE) increases with the atomic number  $Z$ , i.e. with the increase in the number of protons (increases the attractive force of nucleus towards electrons).

The cross-section, which indicates the probability to detect a photoelectron from a certain electronic level, decreases by moving towards the valence band.



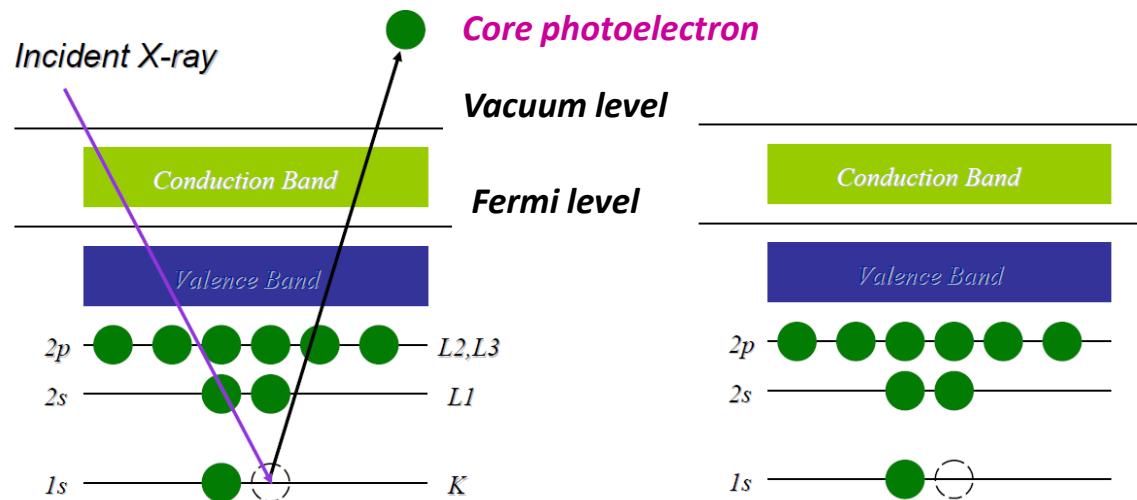
# Which photoelectrons?

An XPS instrument measures the kinetic energies of ALL the electrons reaching the analyser:

- **Core photoelectrons**, those which occupy the most internal electronic levels, i.e. with high binding energy;
- **Valence photoelectrons**, those closer to the Fermi level, i.e. small BE,  $< 20$  eV)
- **Auger photoelectrons**, which are produced as a consequence of atom deexcitation (1100 – 1200 eV)

# Core photoelectrons

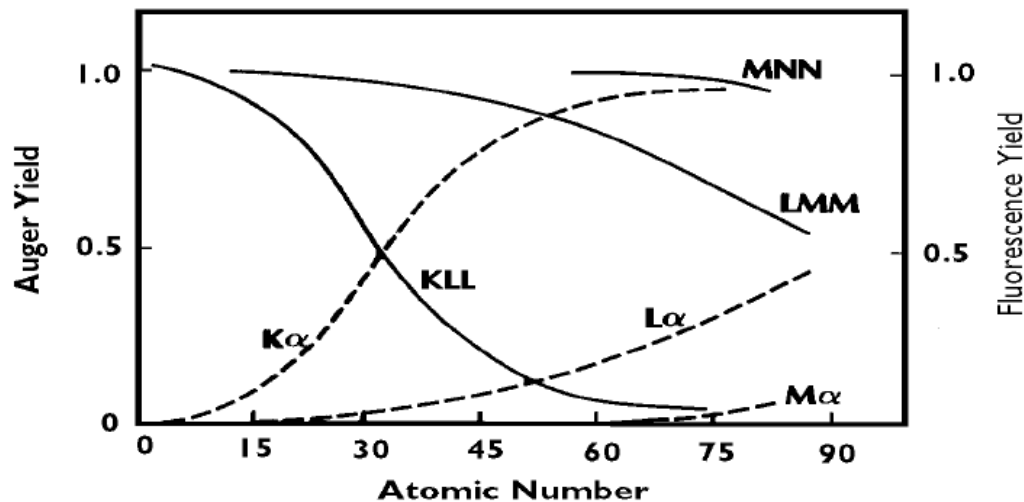
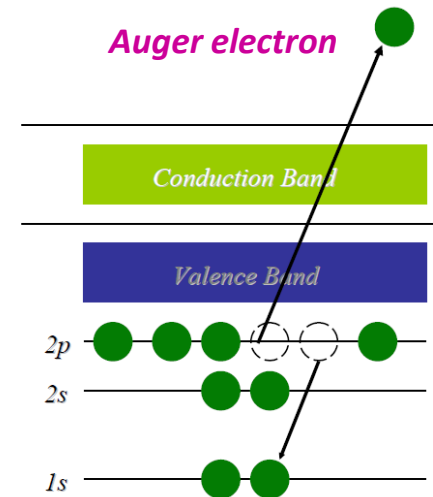
Let's consider the creation of a hole in the K shell. For the ionization process to occur, the incident X-rays must have an energy at least 5 times greater than the BE (typically 5-10 keV).





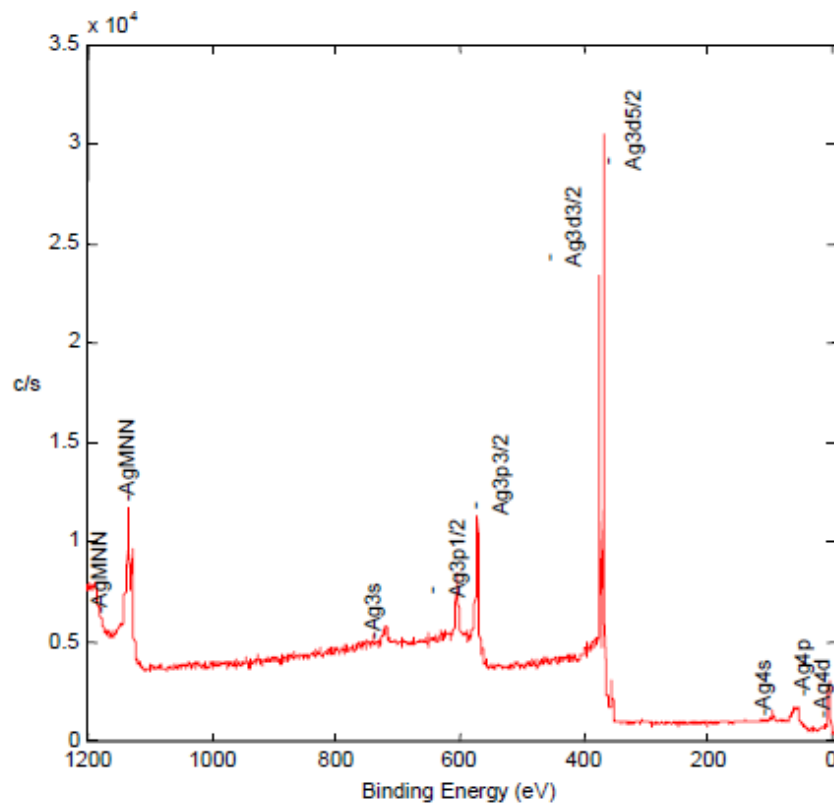
# Auger photoelectrons

The excited atom might relax by filling the hole with an electron from higher shells (e.g. 2p). The energy difference  $E_{2p} - E_{1s}$  can be compensated upon emission of an Auger electron. Note that **the energy of an Auger electron does not depend on the energy of the primary X-rays beam**.



The emission probability for an Auger electron depends on the atomic number  $Z$ .

# Information from XPS spectra



- Narrow and intense peaks due to photoelectrons (elastic scattering)
- Auger peaks
- A background, due to the electrons which are subjected to anelastic scattering inside the material.

## 1. Which are the elements present at the surface of a material

*Different elements are characterized by different BE for the core electrons*

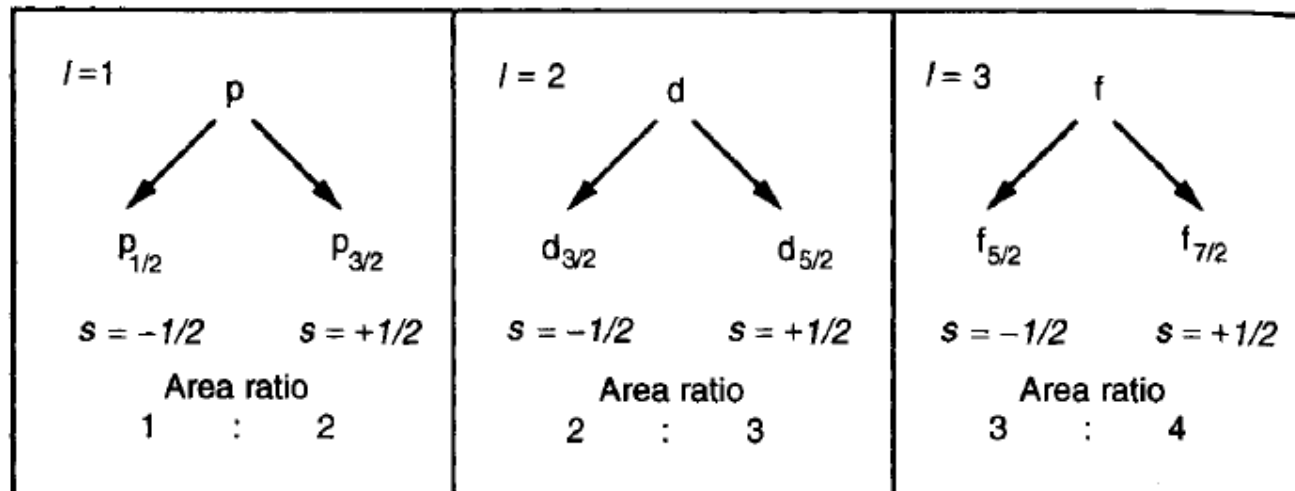
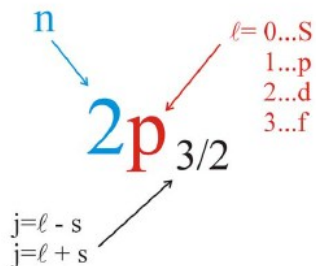
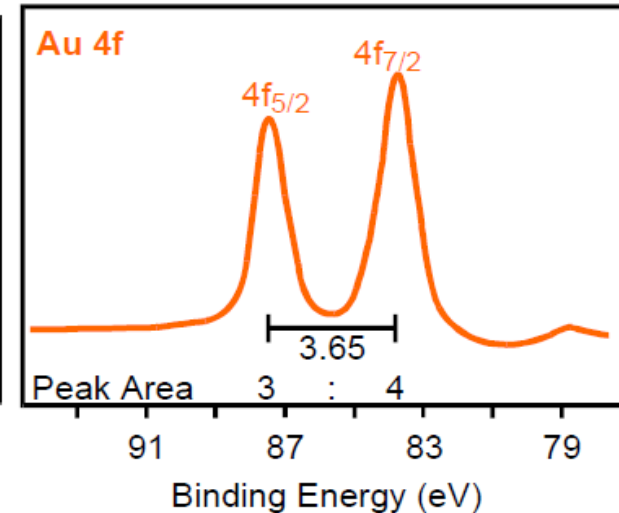
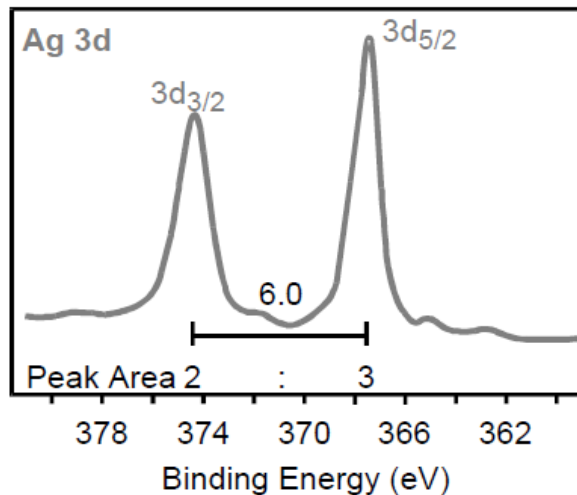
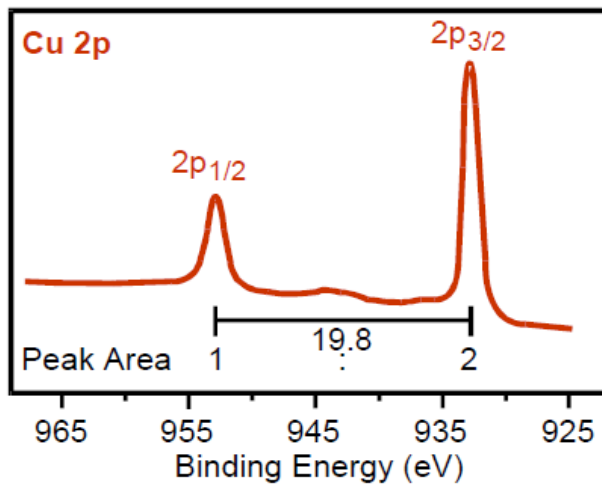
## 2. Chemical state of each element

*e.g. it is possible to discriminate among metal Al and Al-oxide*

## 3. Band structure for a solid

# Spin-orbit coupling

Peaks due to photoelectrons coming from p, d or f orbitals are always doublet due to spin-orbit coupling. The energy splitting and the ratio among the two peaks should be constant for a specific element.



# Qualitative & quantitative analysis

## Qualitative analysis

By **collecting a spectrum in a wide energy range** it is possible to **identify the elements present at the surface** of the sample. Modern data analysis allows the automatic identification of the peaks in a XPS spectrum.

## Quantitative analysis

The intensity of a peak depends not only on the concentration of the emitting element but also on:

- the intensity of the primary beam;
- the probability of ionization and/or Auger transition (cross-section);
- the attenuation length;
- instrumental parameters (e.g. detector efficiency).

# Chemical shift

The XPS spectrum allows not only to identify the elements in the sample, but also their chemical state.

In fact, peaks due to core photoelectrons show a shift in the binding energy (chemical shift) depending on **the chemical bonding with neighboring atoms and the valence of these atoms.**

Chemical shifts are typically of some tens of eV.

## Chemical shift & oxidation state

The removal of valence electrons (**oxidation**) causes **an increase** in the BE (i.e. it is more difficult to remove a further electron from the atom).

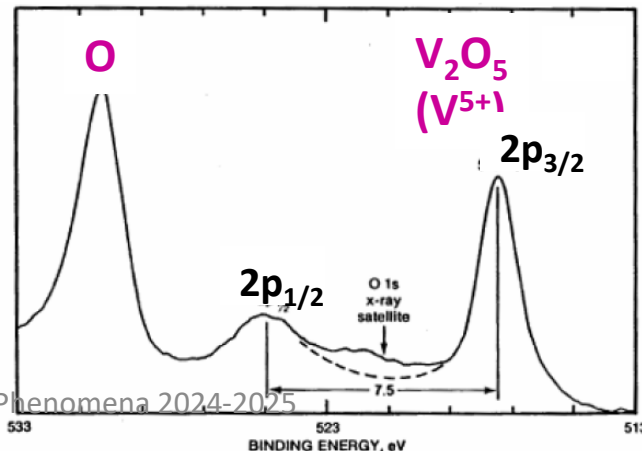
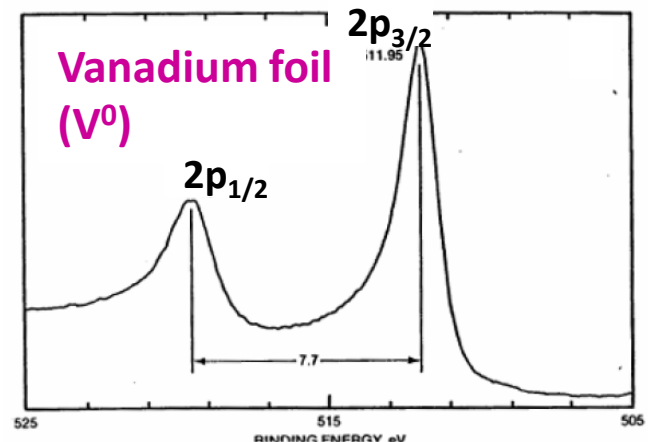
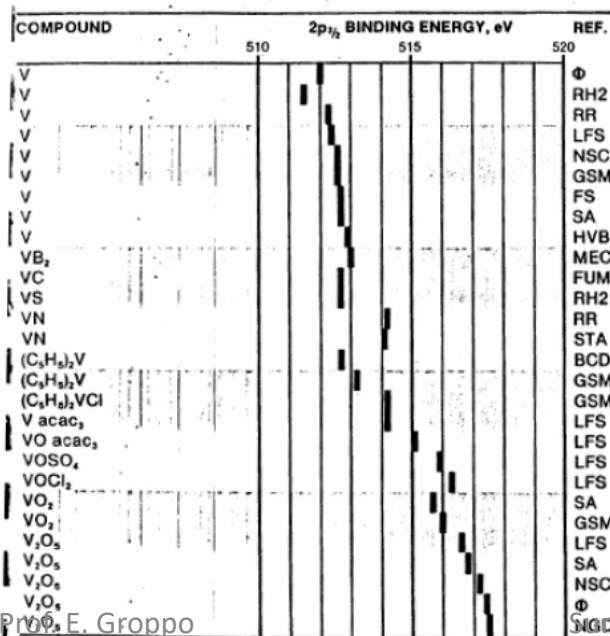
Conversely, the addition of valence electrons (**reduction**) causes a **decrease in the BE** (i.e. it is easier to remove an electron).

 $V^0$ 

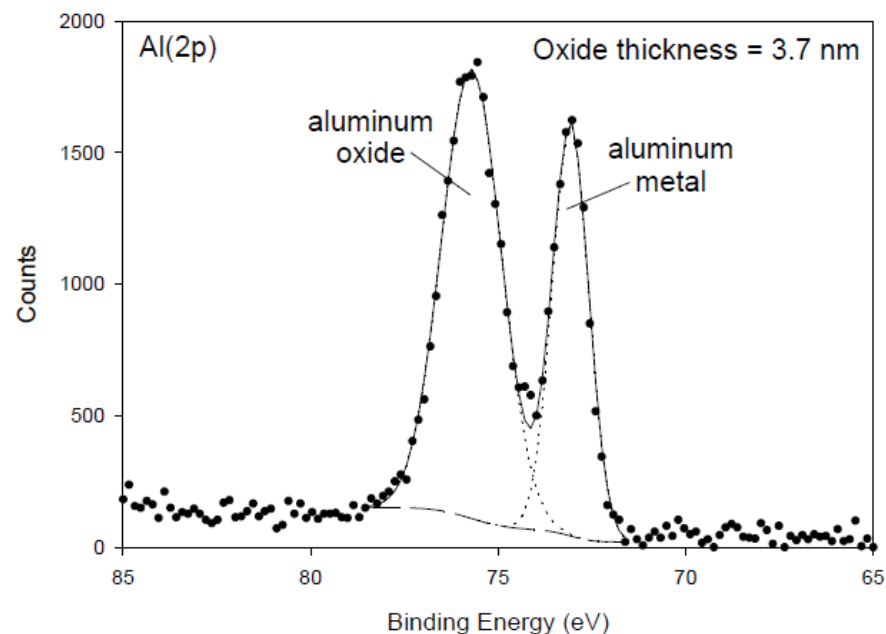
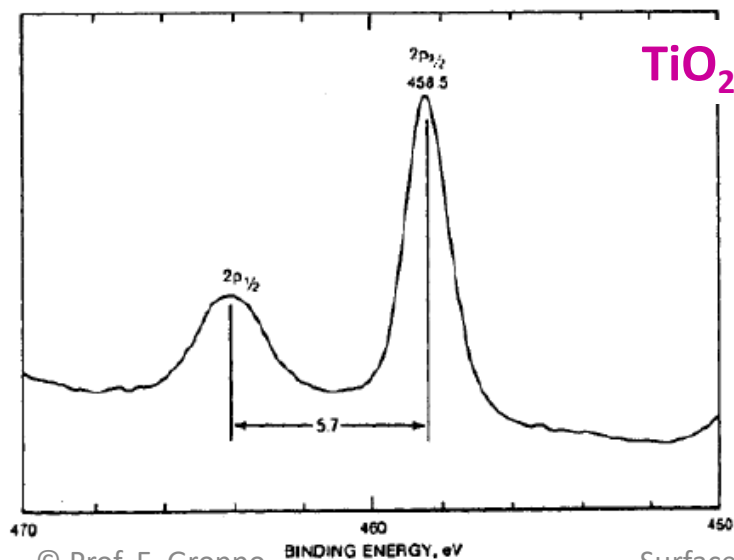
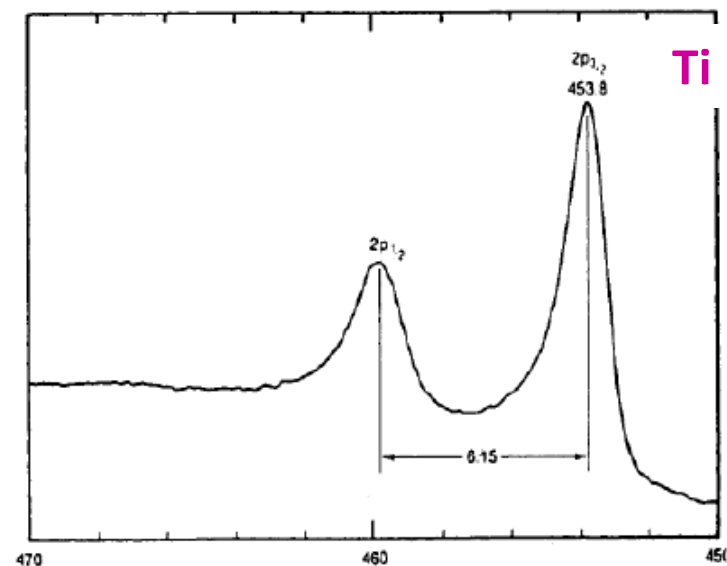
**V+5**

**511.95 eV**

517.45 eV



# Chemical shift & oxidation state (cont.)

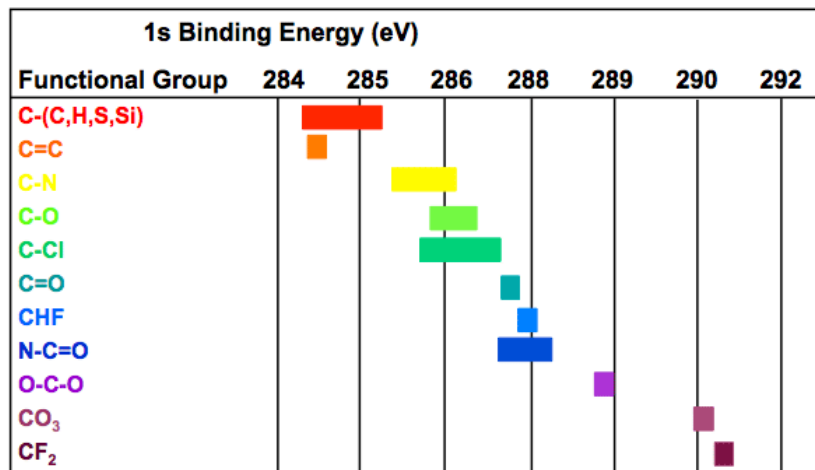


$\text{Al}2p$  XPS spectrum of aluminium surface. The relative intensity of the peaks due to metal Al and Al-oxide can be used to estimate the thickness of the oxide layer.

# Chemical shift & local environment

The chemical shifts can be induced by the local environment around the emitting atom. The origin of the chemical shift is the **electronegativity of the surrounding atoms**. For example, more electronegative elements around C atom decrease its electronic density, and hence cause an increase in the BE of the C1s peak.

## Carbon chemical state (C1s binding energy shift)

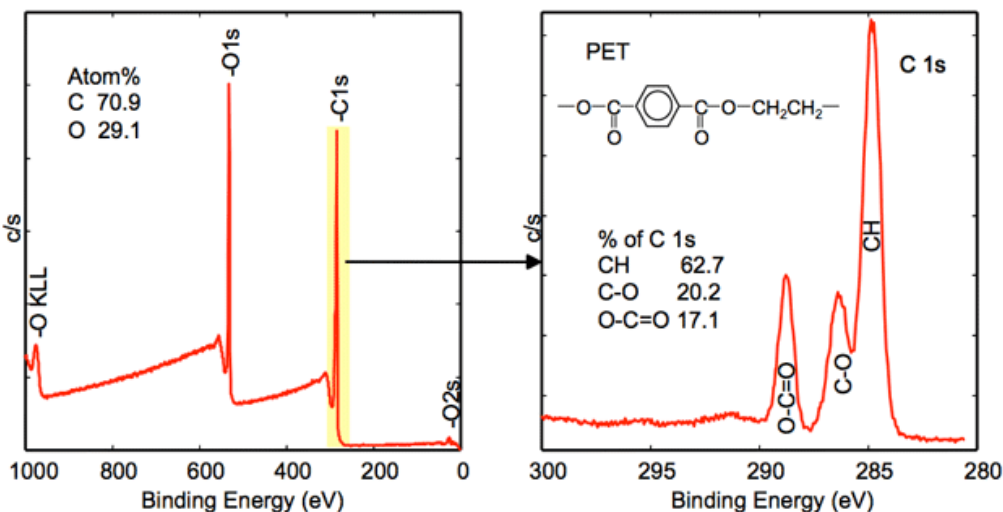


Functional Group		C(1s) Binding Energy (eV)
hydrocarbon	C-H, C-C	285.0
amine	C-N	286.0
alcohol, ether	C-O-H, C-O-C	286.5
Cl bound to C	C-Cl	286.5
F bound to C	C-F	287.8
carbonyl	C=O	288.0

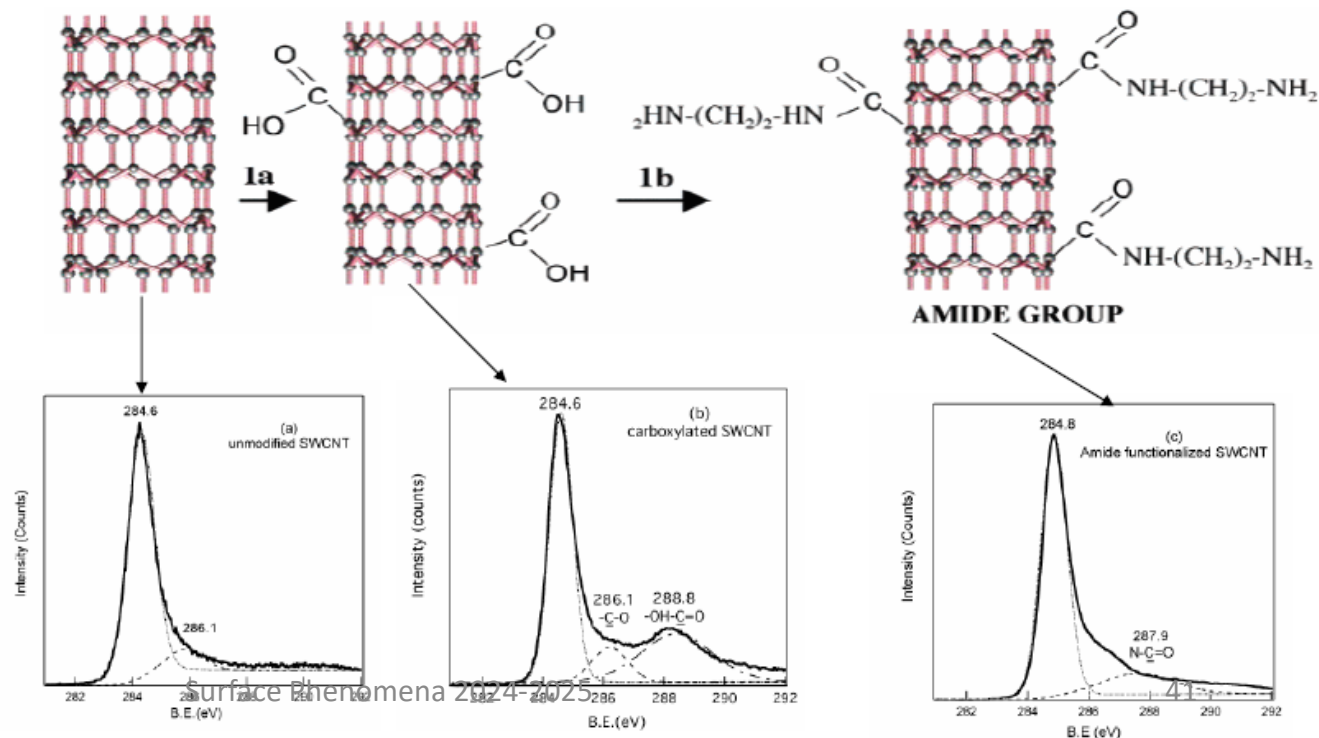


# Chemical shift & local environment (cont.)

XPS spectrum of  
polyethylene  
terephthalate (PET)



XPS spectra of  
functionalized carbon  
nanotubes



# Near ambient pressure XPS (NAP-XPS): why?

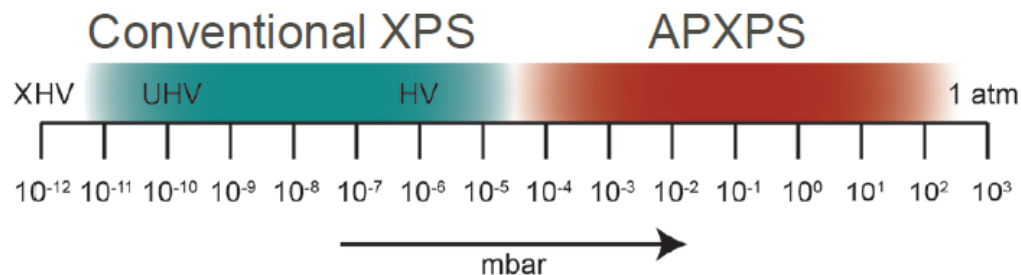
Pressures in  
conventional XPS  
experiments:  
 $10^{-10}$  to  $10^{-6}$  mbar



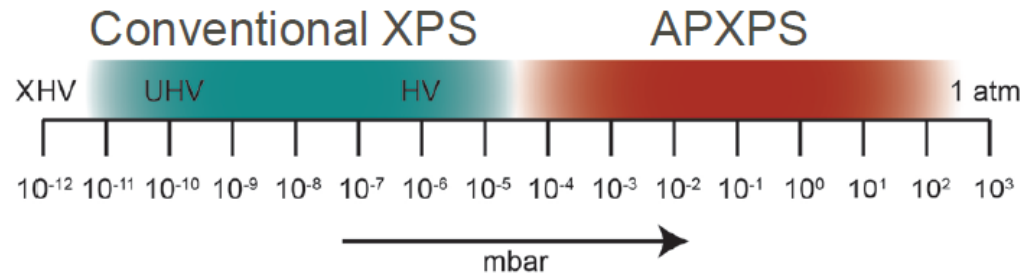
Pressure in a  
car catalyst:  
 $\sim$ atm



Pressures in typical catalytic  
reactors in the chemical  
industry:  
 $10^{-2}$  mbar 100 bar



# Near ambient pressure XPS (NAP-XPS): why? (cont.)



- (Surface) Structures may differ from those observed in UHV
- Materials with a high vapour pressure can be studied
- Dynamic processes can be studied (chemical reactions)

Catalysis  
Oxidation & corrosion  
Film growth  
Electrochemistry  
Liquids and solutions  
Bio/geo samples

Dynamic effects may play a significant, if not decisive, role but ...  
99.9% of all XPS instruments require high vacuum or ultrahigh vacuum

# Why do we need vacuum?

## 1. Control of surface state / cleanness

at  $p = 10^{-6}$  Torr a metal surface is completely covered by gas molecules in about 1 s

## 2. Detector requires vacuum

Microchannel plates in detector do not tolerate moisture and other gases when operated ( $\sim 10^{-6}$  mbar required)

## 3. Limited mean free path of low-energy electrons in gases

# Ambient pressure cell



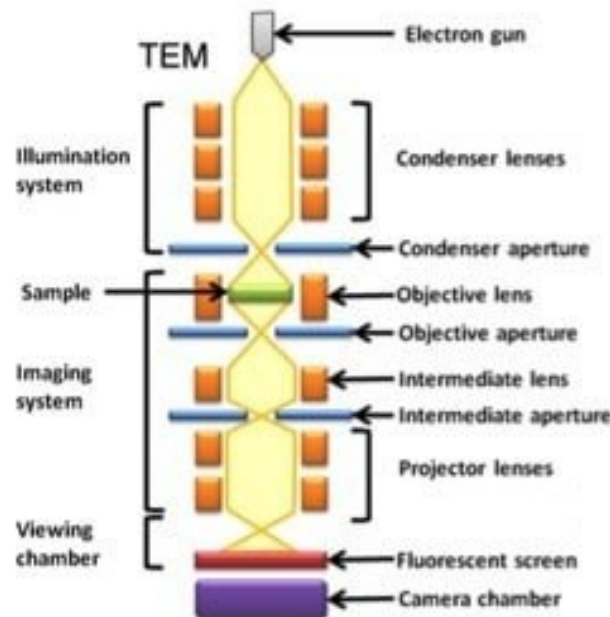
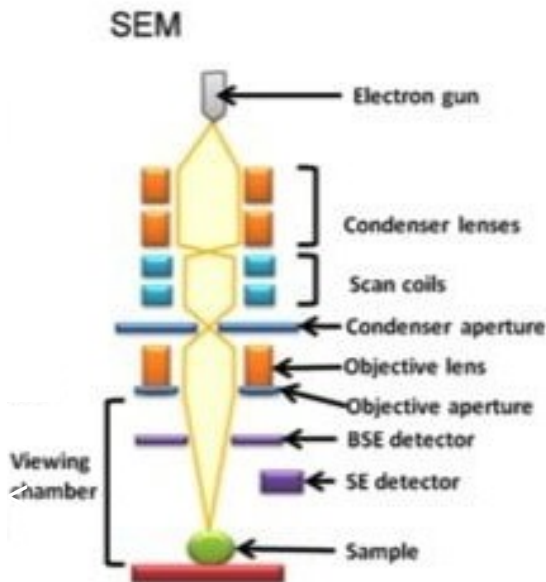
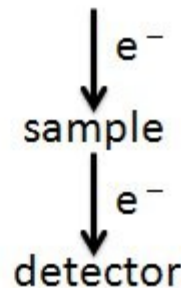
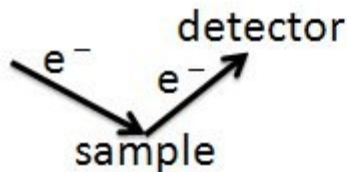
- Working pressure: about 0.1 to 25 mbar  
(pressure in analysis chamber during operation  $<1 \times 10^{-6}$  mbar)
- Temperature range: -50 °C to 500 °C
- Sample can be moved during measurement (beam damage!)

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# Rapid overview on electron microscopies

Scanning Electron Microscopy (SEM) is the electron technique to investigate the morphology of crystalline (and not crystalline) materials with a particle size larger than some tens of nanometers. For smaller details Transmission Electron Microscopy (TEM) is necessary.



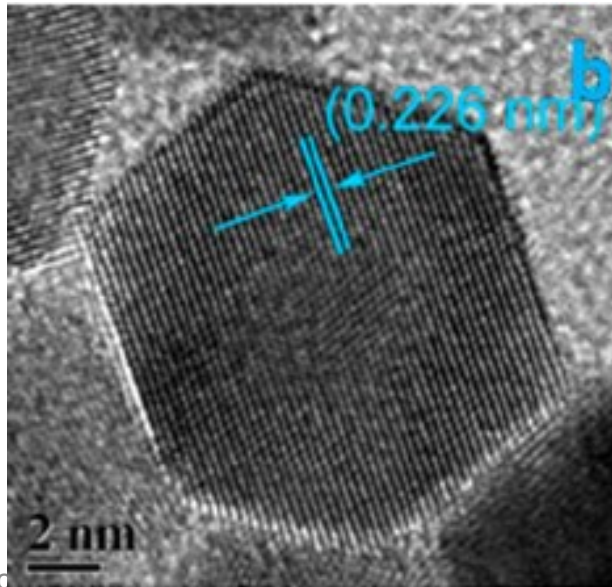
SEM detects electrons which reflected from the **surface** of the sample.

TEM detects electrons which went **through** the sample.

Thus SEM shows the surface of the sample, and TEM can show its inside (sometimes down to seeing individual atoms, if the TEM is very good and the sample very thin).

# Microscopies and crystal morphology (cont.)

The morphological information contained in the HR-TEM micrographs of polycrystalline materials is difficult to extract, since only 2D projections of the single 3D polyhedra in various orientation relative to the electron beam are obtained. However, when one or more crystal planes are parallel to the electron beam, plane fringes are observed, superimposed to the 2D projection of the microcrystals. **From the measured distances between individual fringes it is possible to determine the crystallographic indices of the responsible planes.**



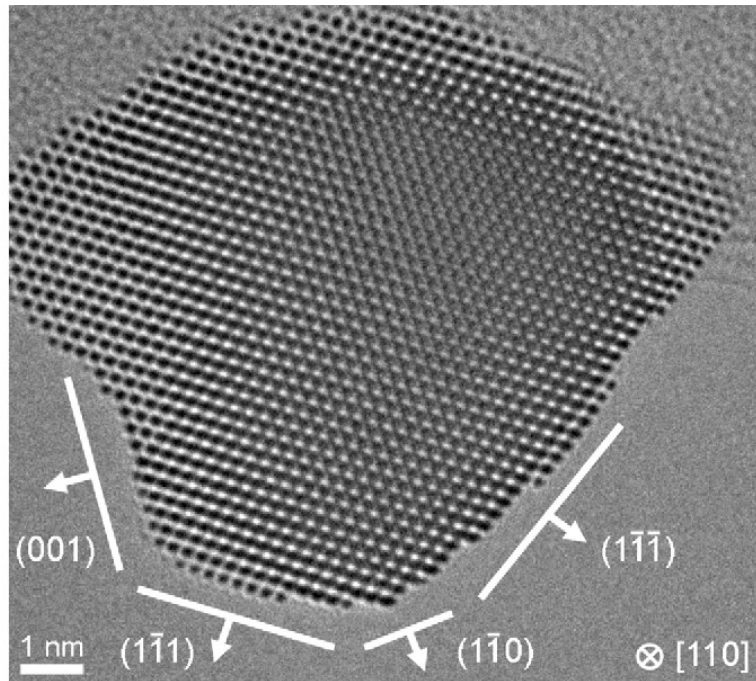
HRTEM image of a single cuboctahedral Pt nanoparticle



# Microscopies and crystal morphology (cont.)

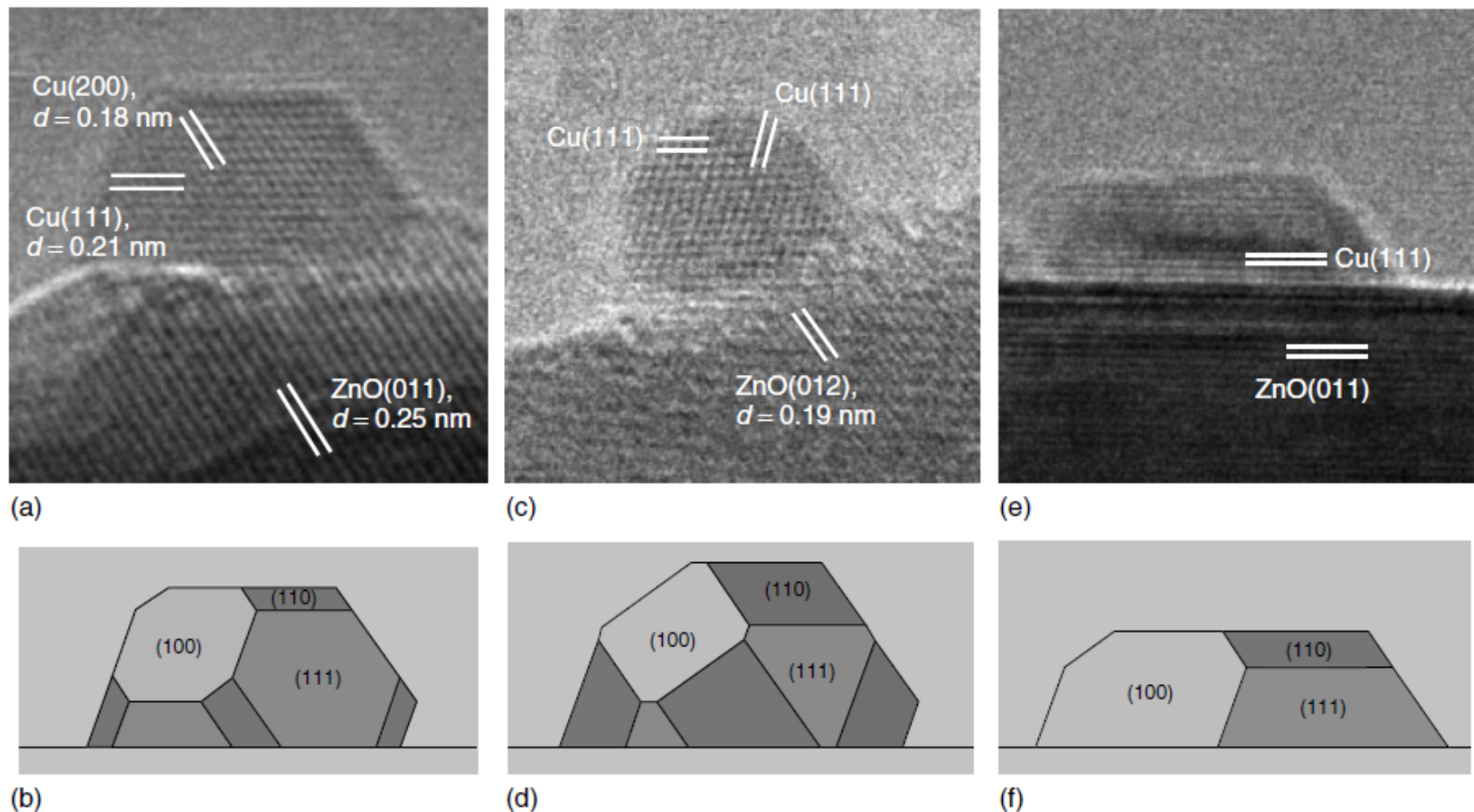
In a few cases, corresponding to favorably oriented microcrystals, two sets of plane fringes are simultaneously present in the planar projection of the same object. This is sufficient to infer the orientation of the planes of the polyhedron.

This procedure allows the **determination of the shapes of the few microcrystals** which show at least two types of intersecting fringes. However, the observation made for these relatively rare (suitably oriented) crystals can be extended with some confidence to the others.



HRTEM image of a Pt nanoparticle oriented in  $[110]$  direction reaching partly into the vacuum. The visible facets are labeled

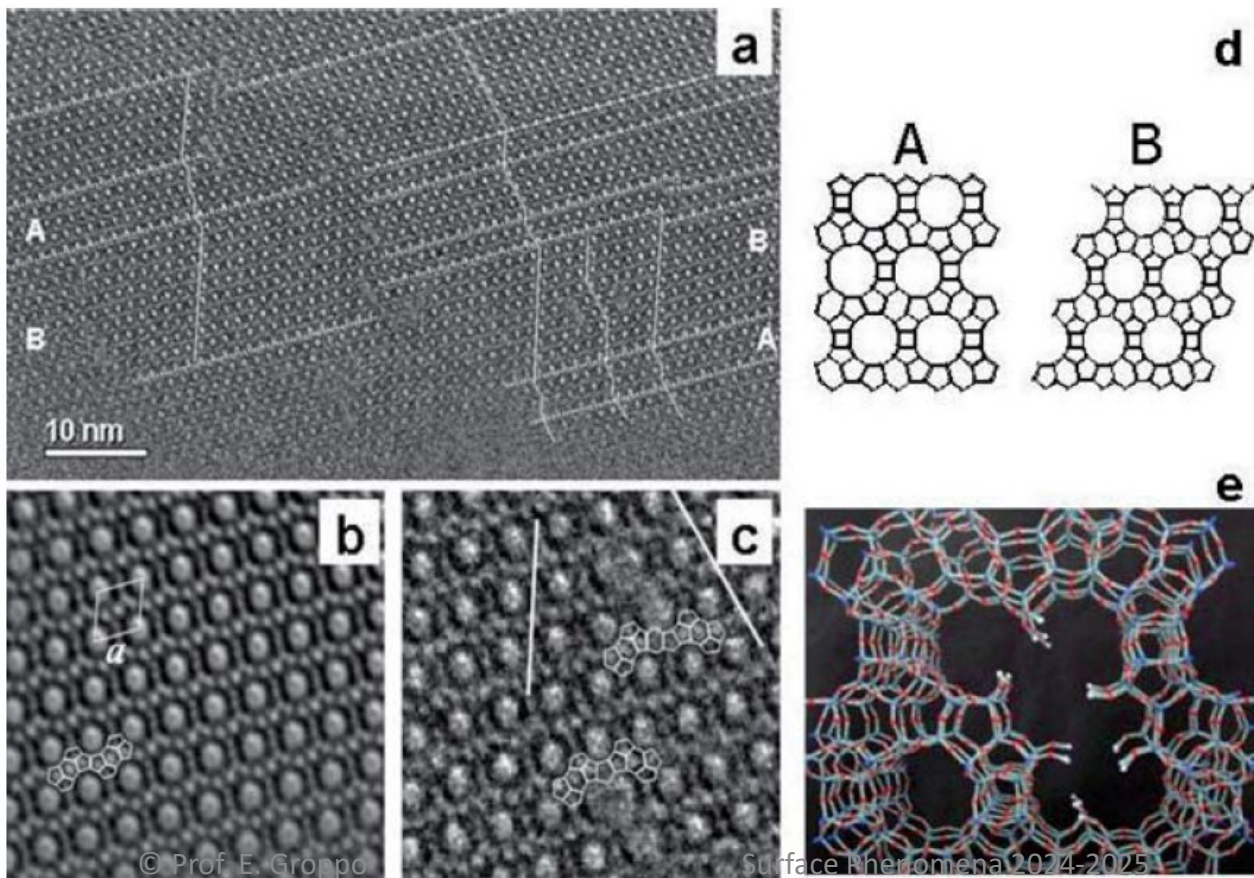
# Microscopies and crystal morphology (cont.)



**Fig. 31** *In situ* high resolution ETEM images [(a), (c) and (e)] of a Cu/ZnO catalyst in various gas environments together with the corresponding Wulff constructions of the Cu nanocrystals [(b), (d) and (f)]. (a) The image was recorded at a pressure of 150 Pa of  $\text{H}_2$  at  $220^\circ\text{C}$ . The electron beam is parallel to the [011] zone axis of copper. (c) Obtained in a gas mixture of  $\text{H}_2$  and  $\text{H}_2\text{O}$ ,  $\text{H}_2 : \text{H}_2\text{O} = 5 : 3$  at a total pressure of 150 Pa at  $220^\circ\text{C}$ . (e) Obtained in a gas mixture of  $\text{H}_2$  (95%) and CO (5%) at a total pressure of 500 Pa at  $220^\circ\text{C}$ . (Reprinted with permission from P. L. Hansen, J. B. Wagner, S. Helveg, J. R. Rostrup-Nielsen, B. S. Clausen, H. Topsøe, *Science* **2002**, 297, 2053.) © Prof. E. Groppo

# Microscopies and porosity

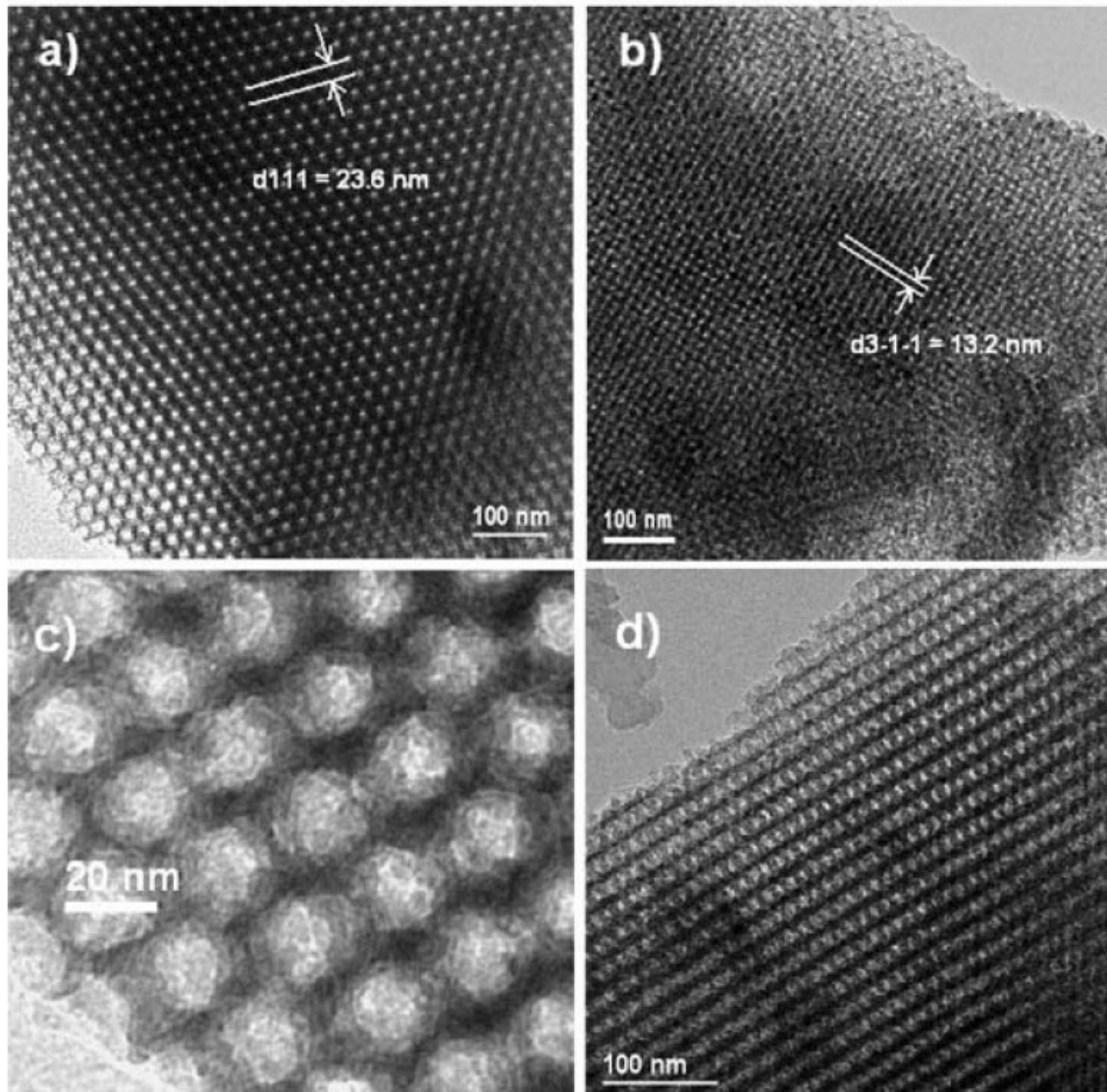
The principal role of HR-TEM in studying micro-porous materials such as zeolites is to directly image the open framework structures and therefore to discover the local microstructures.



**Figure 10.16** (a) HRTEM of an edge of a zeolite  $\beta$  crystallite, annotated to show the stacking directions in different parts. Nanodomains related to polytypes A and B are indicated. Defects are visible in the center of the image, where domains with different stacking directions meet; (b) Fourier-averaged image of a domain of type B, with structural units outlined; (c) Image of two double pore defects, showing different stacking directions and outlining secondary structural details on either side of the defects; (d) Models of the polytypes A (tetragonal) and B (monoclinic); (e) Model of the observed defects, obtained by stacking in the two ways onto a single layer and continuing to the third similar layer.



# Microscopies and porosity (cont.)



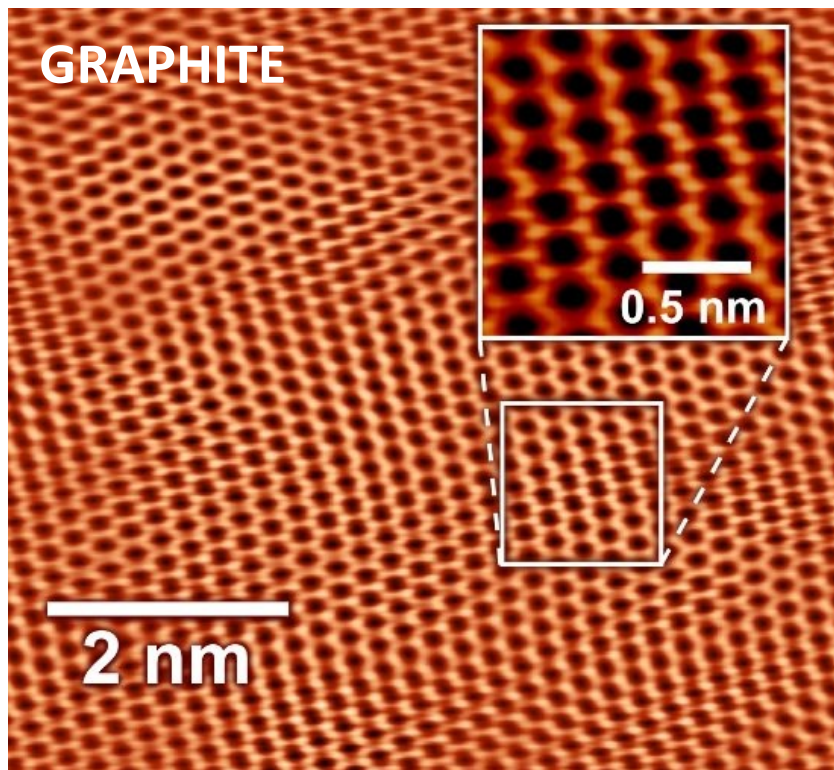
The unit cell dimensions of the mesoporous silicas are much larger than those of the microporous zeolites, and the X-ray powder diffraction method often gives insufficient reflection peaks.

TEM therefore becomes the most powerful technique for structural characterization of these materials.

**Figure 10.17** TEM images of mesoporous silica FDU-12 viewed down the (a) [110] and (b) [233] directions. (c) Enlarged TEM image of an edge area of (a). (d) TEM image of FDU-12 viewed down the [112] direction.

# STM: imaging at atomic scale

Scanning Tunneling Microscopy (STM) is an **imaging technique used to obtain ultra-high resolution images at the atomic scale**, without using light or electron beams.



The scan range of the entire image is less than 7 nm. Each of the yellowish dots in the highlighted magnified area represents one of the atoms which form the typical hexagonal “honeycomb” structure of the graphite lattice.

# STM: history in short

STM was invented in 1981 by two IBM scientists named Gerd Binnig and Heinrich Rohrer. Five years later (1986), the invention earned them the Nobel Prize in Physics.

STM was the first technique developed in the larger class of scanning probe microscopy imaging modes. At the time, it allowed researchers to capture significantly more detail than any previous microscopy—all the way down to atoms and inter-atomic spacing. This ultra-high resolution capability allowed researchers to **precisely map the three-dimensional topography and electronic density of states of conductive materials, and even manipulate individual atoms on the surface of these materials.** Over the following decades, STM has revolutionized the field of nanotechnology and continues to play an important role in fundamental and industrial research across a variety of disciplines.

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# Adsorption – desorption measurements

So far, we have discussed a few characterization methods to determine the structure and/or composition of the surface of different materials. When dealing with high-surface area, porous, materials, however, it is often desired to estimate the surface area and to evaluate the type of pores present in the material.

The most common method used to estimate the specific surface area of (porous) materials is via the measurement of adsorption–desorption isotherms, that is, of the adsorption volume of a gas, typically nitrogen, as a function of its partial pressure.



# Adsorption of probe molecules

When a solid is exposed in a closed space to a gas at pressure  $p$ , the weight of the solid typically increases and the pressure of the gas decreases: the gas is adsorbed by the solid. After a time, the pressure  $p$  does not change any more and correspondingly the weight ceases to increase any further: a dynamic equilibrium is reached.

The amount of gas adsorbed can be experimentally determined:

- (i) by **gravimetry** (the increase in weight of the solid is monitored by a spring balance);
- (ii) by **volumetry** (the fall in the gas pressure is monitored by manometers/transducer gauges);
- (iii) by monitoring the change of any other physical parameter related to the adsorption of matter, such as the **evolved heat** (if the heat of adsorption is known and constant) or the **integrated IR absorbance** (if the specific molar absorbance of adsorbed species is known).

# IR spectroscopy of adsorbed probes

The non dissociative adsorption of probe molecules on the surface of materials is accompanied by distinct perturbations of the vibrational spectra.

The type of interaction and the resulting vibrational perturbation (purely electrostatic or with some orbital overlap contribution) depend on the electronic structure of the adsorption site (with or without d electrons).

At low coverages, the vibrational perturbation induced by adsorption on a site is primarily determined by the **coordinative unsaturation of that site**. **Probe molecules adsorbed on highly coordinatively unsaturated defects (e.g. corners and edges) are usually more strongly perturbed than those adsorbed on flat faces**, and the associated adsorption energy is also stronger. These effects provide qualitative information about the defect structures of surfaces on the atomic scale.

# Adsorption micro-calorimetry

The heat evolved when a gas contacts the solid surface is related to the nature and energy of the adsorbed species/surface atoms interactions. The knowledge of the energetics of chemical and physical events responsible for the process, and the assessment of the associated thermodynamic parameters contributes to a thorough understanding of phenomena taking place at surfaces.