X-ray photoelectron spectroscopy - An introduction

Spyros Diplas
MENA3100

SINTEF Materials & Chemistry, Department of Materials Physics
&
Centre of Materials Science and Nanotechnology, Department of Chemistry, UiO

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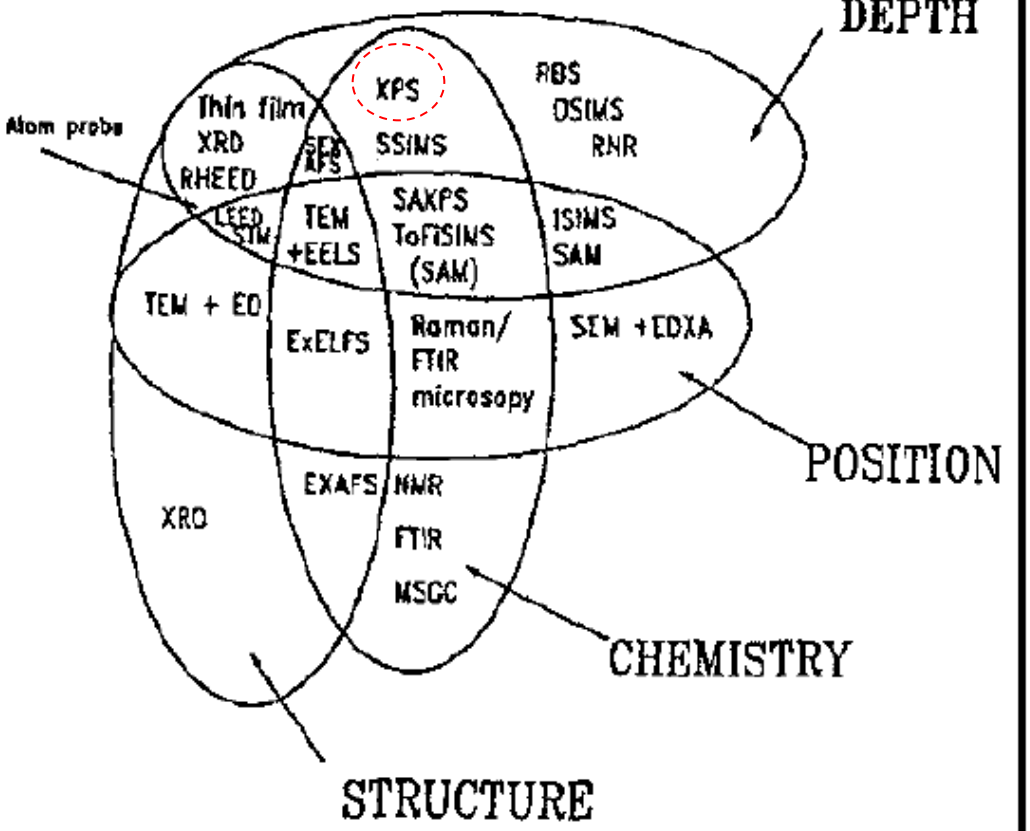
Material Characterisation Methods

Thin Film X-Ray Diffraction
Reflection High Energy Electron Diffraction
Low Energy Electron Diffraction
Scanning Tunnelling Microscopy
Transmission Electron Microscopy
Electron Diffraction
X-Ray Diffraction
Extended X-ray Absorbtion Fine Structure
Surface EXAFS
Extended Electron Energy Loss Fine Structure
Electron Energy Loss Spectroscopy
X-ray Photo-electron Spectroscopy
Static Secondary Ion Spectroscopy
Dynamic SIMS
Imaging SIMS
Small Area XPS
Time-of-Flight (imaging) SIMS
Scanning Auger electron Microscopy
Fourier Transform Infra-Red Spectroscopy
Scanning Electron Microscopy
Energy Dispersive X-ray Analysis
Nuclear Magnetic Resonance
Mass Spectroscopy Gas Chromatography

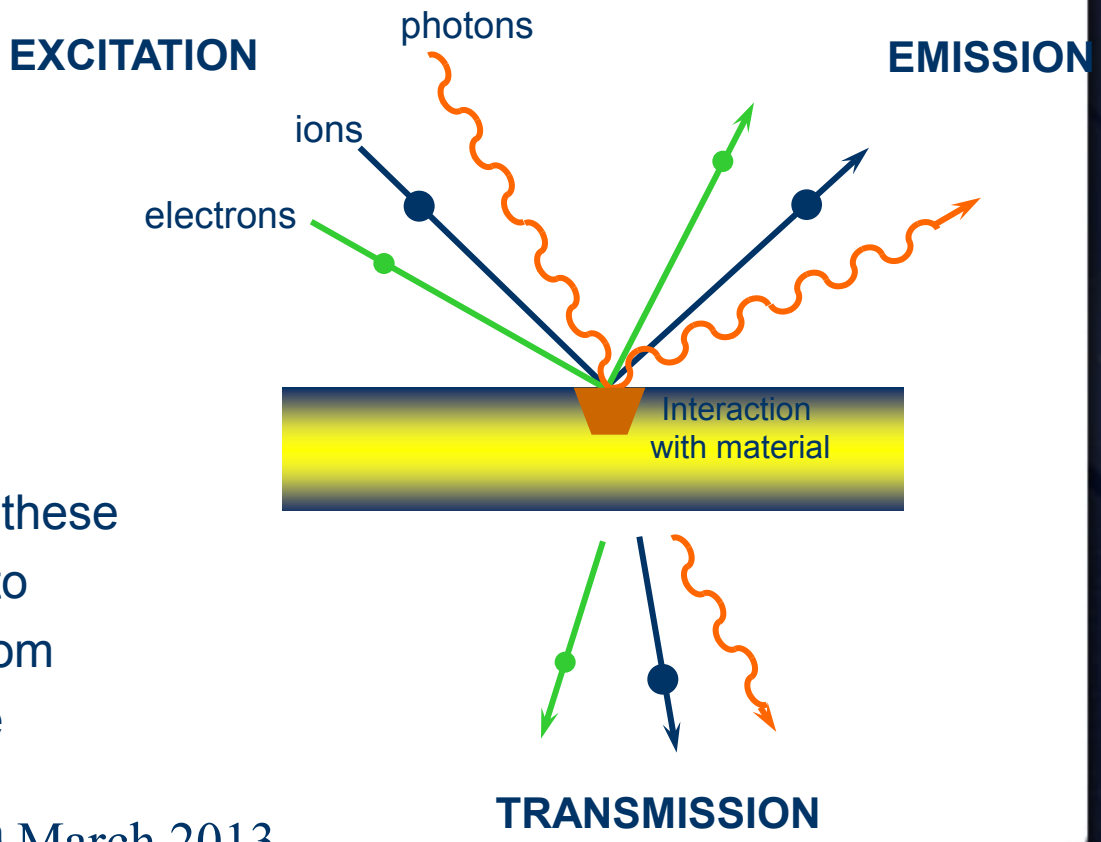


What is the surface?

- What happens at surfaces is extremely important in a vast range of applications from environmental corrosion to medical implants.
- A surface can be thought of as the interface between different phases (solid, liquid or gas).
- We can think of the surface as the top layer of atoms but in reality the state of this layer is very much influenced by the 2 – 10 atomic layers below it (~0.5 – 3 nm).
- Surface modification treatments are often in the range of 10 – 100 nm thick. >100 nm can be thought of as the bulk.
- Surface analysis encompasses techniques which probe the properties in all these ranges.

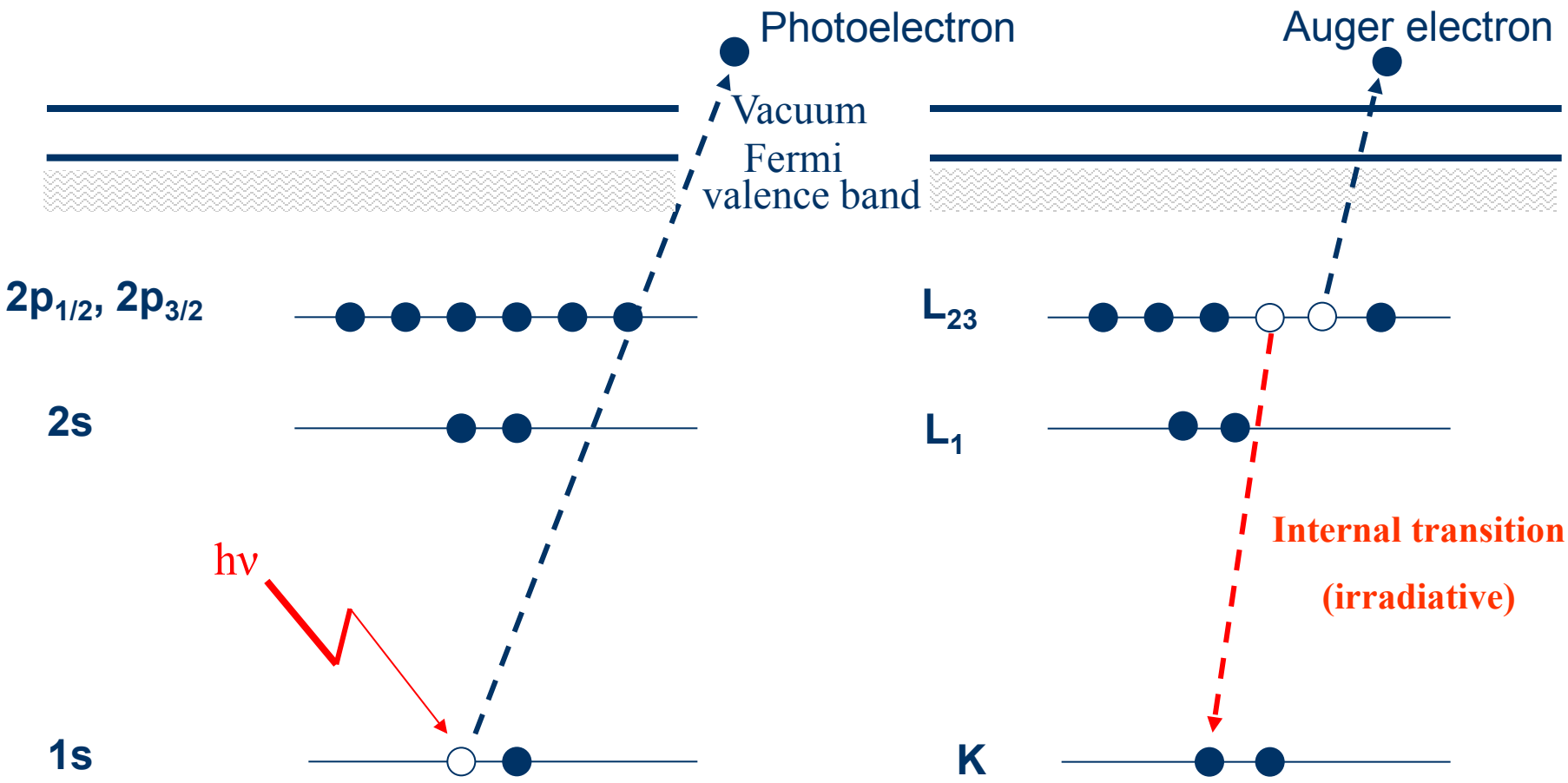
Surface Analysis - Techniques Available

- Properties and reactivity of the surface will depend on:
- bonding geometry of molecules to the surface
- physical topography
- chemical composition
- chemical structure
- atomic structure
- electronic state



No one technique can provide all these pieces of information. However, to solve a specific problem it is seldom necessary to use every technique available.

XPS-Basic Principle



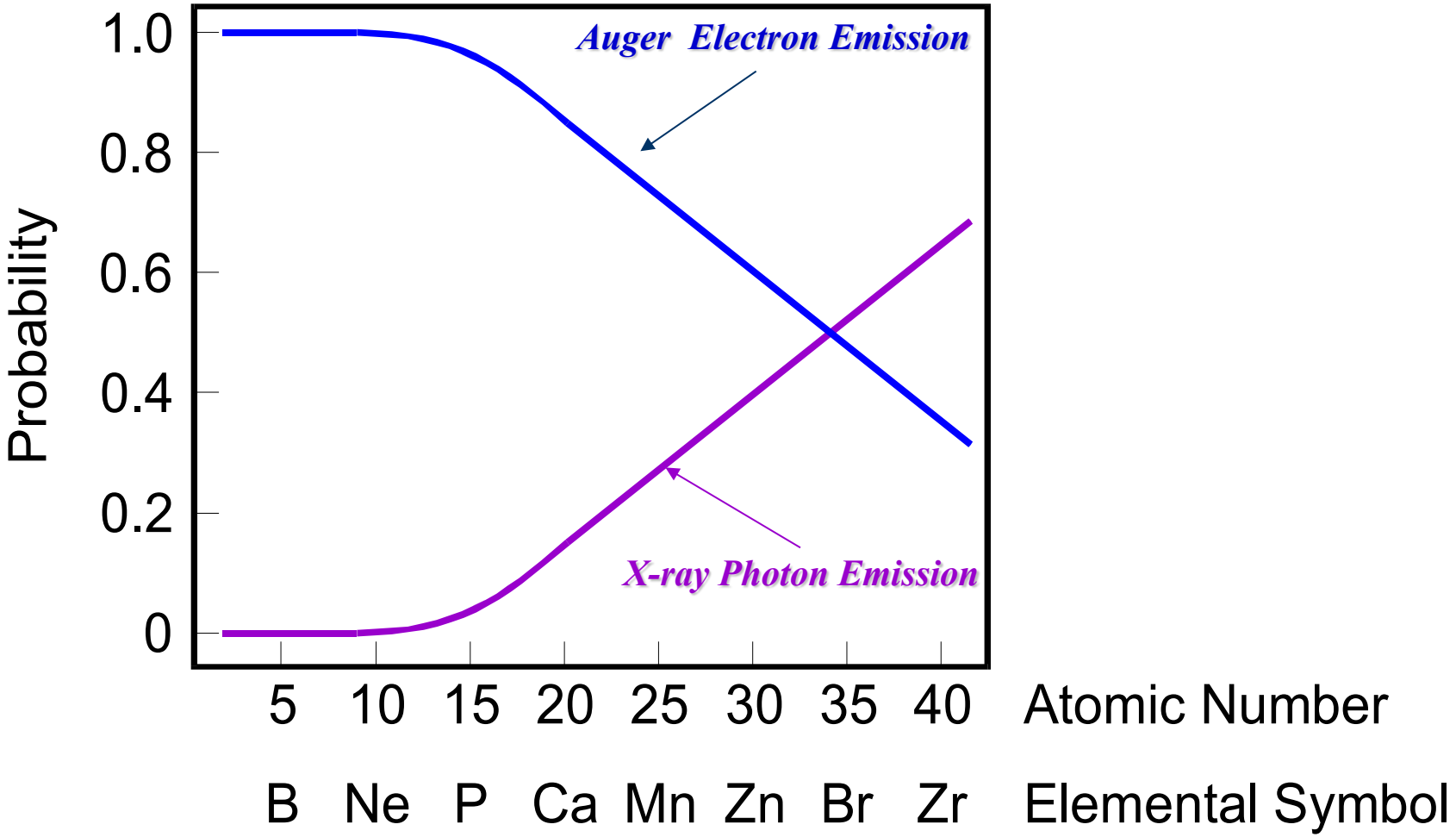
$$E_{kin} = h\nu - E_B - \omega$$

$$E_{KL2,3L2,3}(Z) = E_K(Z) - [E_{L2,3}(Z) + E_{L2,3}(Z+1)]$$

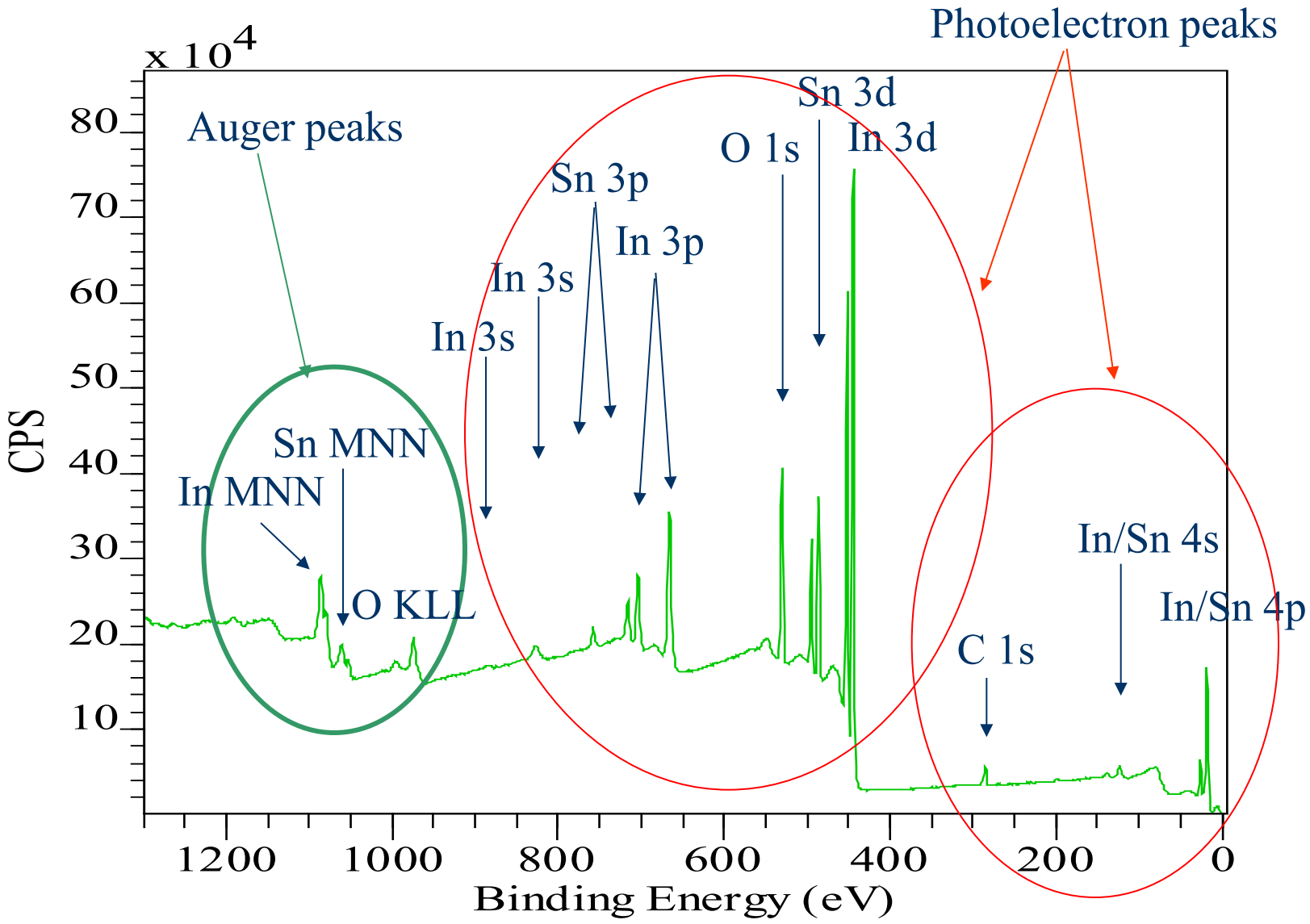
Excitation

De-excitation

Auger electron vs x-ray emission yield



XPS spectrum ITO



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Peak width (ΔE)

$$\Delta E = (\Delta E_n^2 + \Delta E_p^2 + \Delta E_a^2)^{1/2}$$

Natural width

X-ray source contribution

Analyser contribution

- Gaussian broadening:

-Instrumental:

There is no perfectly resolving spectrometer nor a perfectly monochromatic X-ray source.

-Sample

For semiconductor surfaces in particular, variations in the defect density across the surface will lead to variations in the band bending and, thus, the work function will vary from point to point. This variation in surface potential produces a broadening of the XPS peaks.

-Excitation process such as the shake-up/shake-off processes or vibrational broadening.

- Lorentzian broadening.

The core-hole that the incident photon creates has a particular lifetime (τ) which is dependent on how quickly the hole is filled by an electron from another shell. From **Heisenberg's uncertainty principle**, the finite lifetime will produce a broadening of the peak.

$$\Gamma = h/\tau$$

Intrinsic width of the same energy level should increase with increasing atomic number

Examples of XPS spectrometers

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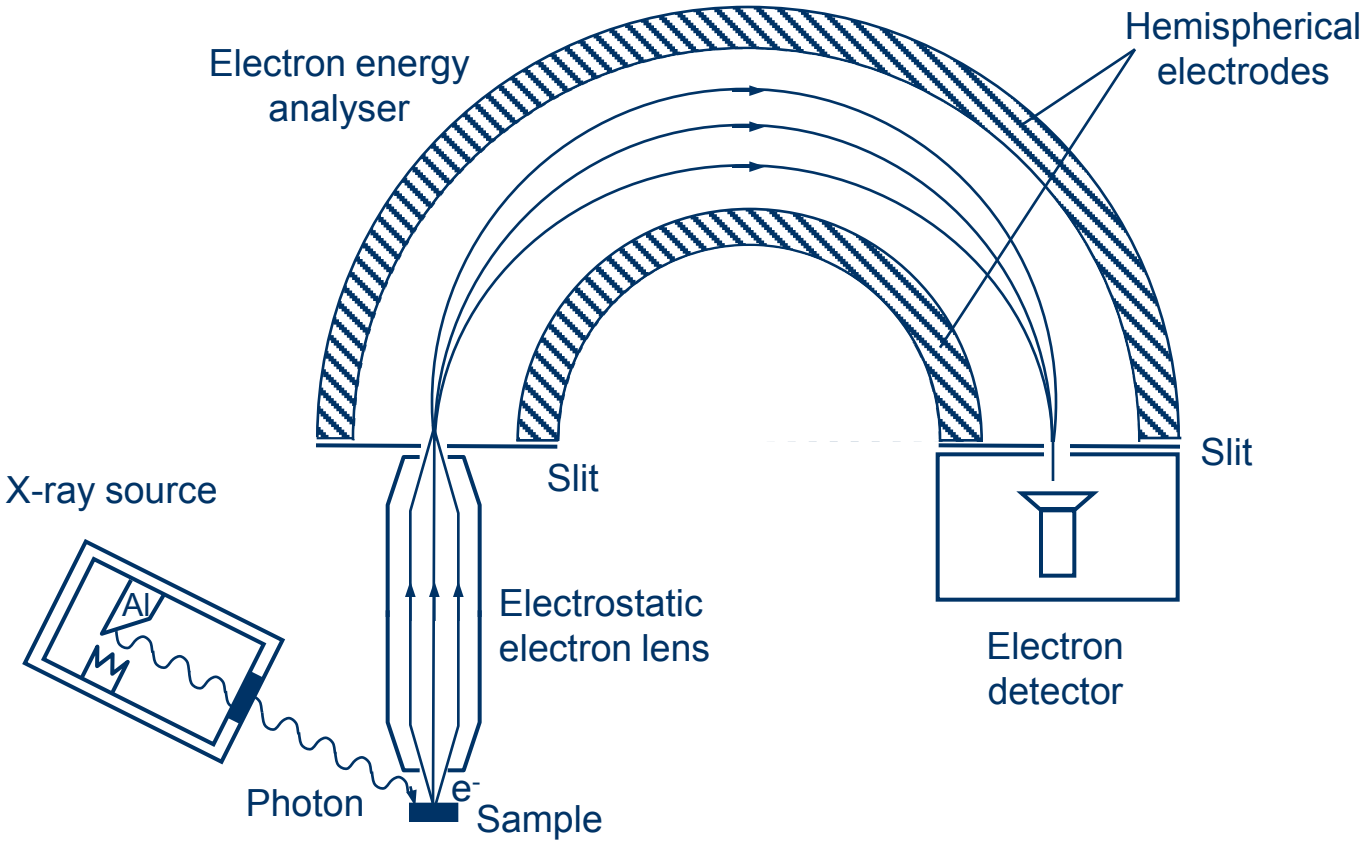
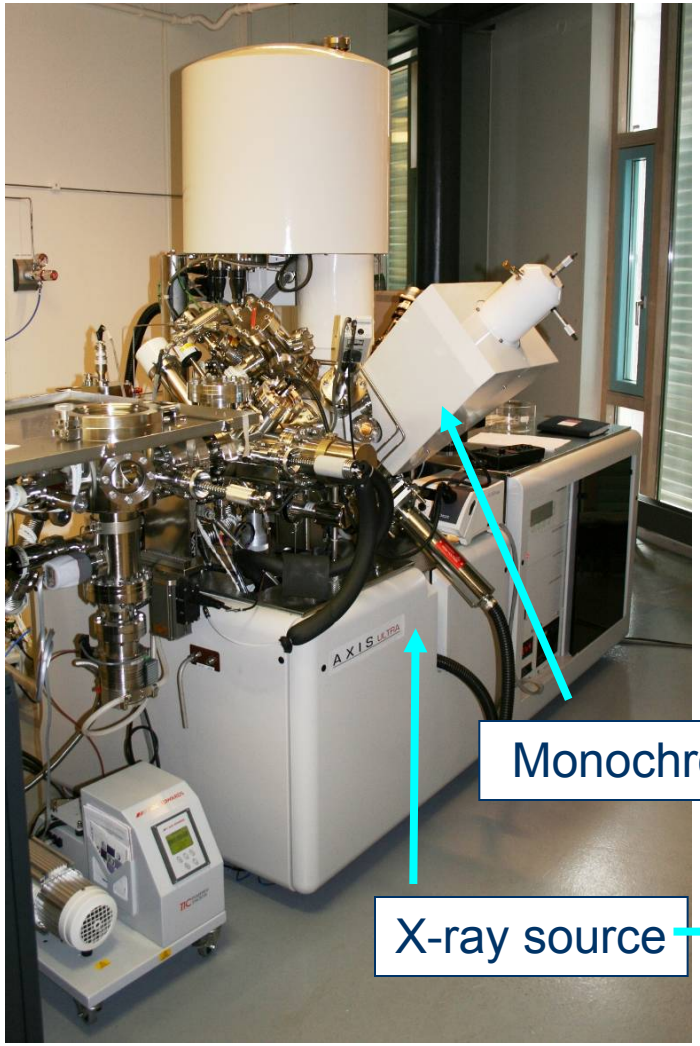
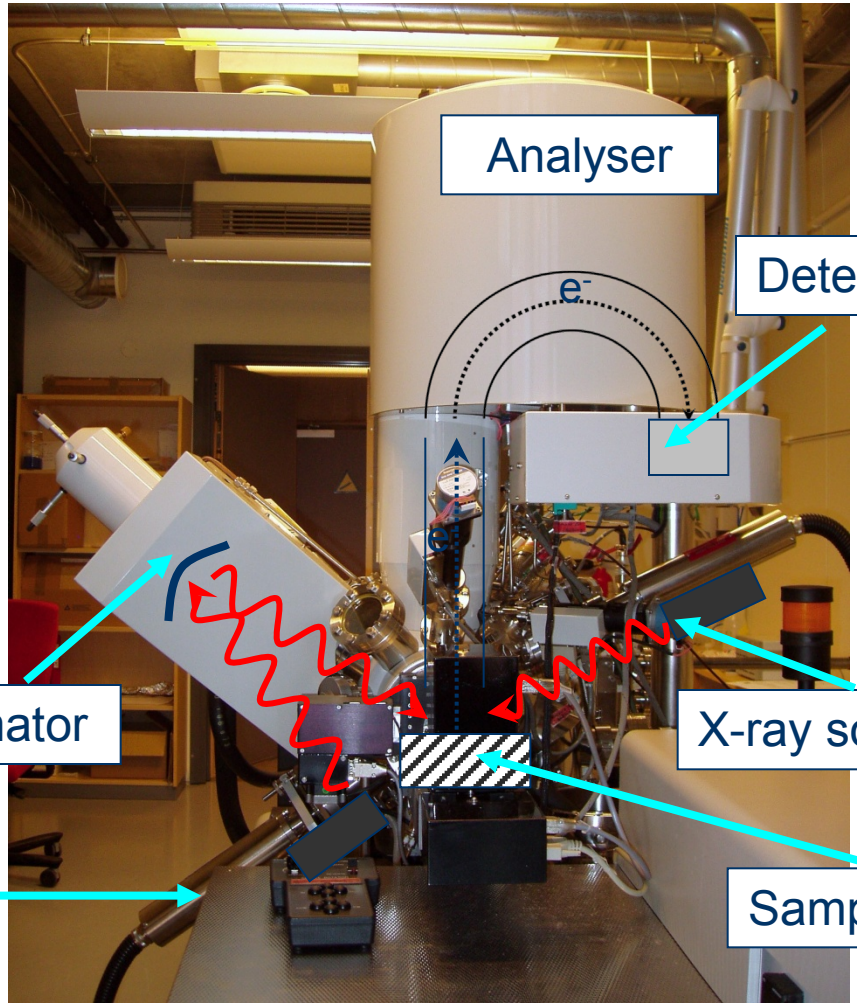
Schematic of an XPS spectrometer



Number of emitted electrons measured as function of their kinetic energy

Instrument: Kratos Axis Ultra^{DLD} at MiNaLab





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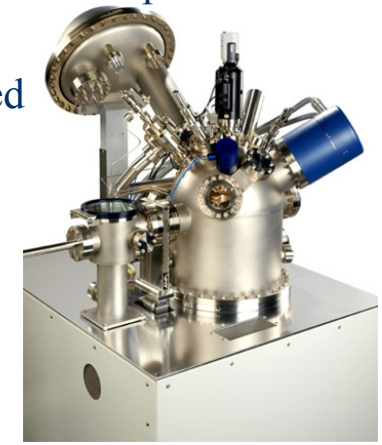
The new XPS instrument-Theta Probe

- Spectroscopy
  - Source-defined small area XPS
    - 15 µm to 400 µm
- Snapshot spectrum acquisition
  - Up to 112 channels
  - Faster serial mapping
  - Faster profiling
- Unique parallel ARXPS with up to 96 channels
- Large samples (70 mm x 70 mm x 25 mm)
- Sputter profiles
- Mapping possible up to full size of sample holder
- ISS included



Target applications

- Thickness measurements
- Surface modification, plasma & chemical
- Self assembly
- Nanotechnology
- Ultra thin film technologies
- Shallow interfaces

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Sample requirements

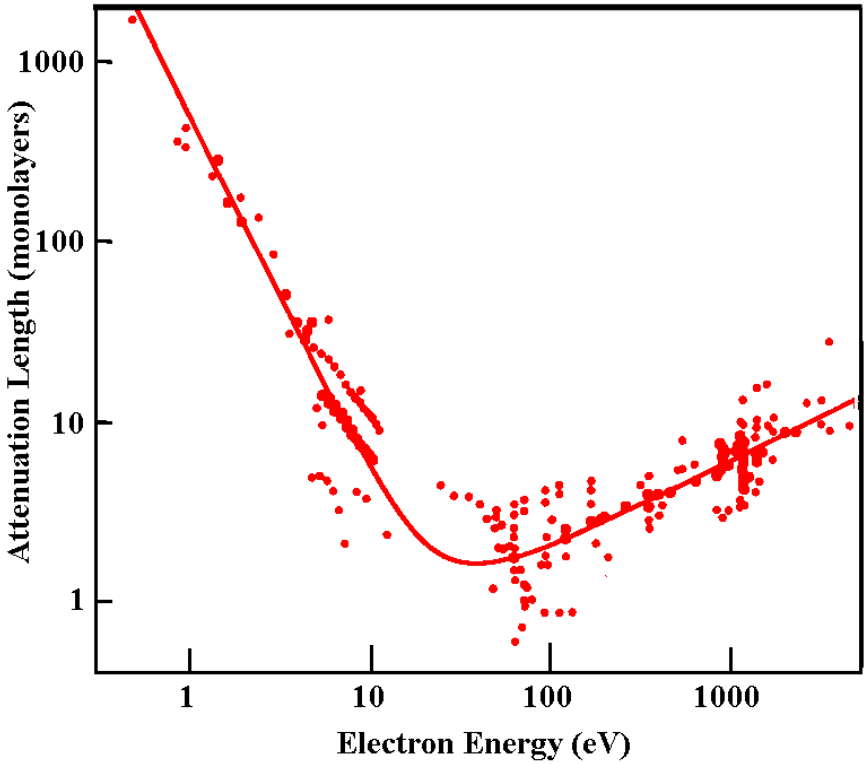
- Has to withstand high vacuum (≤ 10^{-7} Torr).
- Has to withstand irradiation by X-rays
- Sample surface must be clean!
- Reasonably sized.

XPS Depth of Analysis

The probability that a photoelectron will escape from the sample without losing energy is regulated by the Beer-Lambert law:

$$e^{\frac{-z}{\lambda_e(E)\cos\theta}}$$

Where λ_e is the photoelectron inelastic mean free path



Attenuation length (λ) ≈0.9 IMFP

IMFP: The average distance an electron with a given energy travels between successive inelastic collisions

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Features of the XPS spectrum

- Primary structure

  - Core level photoelectron peaks (atom excitation)
  - Valence band spectra
  - CCC, CCV, CVV Auger peaks (atom de-excitation)

- Secondary structure

  - X-ray satellites and ghosts
  - Shake up and shake off satellites
  - Plasmon loss features
  - Background (slope)

Quantification

- Unlike AES, SIMS, EDX, WDX there are little in the way of matrix effects to worry about in XPS. We can use either theoretical or empirical cross sections, corrected for transmission function of the analyser. In principle the following equation can be used:

$$I = J \rho \sigma K \lambda$$

- I is the electron intensity
- J is the photon flux,
- ρ is the concentration of the atom or ion in the solid,
- σ s is the cross-section for photoelectron production (which depends on the element and energy being considered),
- K is a term which covers instrumental factors,
- λ is the electron attenuation length.

- In practice atomic sensitivity factors (F) are often used:
- [A] atomic % = {(IA/FA)/Σ(I/F)}
- Various compilations are available.

Koopmans Theorem

Koopman's Theorem:

The BE of an electron is simply difference between:

initial state (atom with n electrons) and

final state (atom with n-1 electrons (ion) + free photoelectron)

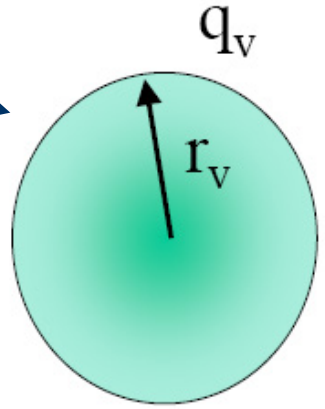
$BE = E_{final\ (n\ -1)} - E_{initial\ (n)}$

If no relaxation followed photoemission, $BE = -\ \varepsilon$

ε = orbital energy which can be calculated from Hartree-Fock method

CHEMICAL SHIFT- (only initial state considered)

- The **charge potential model** **(Siegbahn *et al.* 1969)**
- (atom considered as a hollow sphere)



- $\mathbf{E_i = Ei_0 + kq_i + \Sigma q/r_{i,j}}$ **(i≠j)**

- E_i BE of a core level on atom i
- E_{i0} energy reference
- q_i charge on atom i
- $\Sigma q / r_{i,j}$ potential on atom i due to point changes on surrounding atoms j

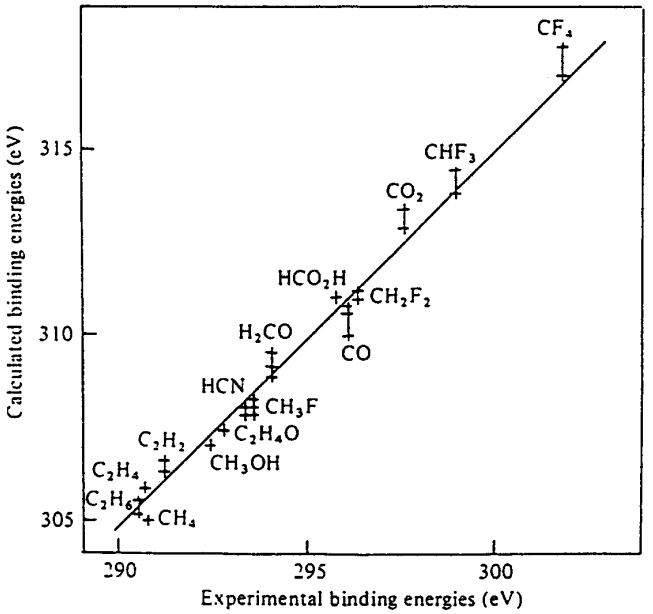
- Potential = q_i/r_v (r_v =average valence orbital radius) is the same at all points inside the sphere
- $\mathbf{\Delta E_i = k\Delta q + \Delta V}$ oxidation → **$\Delta q>0 \rightarrow \Delta E_i>0$**
- Simplifications reduction → **$\Delta q<0 \rightarrow \Delta E_i<0$**
- (a) Intra- and extra-atomic relaxation effects not encountered
- (b) Assumes that the materials involved have same Φ values

Koopmans Theorem-deviation

Measured BE's and calculated orbital energies different by 10-30 eV because of:

- electron rearrangement to shield core hole - the frozen orbital approximation is not accurate
- electron correlation & relativistic effects

Both *initial state effects* and *final state effects* affect measured BE



Comparison of experimental XPS C 1s binding energies with those calculated via Koopman's theorem for C in a range of molecules. Although experimental and theoretical values differ by 15 eV (associated with relaxation effects) the systematic comparison is excellent as indicated by the straight line of unity gradient (after Shirley, 1973).

Chemical shift

$$\Delta E_{(i)} = k\Delta q + \Delta V_M - \Delta R$$

Initial state contribution

final state contribution

- Δq: changes in valence charge
- ΔV_M : Coulomb interaction between the photoelectron (i) and the surrounding charged atoms.
- ΔR: relaxation energy change arising from the response of the atomic environment (local electronic structure) to the screening of the core hole

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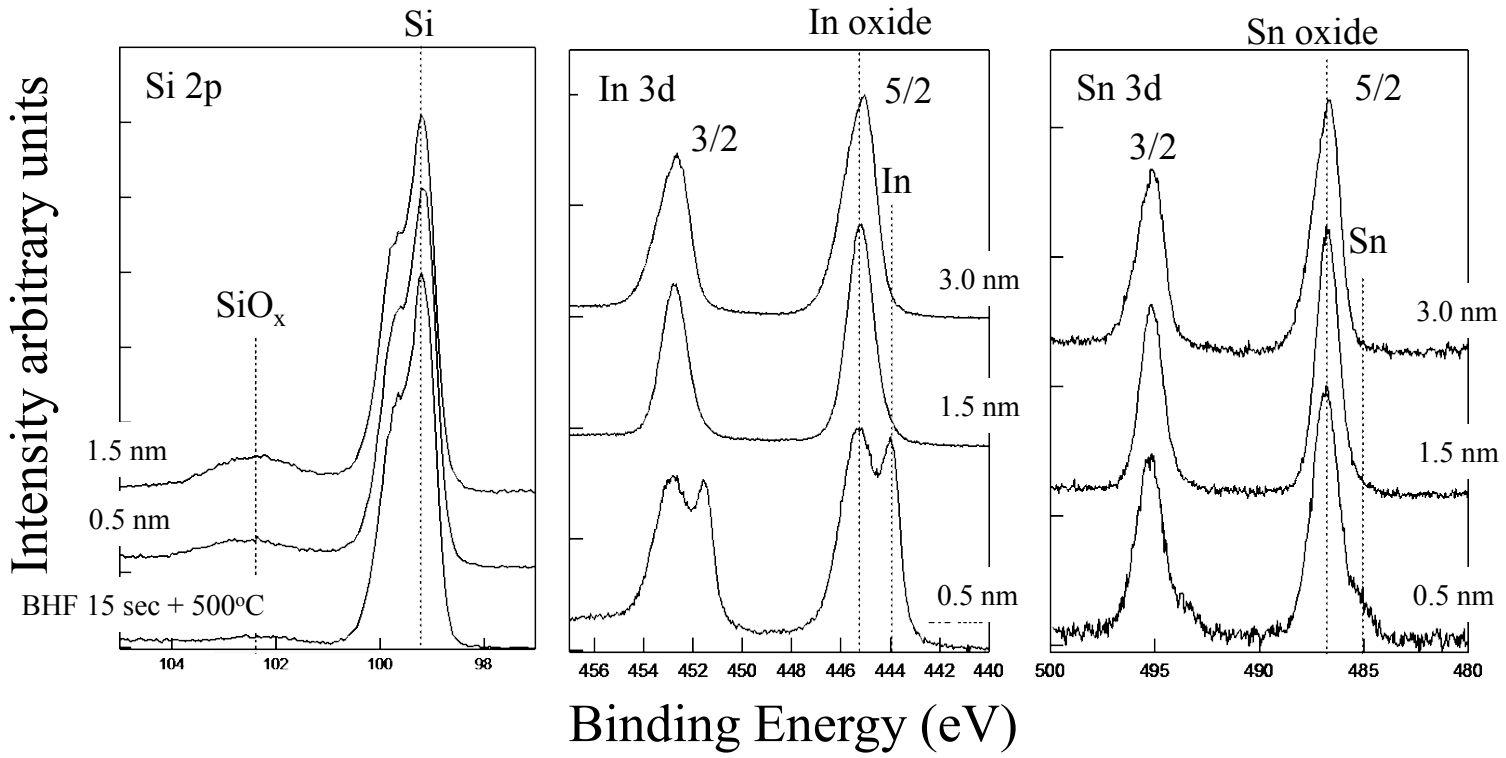
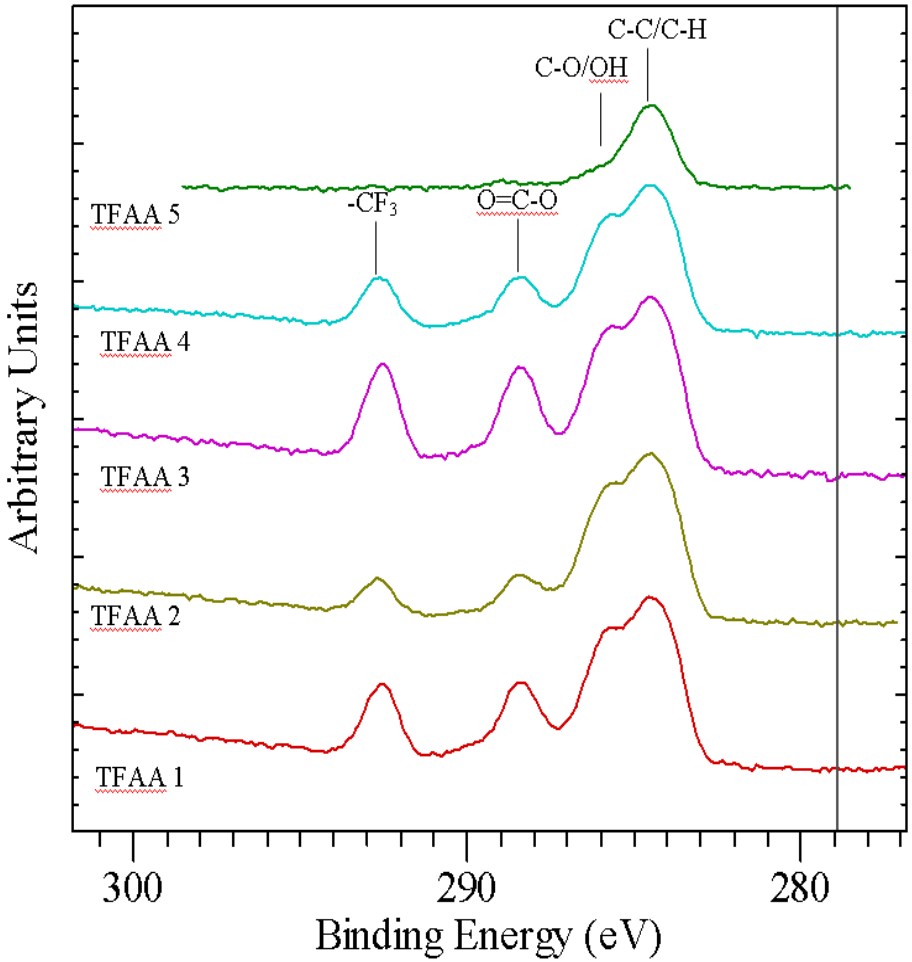
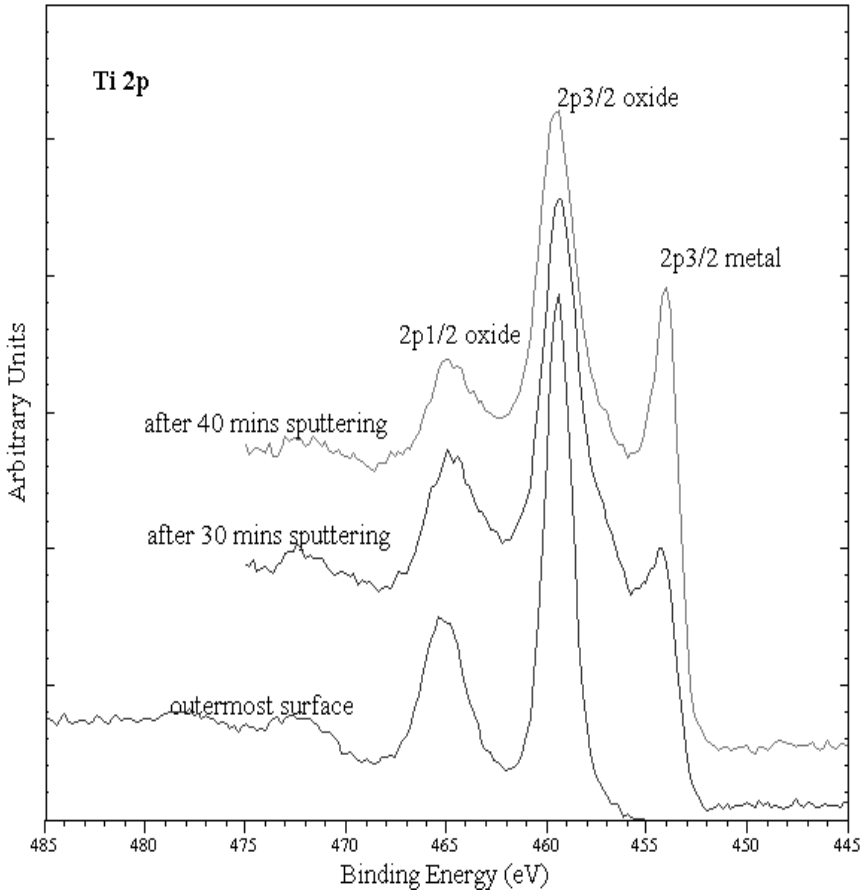
Chemical shift - Growth of ITO on p c-Si

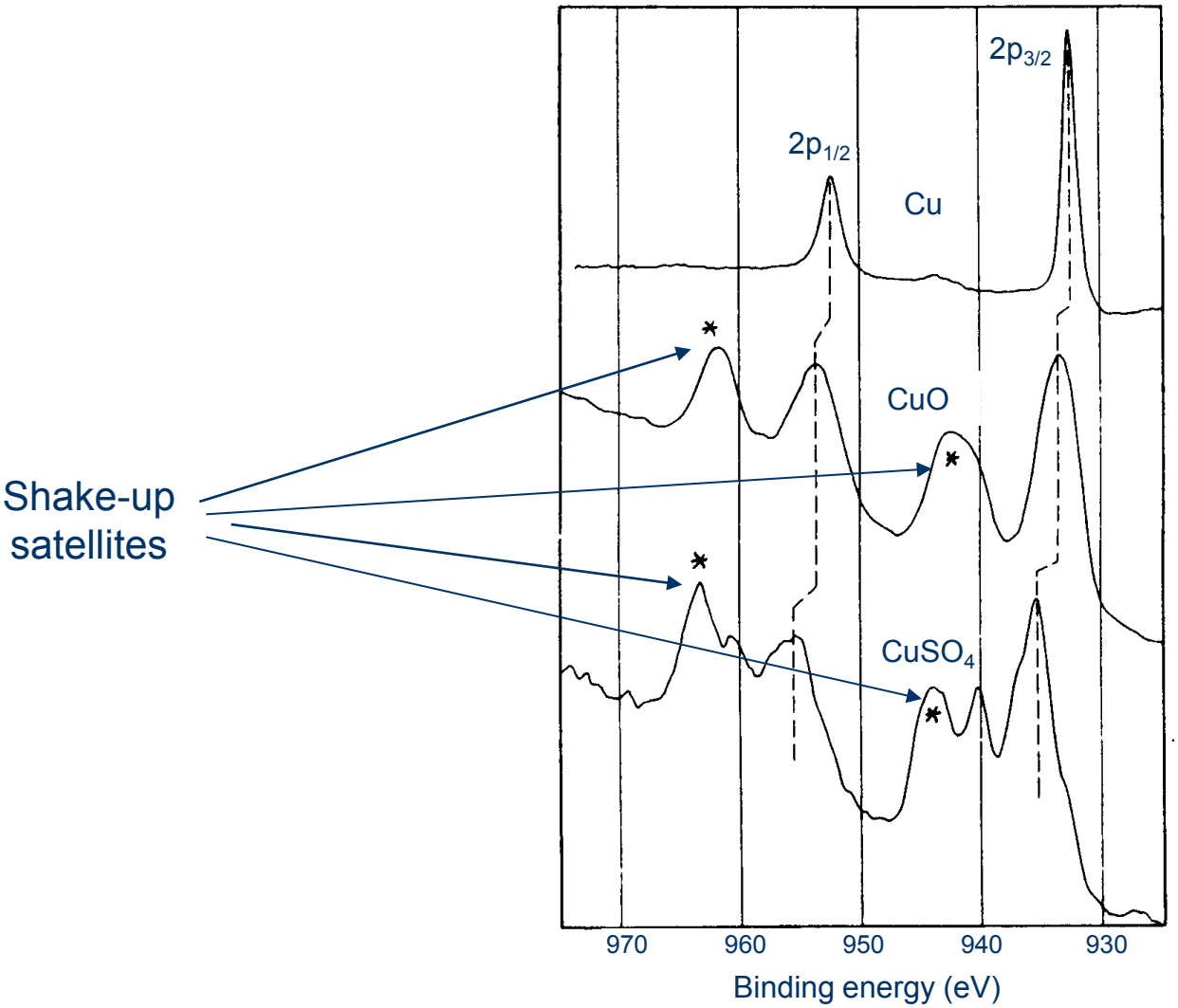


Chemical shift





Shake-up satellites in Cu 2p

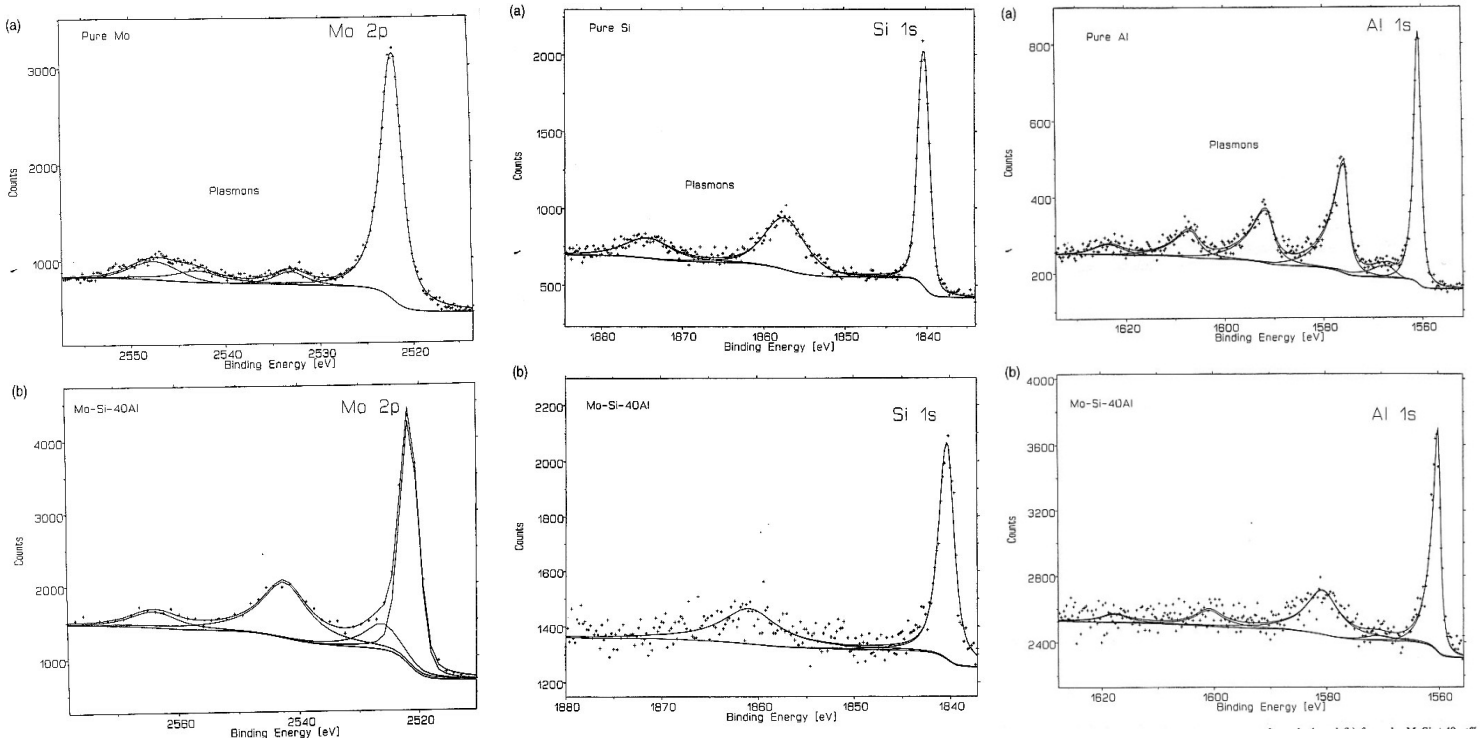


Plasmons

- They describe the interaction (inelastic scattering) of the PE with the plasma oscillation of the outer shell (valence band) electrons
- Plasmons in their quantum mechanical description are pseudoparticles with energy $E_p=h\omega$
- $\omega = (ne^2/\varepsilon_0 m)^{1/2}/2\pi$ **n =valence electron density,**
  e, m electron charge and mass
  ε_0=dielectric constant of vacuum

Pure elements

Mo-Si-Al Compound



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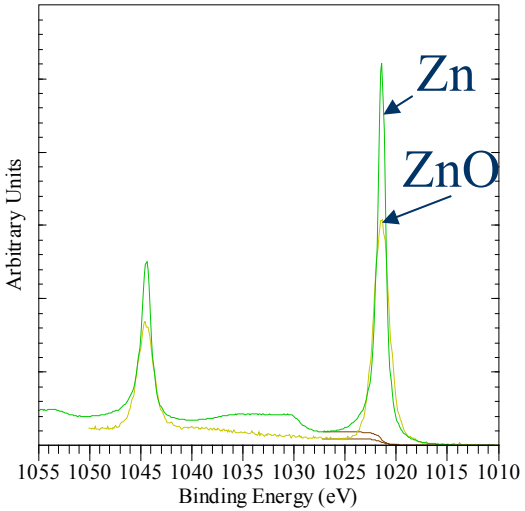
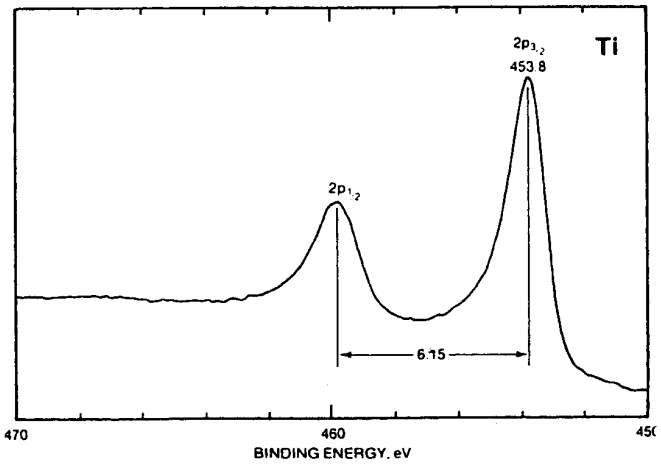
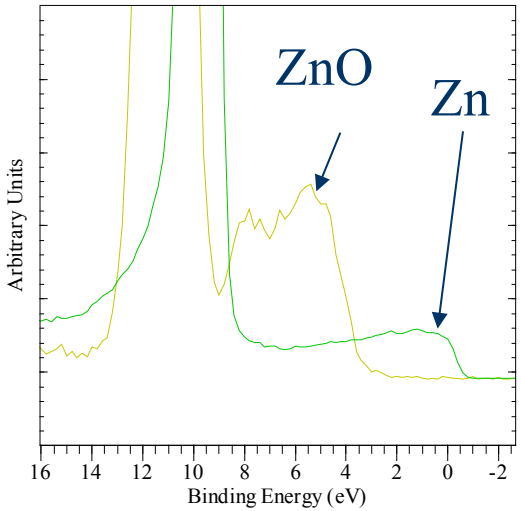
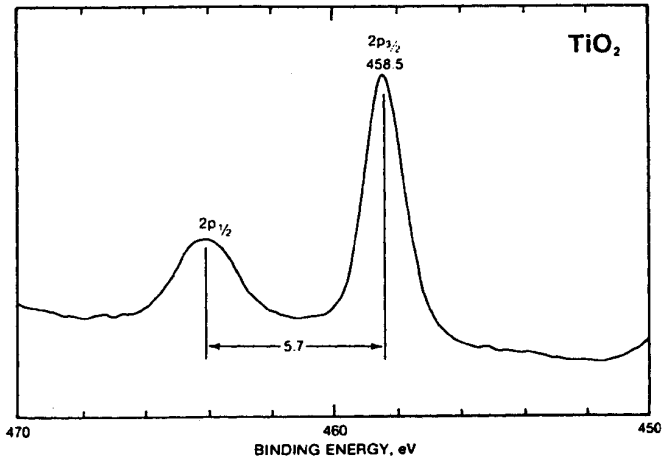
Peak asymmetry









Peak asymmetry in metals caused by small energy electron-hole excitations near E_F of metal

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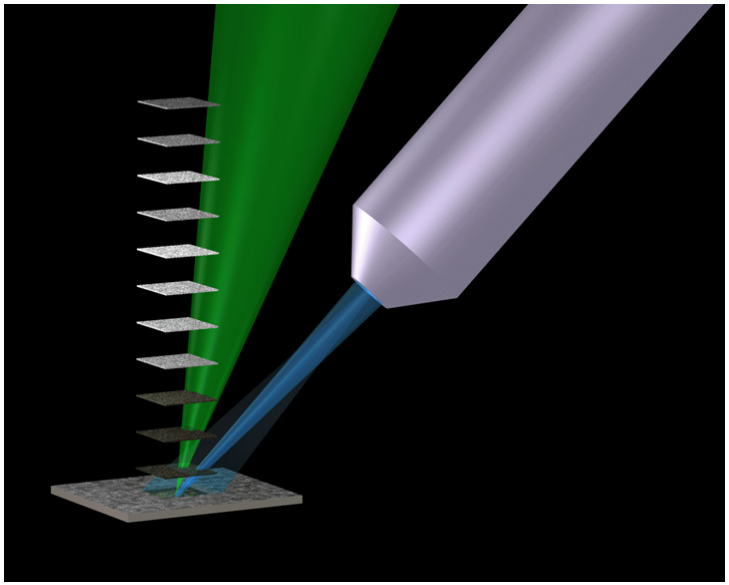
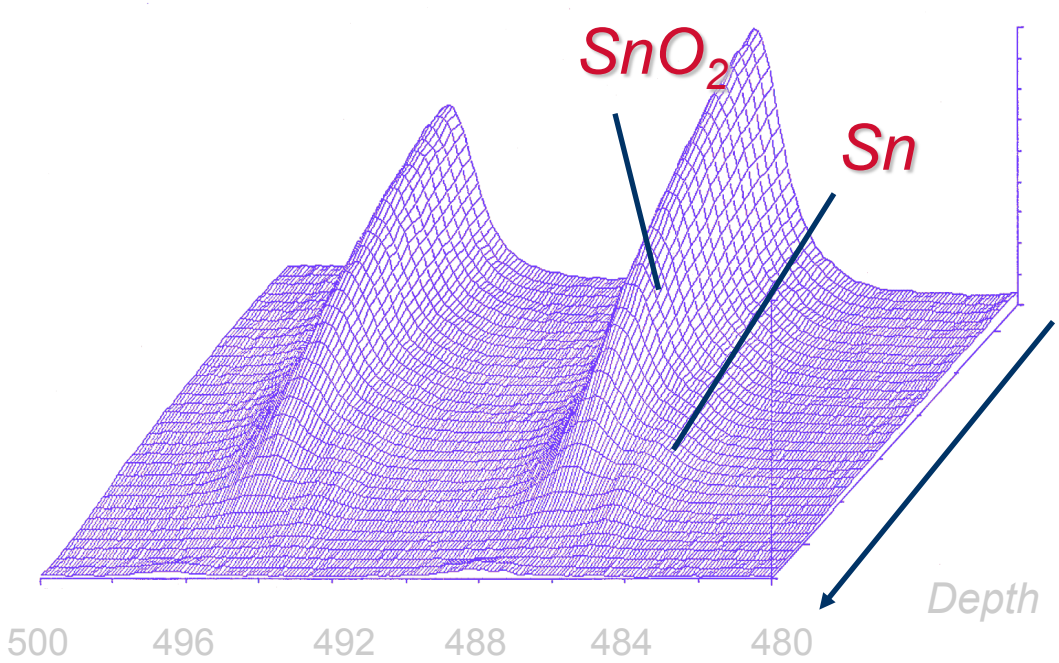
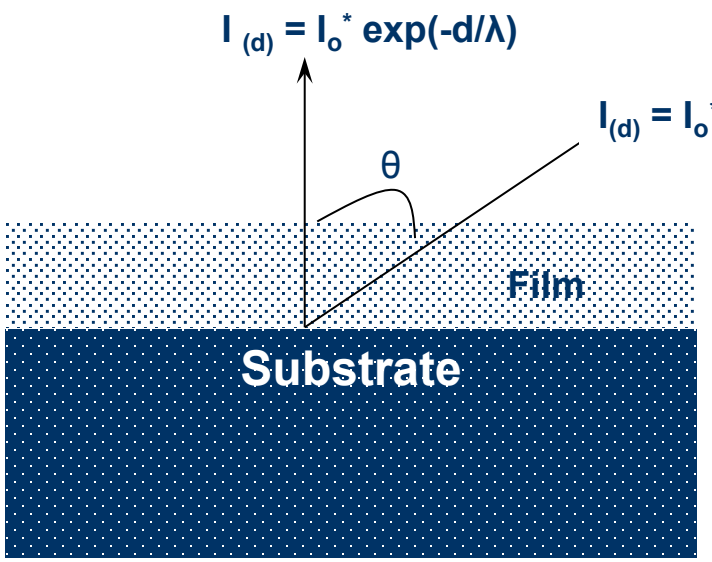
Depth profile with ion sputtering

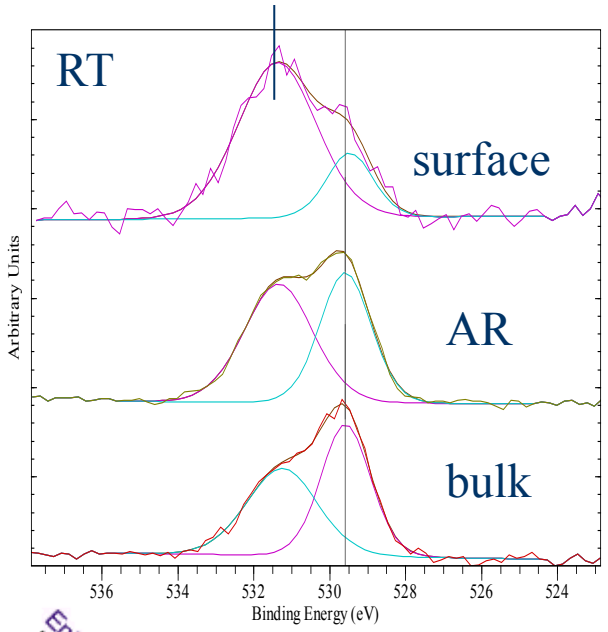




- Use of an ion gun to erode the sample surface and re-analyse
- Enables layered structures to be investigated
- Investigations of interfaces
- Depth resolution improved by:
  - Low beam energies
  - Small ion beam sizes
  - Sample rotation

Angle Resolved XPS (ARXPS) for non-destructive depth profile

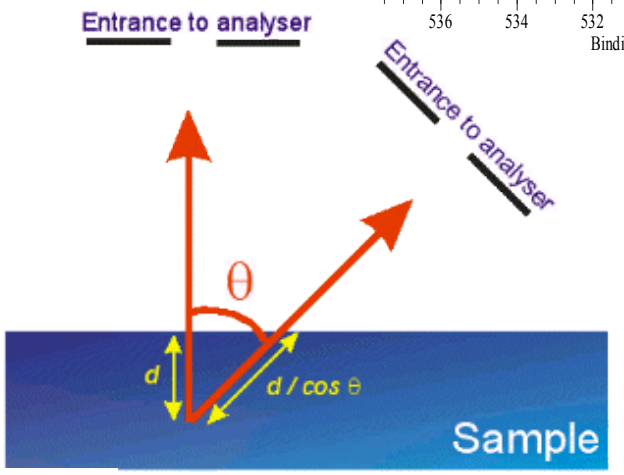




λ=attenuation length (λ ≈0.9 IMFP)

$\lambda = 538\alpha_A/E_A^2 + 0.41\alpha_A(\alpha_A E_A)^{0.5}$

(α_A^3 volume of atom, E_A electron energy)



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XPS-Check list

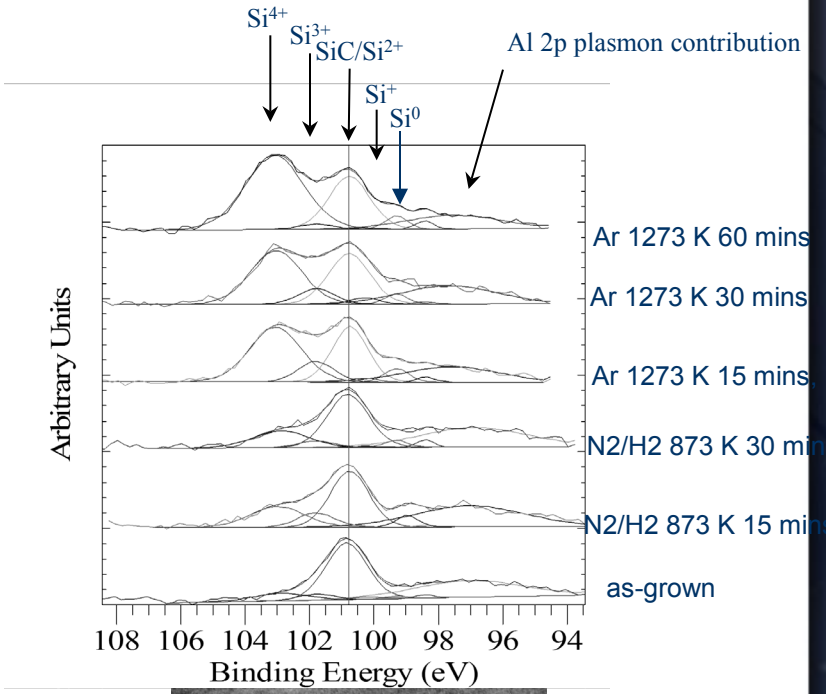
- Depth of analysis ~ 5nm
- All elements except H and He
- Readily quantified (limit ca. 0.1 at%)
- All materials (vacuum compatible)
- Chemical/electronic state information
  -Identification of chemical states
  -Reflection of electronic changes to the atomic potential
- Compositional depth profiling by
  -ARXPS (ultra thin film <10 nm),
  -change of the excitation energy
  -choose of different spectral areas
  -sputtering
- Ultra thin film thickness measurement
- Analysis area mm^2 to 10 micrometres

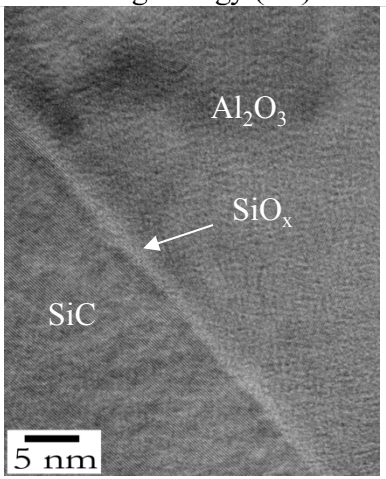
Interfacial studies of Al_2O_3 deposited on 4H-SiC(0001)

Avice, Diplas, Thøgersen, Christensen, Grossner, Svensson, Nilsen, Fjellvåg, Watts

Appl. Physics Letters, 2007;91, 52907, Surface & Interface Analysis,2008;40,822

- $d=\lambda_{Si} \cos\theta \ln(1+R/R\infty)$
- d: SiOx film thickness
- λ_{Si}:inelastic mean free path for Si,
- Θ: the angle of emission,
- R: the Si 2p intensity ratios ISiox/ISiC,
- R∞ the Si 2p intensity ratios I∞Siox/I∞SiC where I∞ is the intensity from an infinitely thick substrate.
- $R\infty=(\sigma_{Si,SiO_2} \cdot \lambda_{Si,SiO_2}) / (\sigma_{Si,Si} \cdot \lambda_{Si,Si})$
- where $\sigma_{Si,SiO2}$ and $\lambda_{Si,SiO2}$ are the number of Si atoms per SiO_2 unit volume and the inelastic mean free path respectively
- The $\sigma_{Si,SiO2} / \sigma_{Si,Si}$ ratio is given by
- $\sigma_{Si,SiO2} / (\sigma_{Si,Si} = (D_{SiO2} \cdot F_{Si}) / D_{Si} \cdot F_{SiO2}$
- where D is the density of the material and F the formula weight.
- For the calculations we also assumed that the Si 2p photoelectrons from both SiC and Si oxide film will be attenuated by the same amount as they travel through the Al2O3 film therefore, their intensity ratio will reflect the attenuation of the Si 2p electrons coming from the SiC through the Si oxide film.





From XPS

d= 1nm at RT, d=3nm at 1273 K

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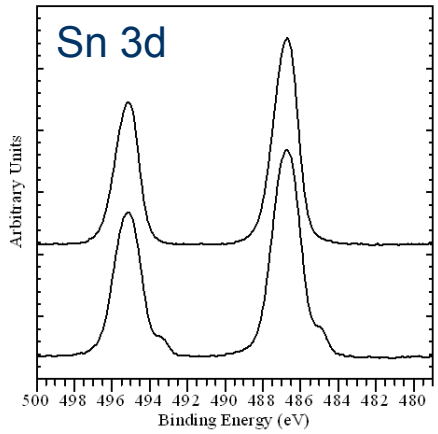
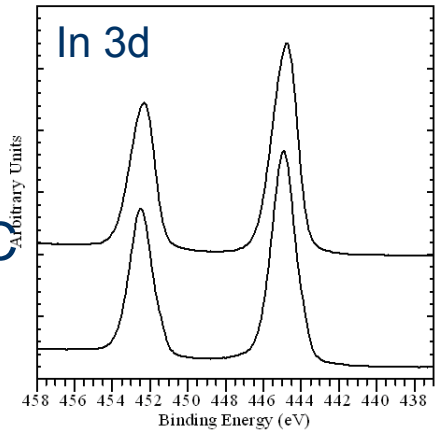
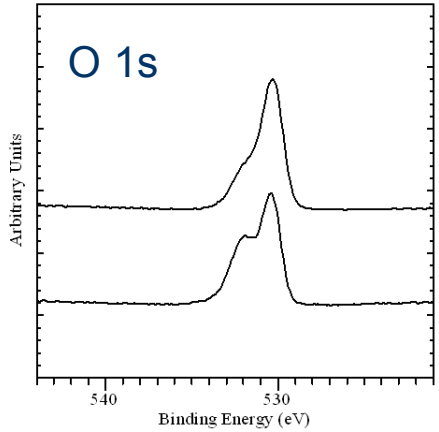
XPS on ITO e-beam deposited prior and after annealing (SINTEF SEP 09)



Air annealed 300 C

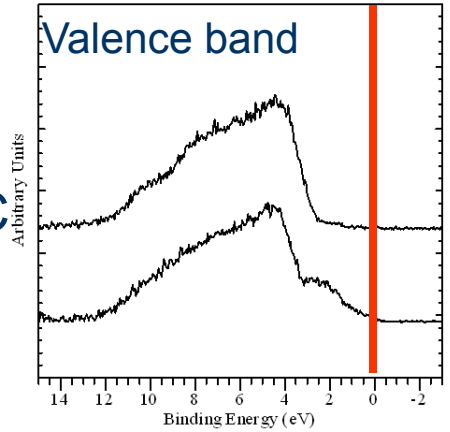
e-beam deposited





Air annealed 300 C

e-beam deposited



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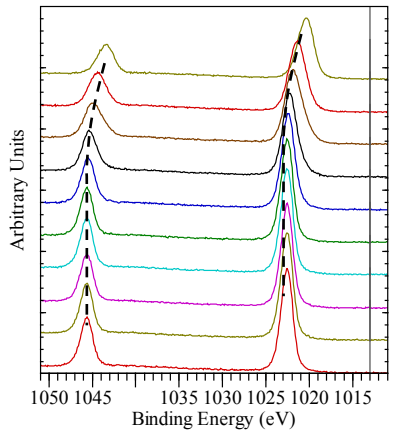
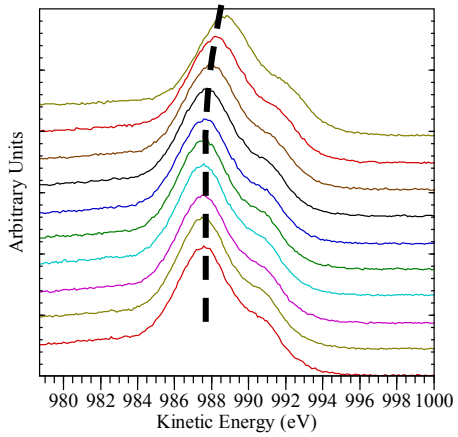
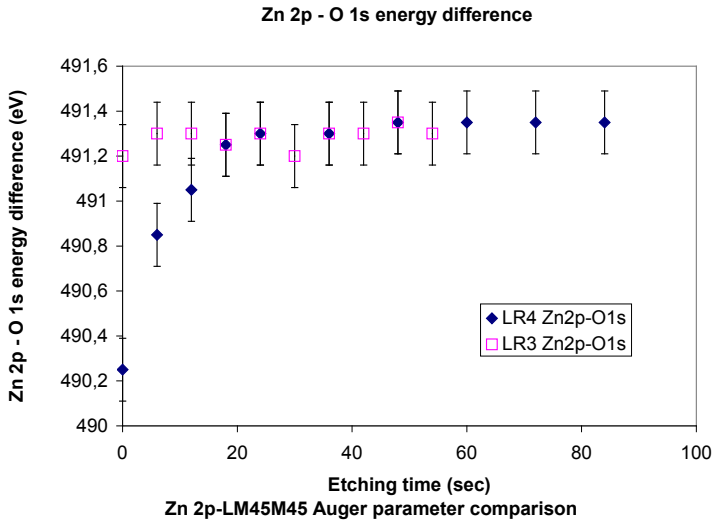
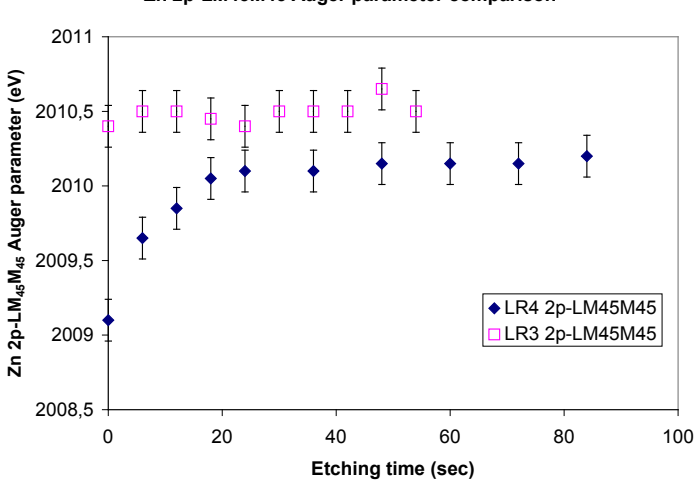
Band bending in ZnO

R. Schifano, E. V. Monakhov, B. G. Svensson, and S. Diplas, 2009, Appl. Phys. Lett. 94, 132101









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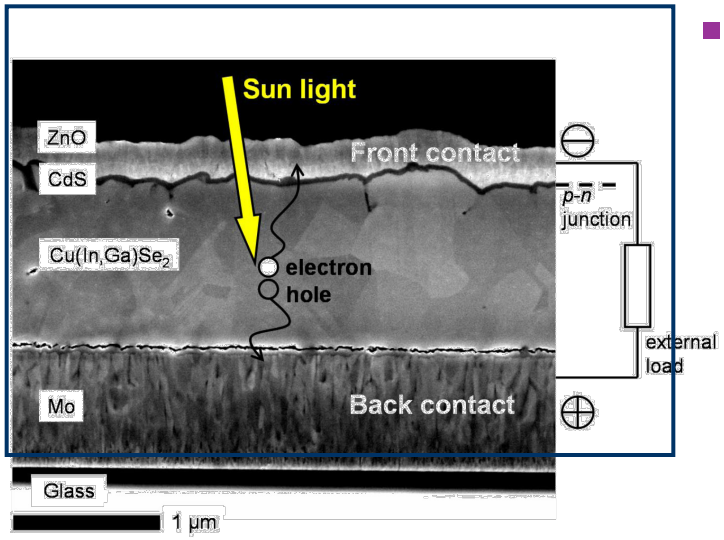
CIGS solar cell



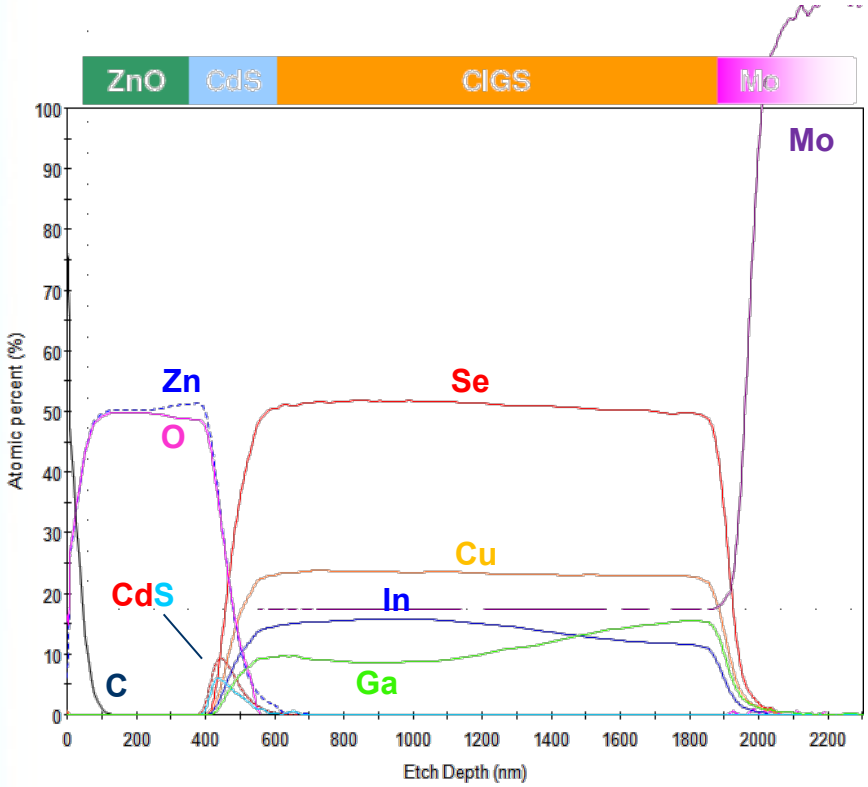
[3]SEM of a $Cu(In,Ga)Se_2$ solar cell (cross-section) and its mode of operation

- CIGS solar cell
  - Energy/environmental application
    - Solar cells based on $Cu(In, Ga)Se_2$ (CIGS)
      - Thin-film stack on glass
      - Mo and Zn oxide layer form electrical contacts
      - *p*-type CIGS film (sunlight absorber) and *n*-type CdS film form *p-n* junction
    - Excellent efficiency
    - Low cost compared to thicker silicon-based solar cells
  - Practical problem
    - Controlling film composition and interfacial chemistry between layers (affects electrical properties)
  - XPS solution
    - XPS sputter depth profiling
      - *Elemental and composition information as a function of depth*
      - *Identify chemical gradients within layers*
      - *Investigate chemistry at layer interfaces*

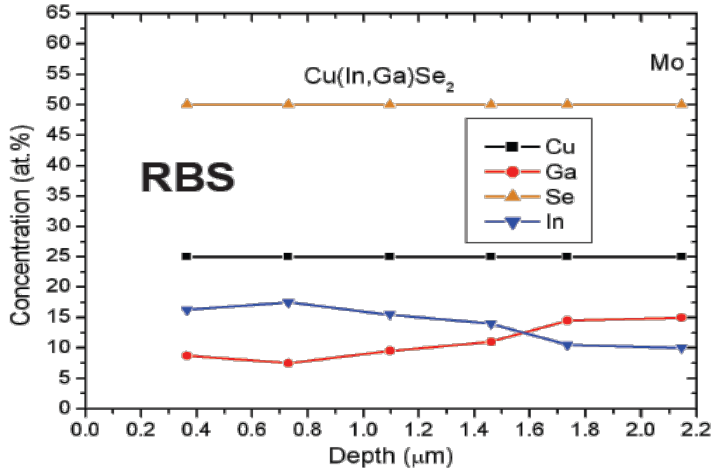
Acknowledgement: Thermo Electron Corporation

CIGS solar cell

- CIGS solar cell
  - Depth profile of CIGS film stack
    - Demonstrates standardless quantification of XPS
      - Excellent quantification agreement between XPS and Rutherford BackScattering (RBS)
      - Both techniques show cross-over of In and Ga close to 1.6μm depth
        - XPS tool is able to analyze product solar cell device



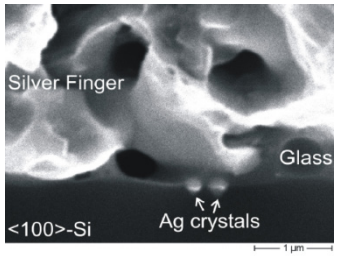
Sputter depth profile of CIGS film stack

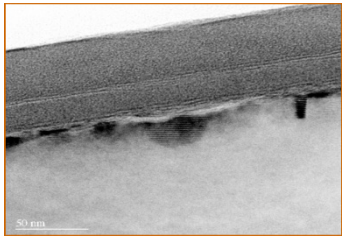


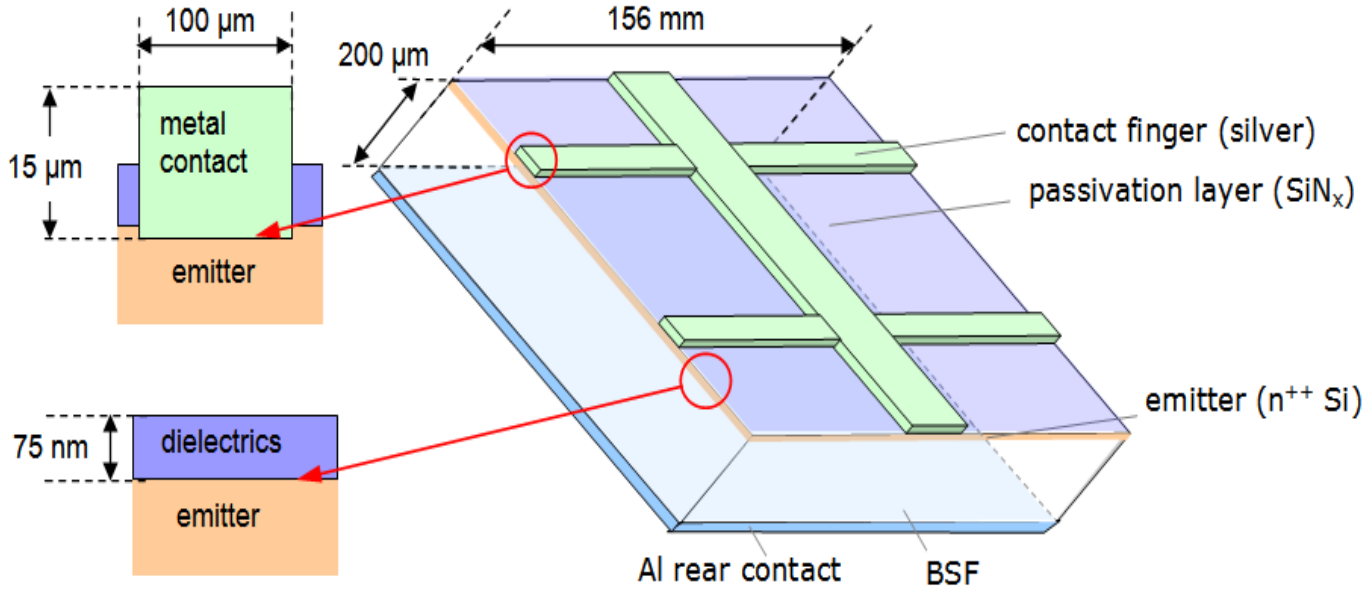
Rutherford BackScatter profile of CIGS film stack

Acknowledgement: Thermo Electron Corporation

Interfaces in Solar cells

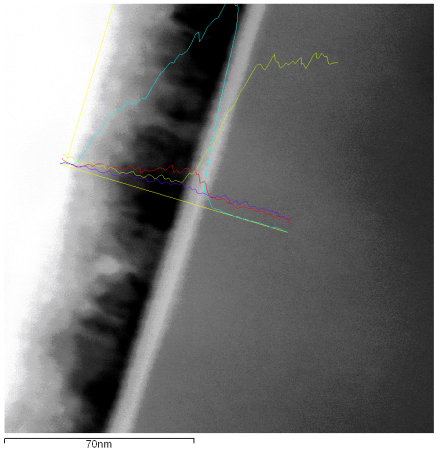


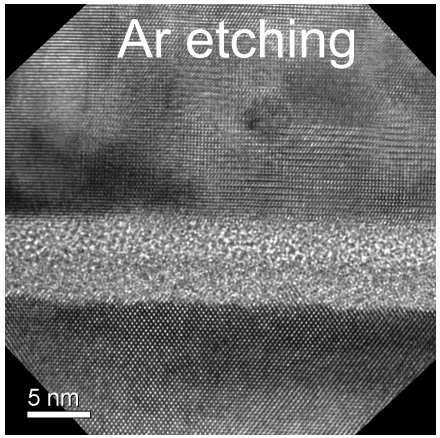


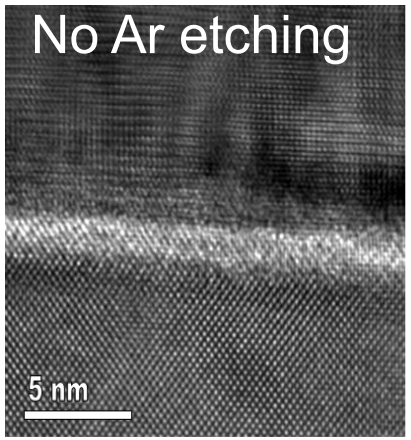


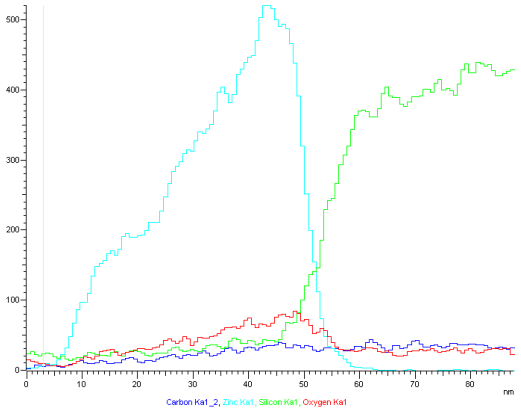
6th March 2013

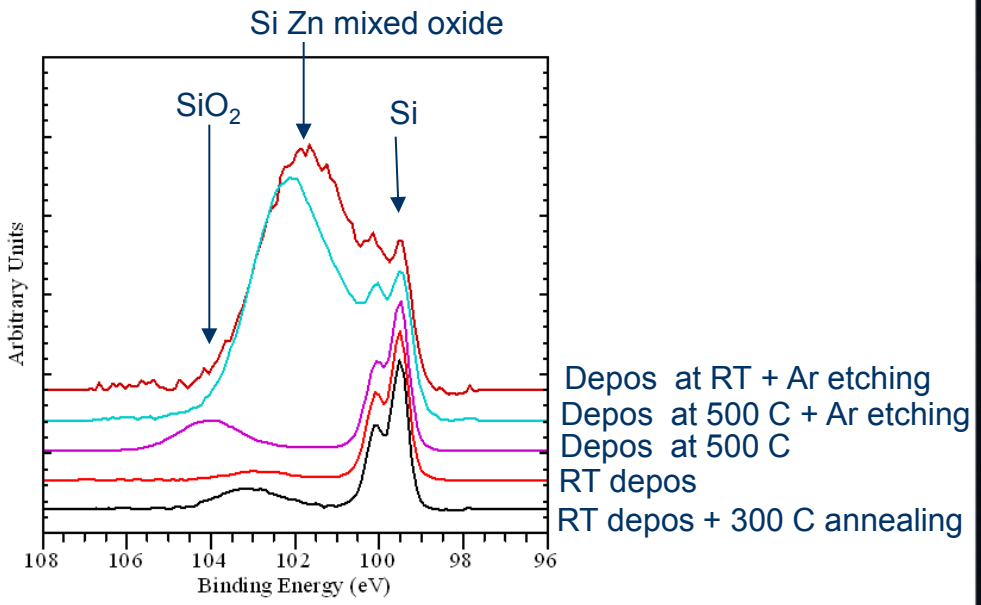
Interface between p-Si/ZnO: Si HF with and without Ar etched (SINTEF SEP 09)











6th March 2013

Elemental distribution and oxygen deficiency of magnetron sputtered ITO films

A. Thøgersen, M.Rein, E. Monakhov, J. Mayandi, S. Diplas

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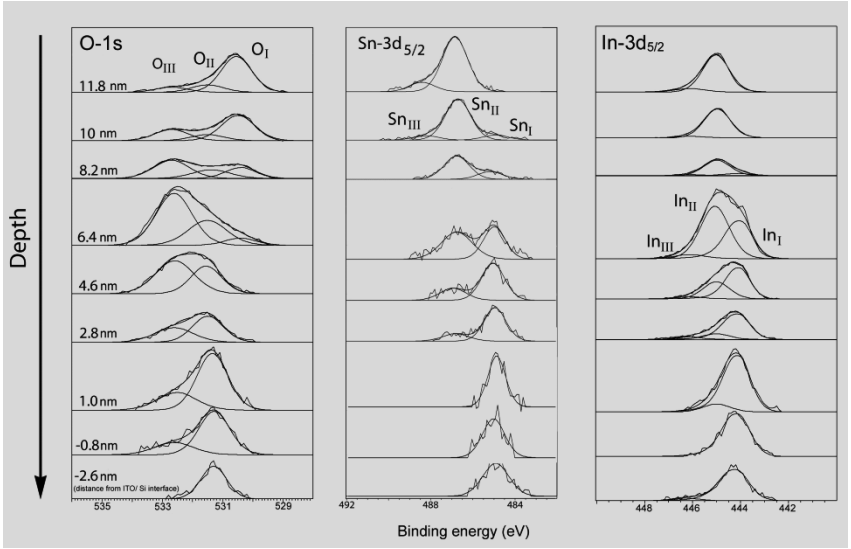

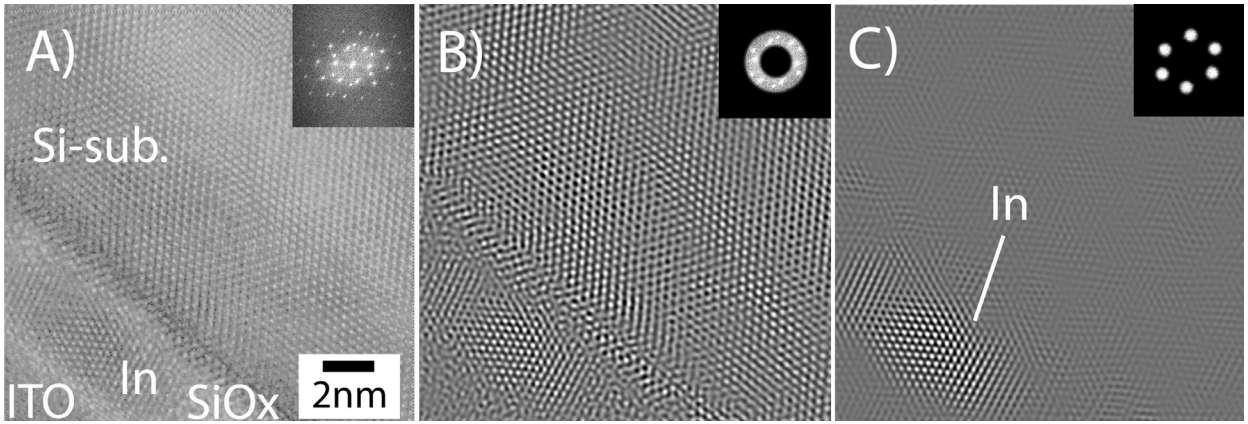

6th March 2013

Thank you for your attention

6th March 2013