Surface analysis tools: application to glass and thin films

R. Lazzari

Institut des NanoSciences de Paris, CNRS/Sorbonne Université, Paris, France

Outline

Photon based-tools to characterize glass surface and thin films ontop

1- Photoemission spectroscopy

2- X-ray absorption spectroscopy

3- X-ray diffraction

4- Optical spectroscopies [(except vibrational spectroscopies (IR/Raman)]

5- Wandering towards surface science : 2D silica films

A list of references

Photoemission

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XPS guide: Charge neutralization and binding energy referencing for insulating samples, *J. Vac. Sci. Technol. A,* 2020*, 38,* 031204

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http://www.lasurface.com/accueil/

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X-ray absorption spectroscopy

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Fischer, H.; Barnes, A. & Salmon, P., Neutron and x-ray diffraction studies of liquids and glasses, Rep. Prog. Phys., 2005, 69, 233

Optics and ellipsometry

Oates, T.; Wormeester, H. & Arwin, H., Characterization of plasmonic effects in thin films and metamaterials using spectroscopic ellipsometry *Prog. Surf. Sci., Elsevier BV,* 2011*, 86,* 328-376

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Photoemission spectroscopy : history

- Photoemission spectroscopy based on the photoelectric effect discovered by Hertz in 1887 and explained in 1905 by Einstein

Ann. Phys. (Leipzig) **14**, Supplement, 194-224 (2005)   A. Einstein, Annalen der Physik, Band 17, 1905

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3. *Zur Elektrodynamik bewegter Körper;*
von A. Einstein.

H. Hertz

- In the 1960's, Kai Siegbahn (Nobel prize 1981) at the University of Uppsala (Sweden) significantly developed the technique as a tool for chemical analysis.
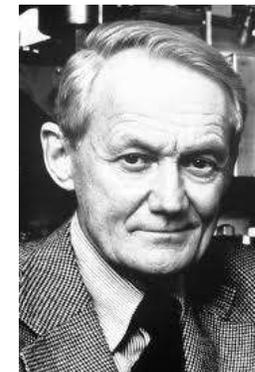
K. Seigbahn

Photoemission spectroscopy (1): basis

- Interactions between photons or electrons and matter to probe the electronic structure

- Measure the energy distribution of filed electronic states in atoms, molecules, liquid or solid state materials

- Depending on the energy of light source
  - Ultraviolet Photoemission Spectroscopy (UPS ➔ 10 to 50 eV), which employs low energy photons to excite valence electrons.
  - Soft X-ray (SXPS), and X-ray Photoemission Spectroscopy (XPS ➔ 100eV to 1.5 keV).
  - HArd X-Ray Photoemission Spectroscopy (HAXPES ➔1.5keV) to probe "deep" interfaces

- Also known as ESCA (Electron Spectroscopy for Chemical Analysis) ; except H

- Qualitative and quantitative information on the sample chemical composition

Photoemission spectroscopy (2): basis

- Surface irradiated with photons of energy $h\nu$

- Electrons excited from deep energy levels of binding energy E_b ejected from the sample with kinetic energies $E_{k,emitted}$ given by Koopman's equation:

$$E_{k,emitted} = h\nu - E_b - \phi_s$$

- ϕ_s :sample work function, *i.e.* minimum energy required to remove an electron

- Photoemitted electrons are analysed in kinetic energy by an electrostatic analyser, to give the typical XPS spectrum showing the intensity versus electron kinetic energy

- Atomic orbital binding energies are specific to each element: possible to identify the elements and gain information on the sample chemical composition

- UPS = valence band, XPS = more strongly bound core levels
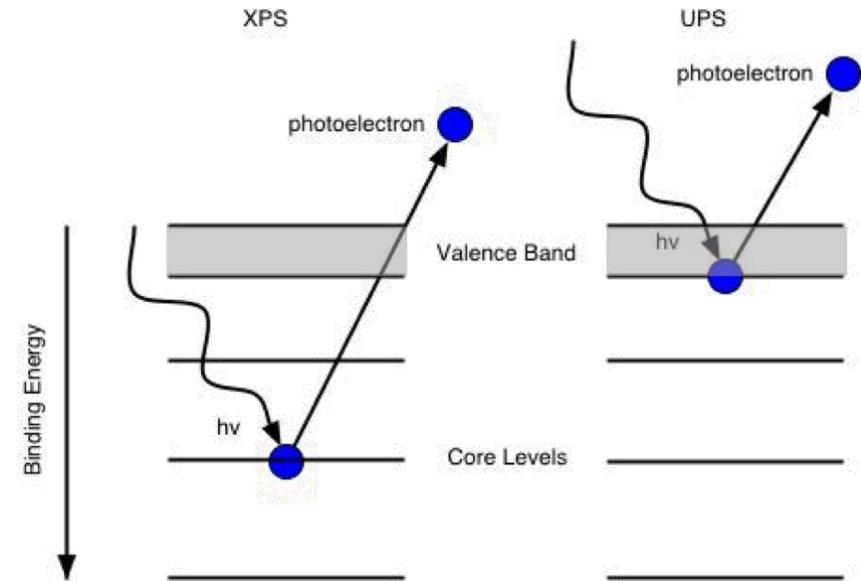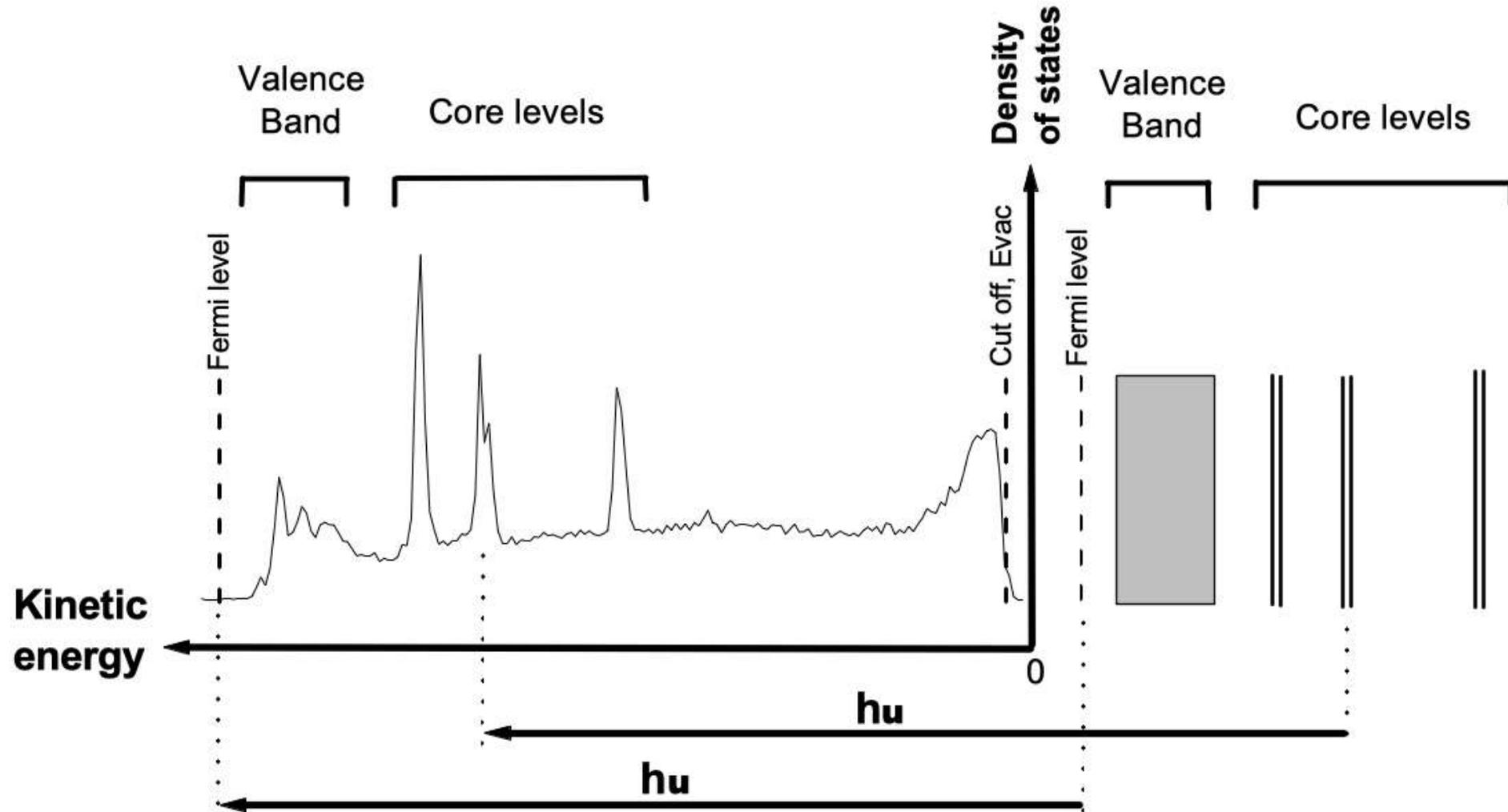
Photoemission surface sensitivity (1) : why ?

- Incident photons: long penetration depths and ionisation process occurs over several micrometers from the sample surface

- Probability for an electron to interact with matter significantly higher than for a photon

- Electrons coming from the topmost layers, within tens of angstroms, will reach the detector without suffering energy losses

- Leads to plasmon losses, phonon losses and valence band electronic excitations

- Because of such attenuation and inelastic effects, the photoelectron escape probability is well described by an exponential law

Surface sensitivity (2): the inelastic mean free path
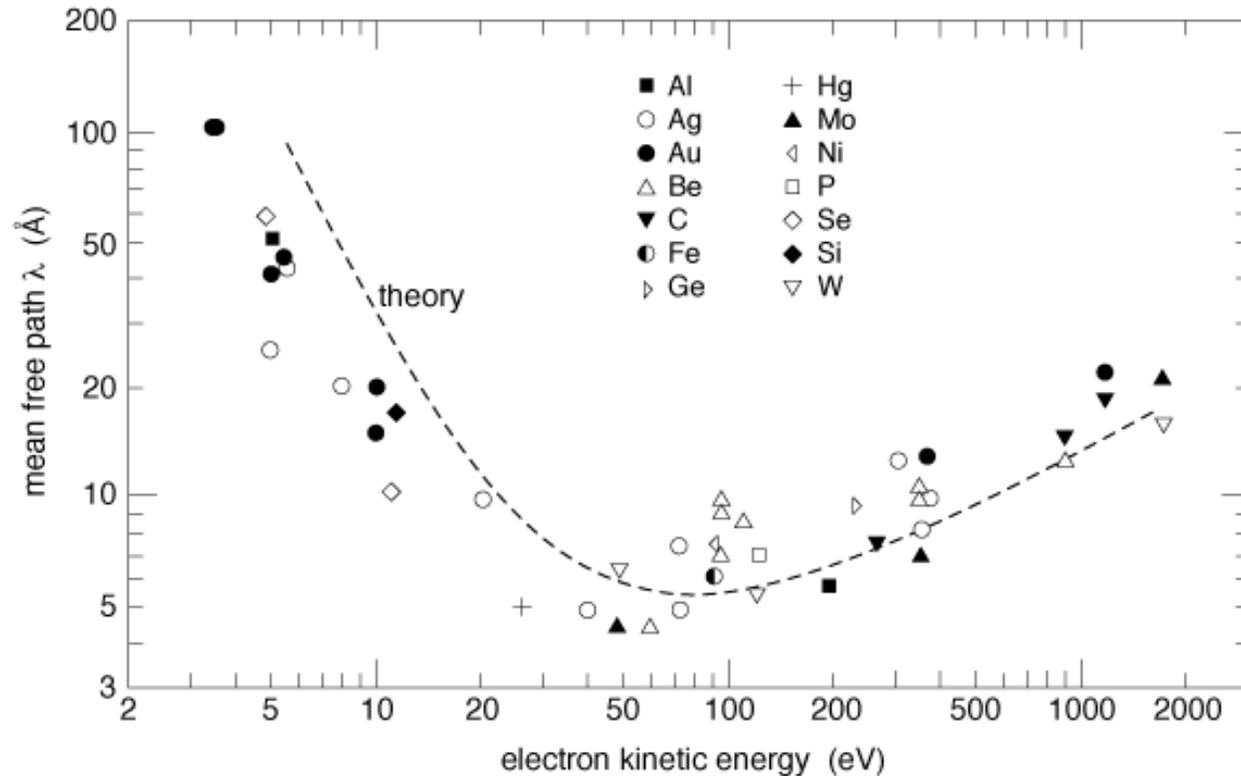
Inelastic Mean Free Path: IMFP (λ).
Thickness of matter through which 63%
of the traversing electrons lose energy.
(Beer-Lambert's or Beer's law).

- Good choice of photon energy as a function of core level probed to maximise surface sensitivity

- Minimum at emitted photoelectron with $E_K \approx 70$ eV

- λ from dielectric theory of losses; effective formula ± 20%

Instrumentation (1) : the electrostatic analyser

Outer Hemisphere

Inner Hemisphere

Entrance Slit

Electron Retarding Lenses

Multichannel Detector

Extraction Lenses

Electron Collection Lenses

X-ray Source

Sample
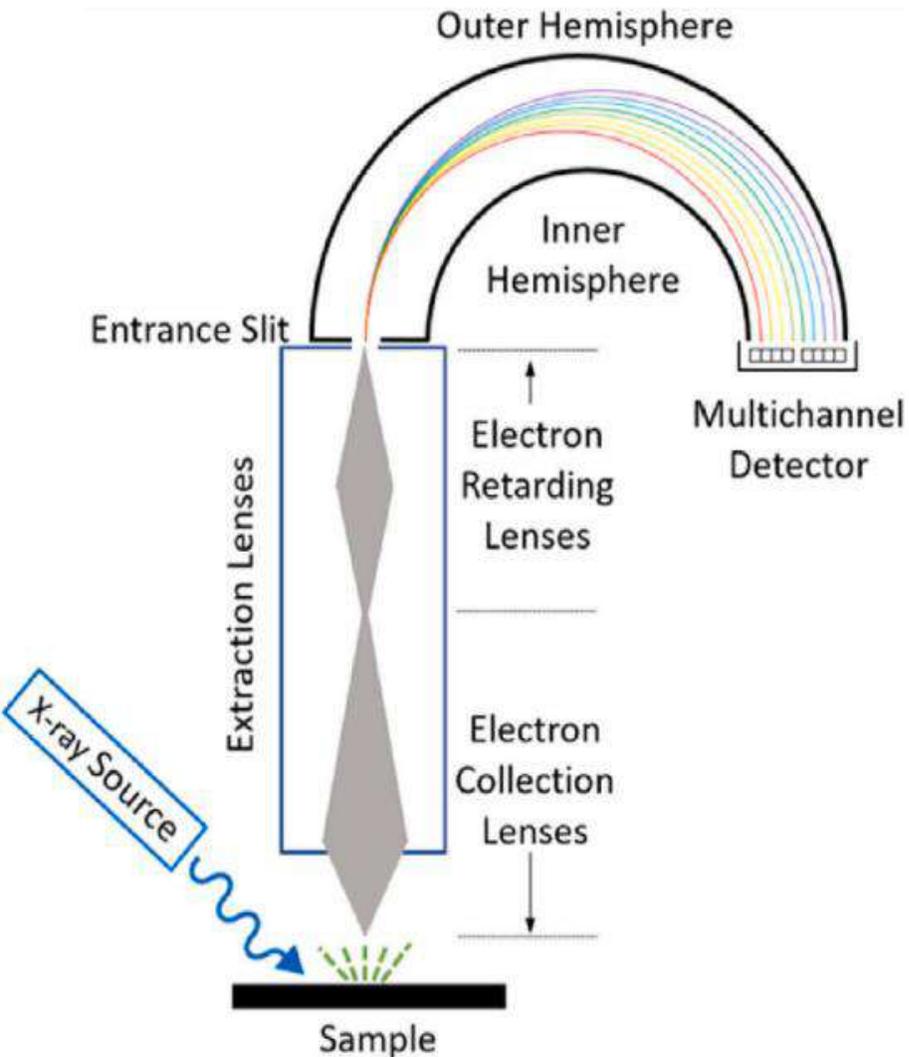
- Ultra-high vacuum ($p < 10^{-6}$ mbar): signal damping and contamination
- Collection lenses: angular acceptance/analyzed area
- Concentric Hemispherical Analyser : band-pass filter at

  pass energy E_P with resolution $\Delta E = E_p \left(\frac{d}{2R_0} + \alpha^2 \right)$

    - d slit width along dispersive direction
    - α angular spread at entrance slit
- Constant E_P ; fixed resolution
- Detector : channeltron, 1D, 2D
- Magnetic shielding with μ-metal

Instrumentation (2) : the X-ray source

- Typical lab source: Al$K\alpha$ or Mg$K\alpha$

- Emission of X-rays upon electron bombardment of a anode (~10kV, few 100W)

- Non-monochromatic sources: additional emission lines due to less probable (less intense) transitions w.r.t. the main Kα line.

Source	Photon energy (eV)	Linewidth (eV)
Mg Kα	1253.6	0.7
Al Kα	1486.6	0.85
Cr Kα	5414.7	~1
Ga Kα	9251.8	~1

- Gives rise to the so-called satellite peaks

Line	$\alpha_{1,2}$	α_3	α_4	α_5	α_6	β
Mg displacement, eV	0	8.4	10.2	17.5	20.0	48.5
Mg relative height	100	8.0	4.1	0.55	0.45	0.5
Al displacement, eV	0	9.8	11.8	20.1	23.4	69.7
Al relative height	100	6.4	3.2	0.4	0.3	0.55

Table 2.1: X-ray satellite energies and intensities for given X-ray sources [50].

- Ghost peaks in twin anode sources
- Bremsstrahlung emission
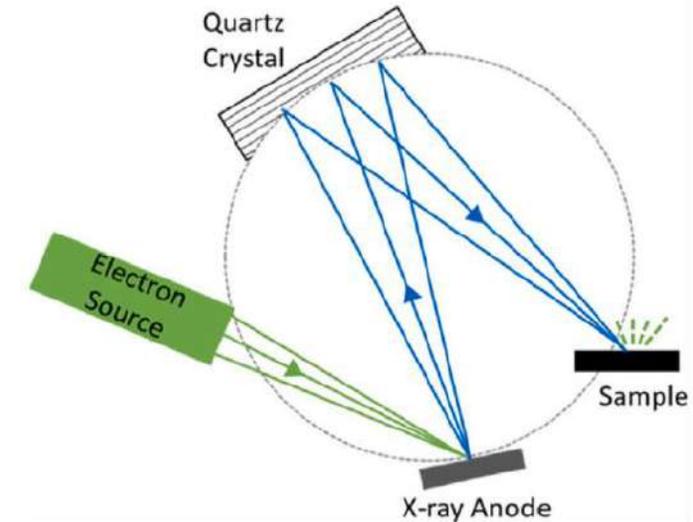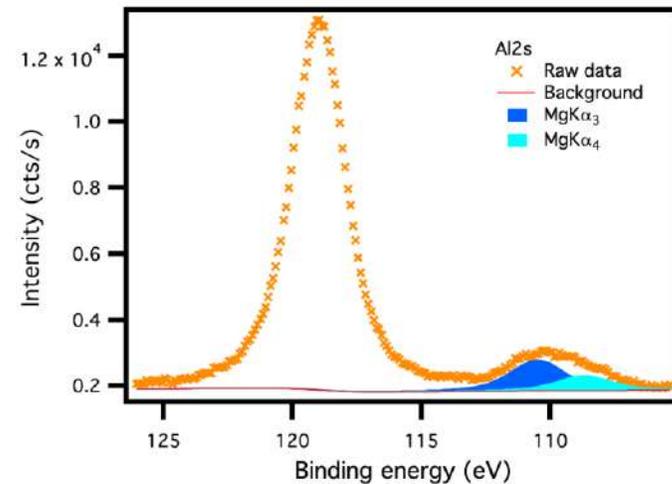
- The use of monochromator facilitates the spectrum interpretation since a better resolution is achieved

- Use also of synchrotron radiation (variable $h\nu$)

- Conductive sample➔ analyser and sample put in electrical contact: their Fermi levels E_F are aligned.

- Due to analyser work function ϕ_a, a contact potential $\phi_s - \phi_a$ is established, which shifts the measured E_k to:

$$E_k = h\nu - E_b - \phi_s + (\phi_s - \phi_a) = h\nu - E_b - \phi_a$$

- E_k depends only on ϕ_a determined by calibrating the analyser kinetic energy scale with standards (known core level or E_F of a metal)
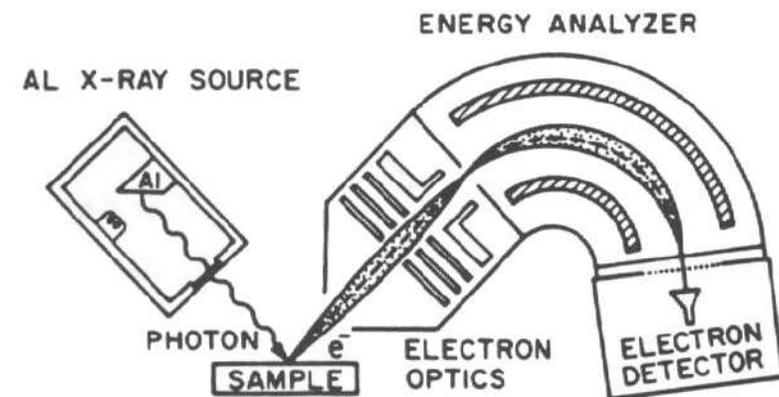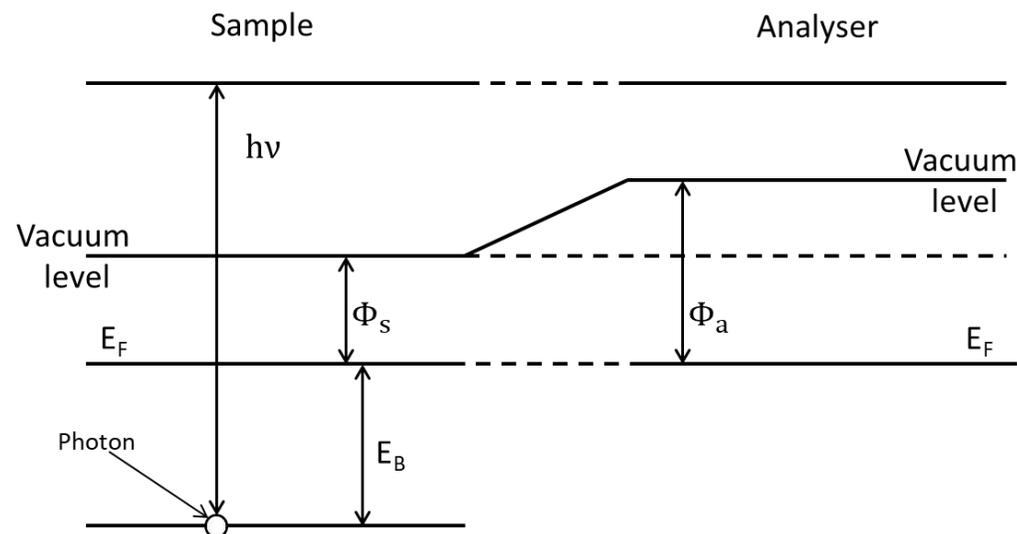
Charge effect and compensation for insulators

Focused X-ray beam

Low Energy Electron beam

Low Energy Positive Ion beam

Insulating Sample

a) C 1s

b)

Intensity (a.u.)

Binding Energy (eV)
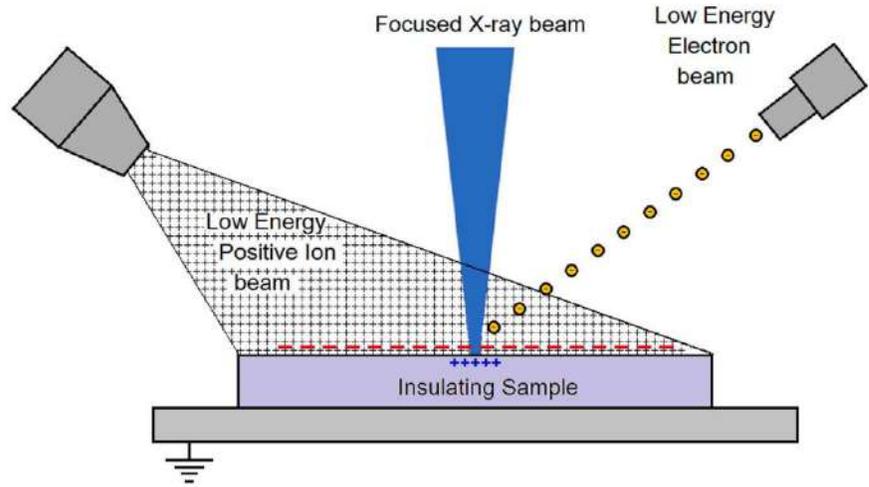
- In insulator, positive charge build-up upon electron emission
  ➔ peaks at lower E_K / higher E_B

- Depend on sample nature, topography, mounting, X-ray source focusing

- Charge compensation with low-energy electrons (flood gun) and/or ions (<5eV), graphene sheet

- Differential charging and sample inhomeneities ➔ lineshape distorsion

- Potential complex optimisation of measurement conditions

- Beam damage (desorption, irradation point defects, diffusion of alkaline)

- Binding energy reference (adventitious C 1s $E_B = 284.5$ eV; internal reference O 1s; gold deposition; inert gas implantation)

- Auger parameter : free of charge effect
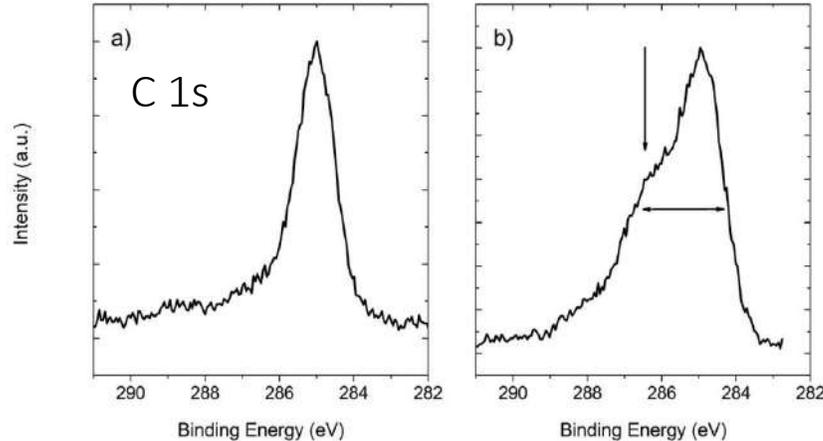
The mean features of a XPS spectrum

- XPS spectrum reflects the density of the occupied states

- Complications due to the presence of other features : Auger peaks, plasmon losses and satellite peaks, shake-up/shake-off superimposed to a continuous background arising from electrons that have suffered energy losses
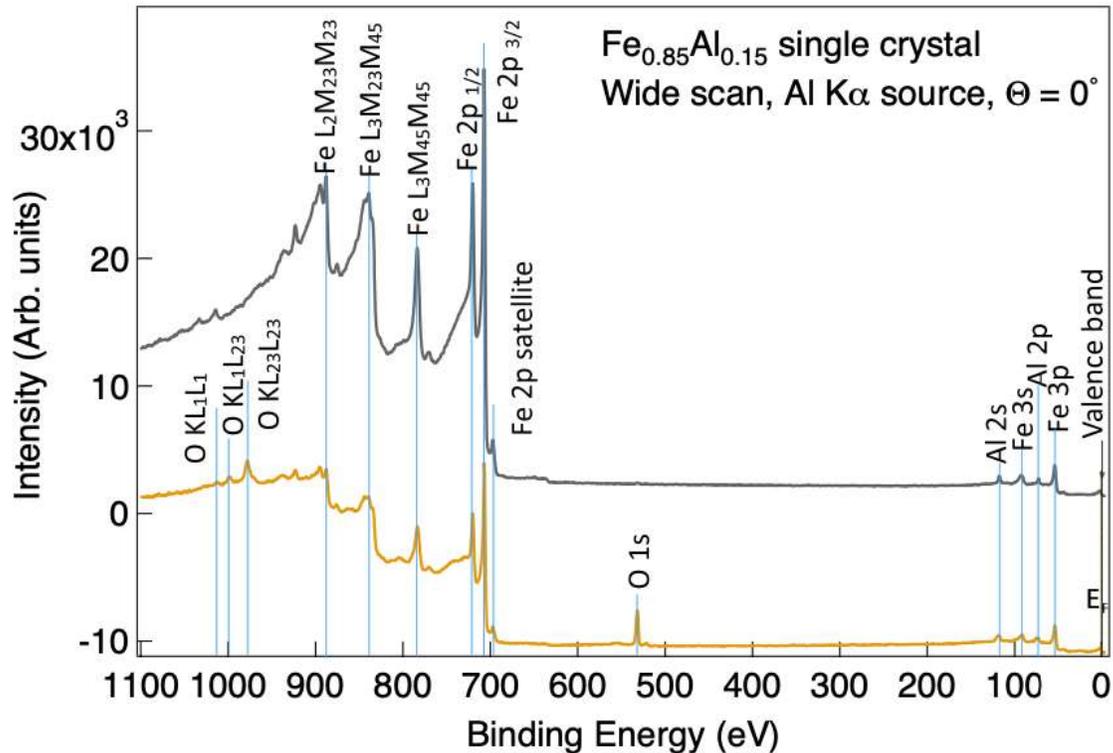
Typical XPS survey spectrum
Intensity vs binding energy
Usually E_B increasing from left to right
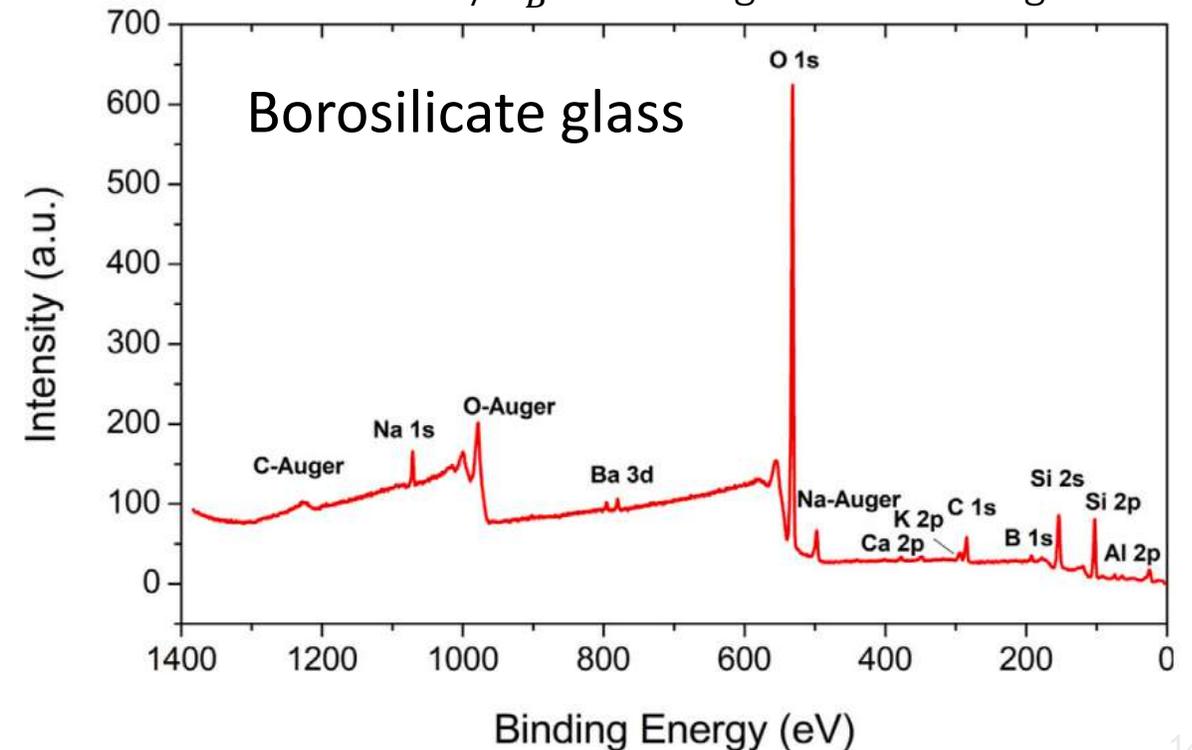
Core level peaks (1) : chemical shift

- Sharpest and most prominent peaks

- Labelling with electronic n and orbital quantum numbers $l = 1,2,3,4$ [s, p, d, f]

- Give information on sample composition

- But also on chemical environment (e.g. oxidation states)

- Different chemical states of the same element give rise to the so-called chemical shifts

- Small changes in E_b from fractions of eV up to several eV.
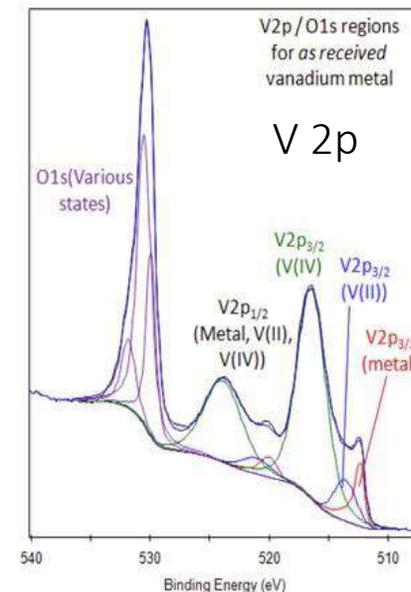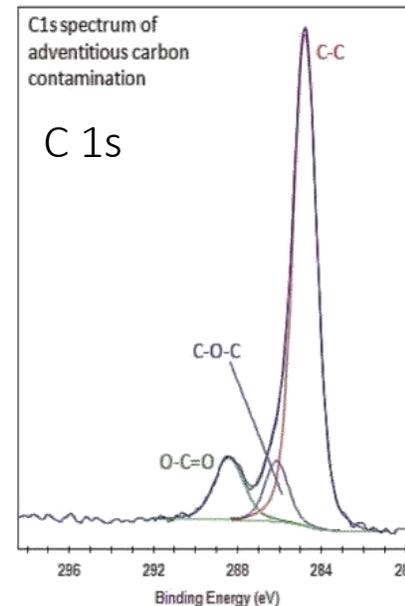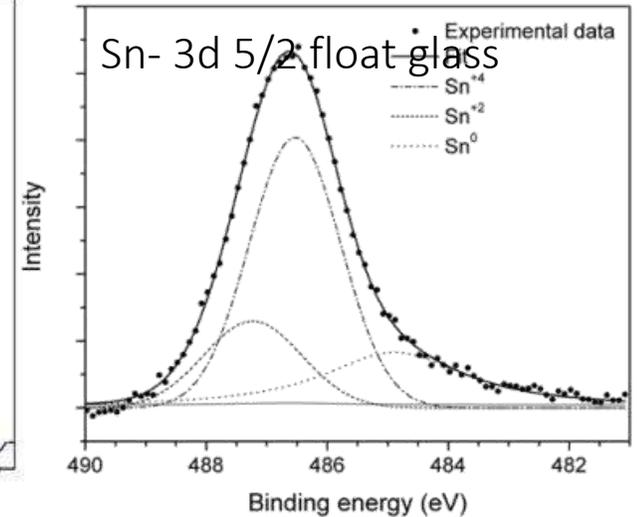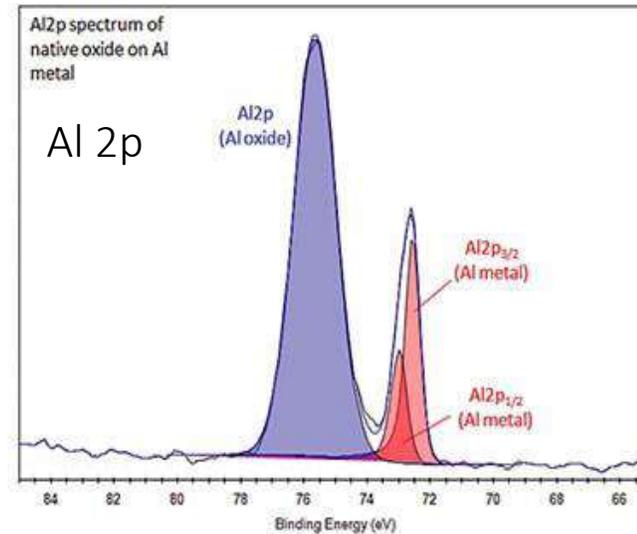
- E_b depends on iono-covalence bonds

- In chemical bonds, charge transfers occur between the atoms, affecting the charge density and the screening of the nucleus Coulomb attraction

- Generally speaking, the greater the electronegativity, the higher the shift to lower binding energies.

- Initial versus final state effects (ex Ag, Cd)

- Peak fitting often required for an accurate analysis

Al2p spectrum of native oxide on Al metal

Al 2p

Al2p (Al oxide)

Al2p$_{3/2}$ (Al metal)

Al2p$_{1/2}$ (Al metal)

Sn- 3d 5/2 float glass

Experimental data
Sn^{+4}
Sn^{+2}
Sn^0

C1s spectrum of adventitious carbon contamination

C 1s

C-C

C-O-C

O-C=O

V2p / O1s regions for as received vanadium metal

V 2p

O1s(Various states)

V2p$_{3/2}$ (V(IV))   V2p$_{3/2}$ (V(II))

V2p$_{1/2}$ (Metal, V(II), V(IV))

V2p$_{3/2}$ (metal)

O1s spectrum of *as received* copper (II) carbonate dihydroxide

Each component has the same width

[Carbonate]/[hydroxide]=4

Metal carbonate

Metal hydroxide

- E_b depends on the chemical environnement

- Important to know the energy reference of the analyser (E_F ,VB) and to calibrate all spectra to that reference

- Especially when charging occurs (insulators)

Core level peaks (4) : spin-orbit splitting

- When photoelectrons ejected from energy levels p,d,f with an orbital angular momentum $l > 0$, core level splitting due to spin-orbit coupling, i.e. the coupling between the electron spin momentum and its orbital angular momentum.

- 2 states with different values of the total angular momentum

  - $j_1 = |l - 1/2|$: high E_b
  - $j_2 = |l + 1/2|$: low E_b

- Area ratio (branching ratio) is given by the ratio of their respective degeneracies:

Core level	2p	3d	5f
j	$\frac{1}{2}$: $\frac{3}{2}$	$\frac{3}{2}$: $\frac{5}{2}$	$\frac{5}{2}$: $\frac{7}{2}$
Intensity Ratio	1:2	2:3	3:4

- Also dependant on chemical environment
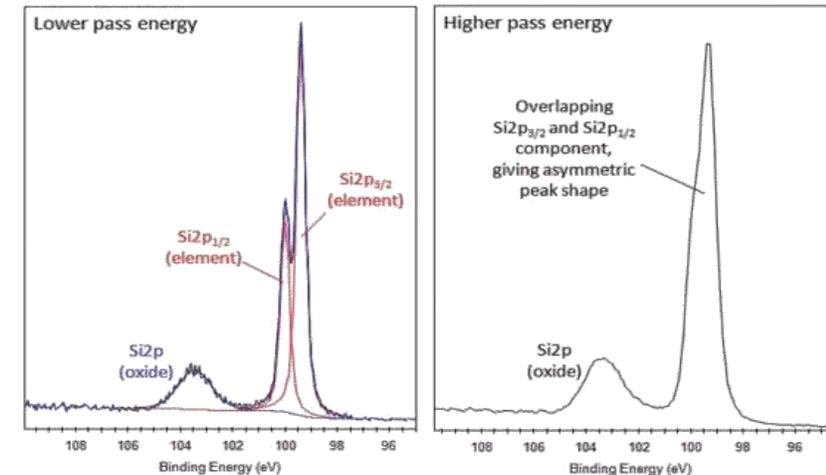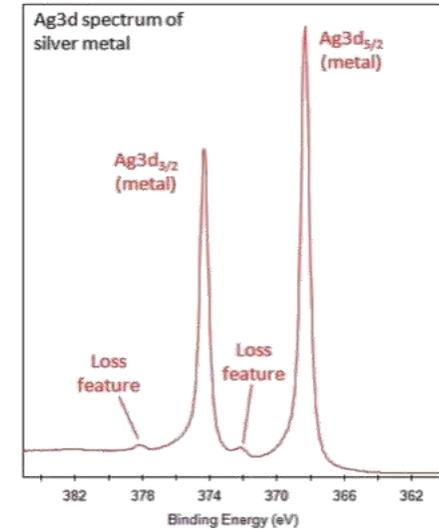
Core level peaks (4): broadening

<p style="color:red; text-align:center;">Full width at half maximum:</p>

$$\Delta E_{exp}^2 = \Delta E_c^2 + \Delta E_n^2 + \Delta E_a^2 + \Delta E_s^2$$

- ΔE_{exp} : experimental peak width (mix gaussian lorentzian)
- ΔE_c : natural linewidth of the electronic distribution- core-hole lifetime (lorentzian)
- ΔE_n : linewidth of the X-ray emission line (lorentzian and gaussian)
- ΔE_a : analyser resolution (gaussian)
- ΔE_s : sample related broadening (potential/distribution of binding energies)

Auger electron spectroscopy (1)

- Named after the 3 energy levels involved, in the order of intervention

- Generic *XYZ* Auger transition:
  - photoemitted electron ejected from level X
  - core hole created filled by a 2nd electron from level Y
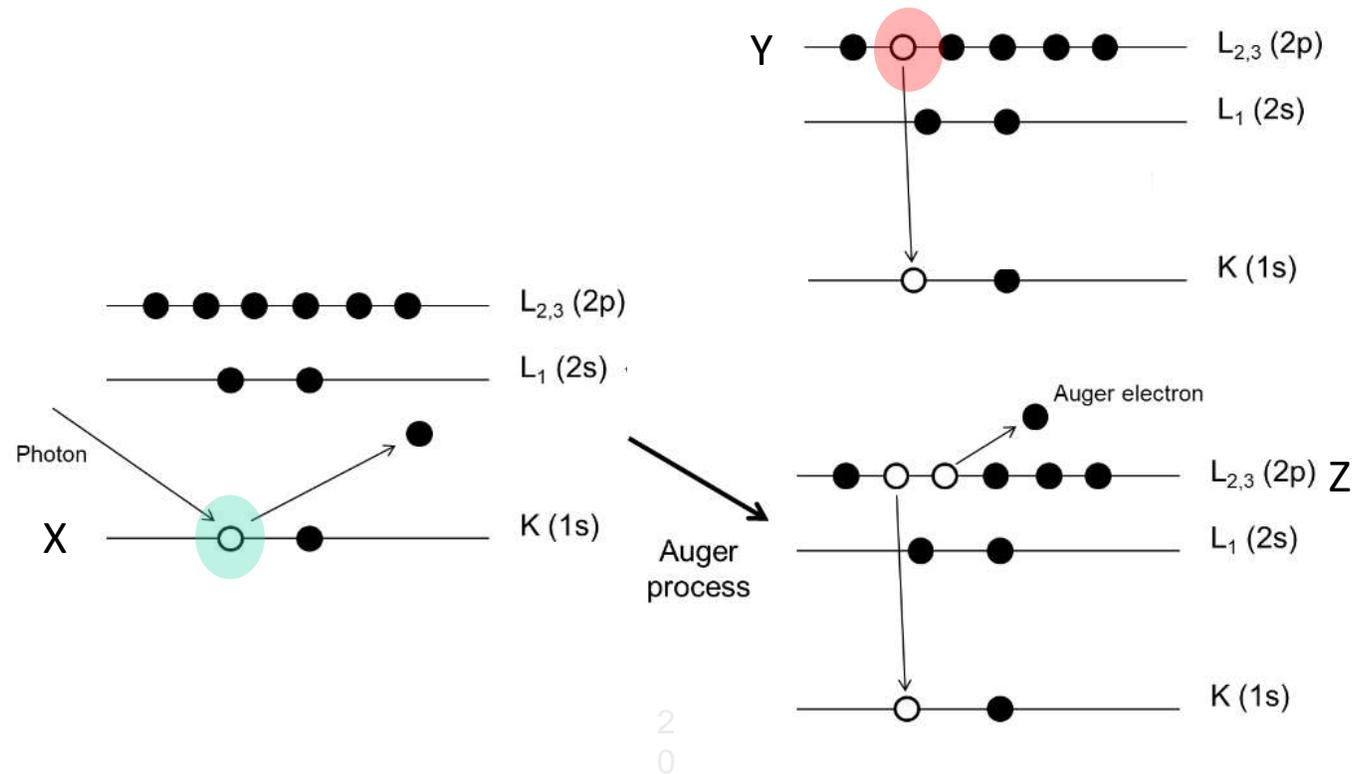
Auger electron spectroscopy (2)

- Excess energy released by ejection of an Auger electron from level Z with kinetic energy

$$E_{K,Auger} = E_{b,X} - E_{b,Y} - E_{b,Z} - \Phi_S$$

$E_{b,X}, E_{b,Y}, E_{b,Z}$ binding energies of electrons in levels X, Y, Z
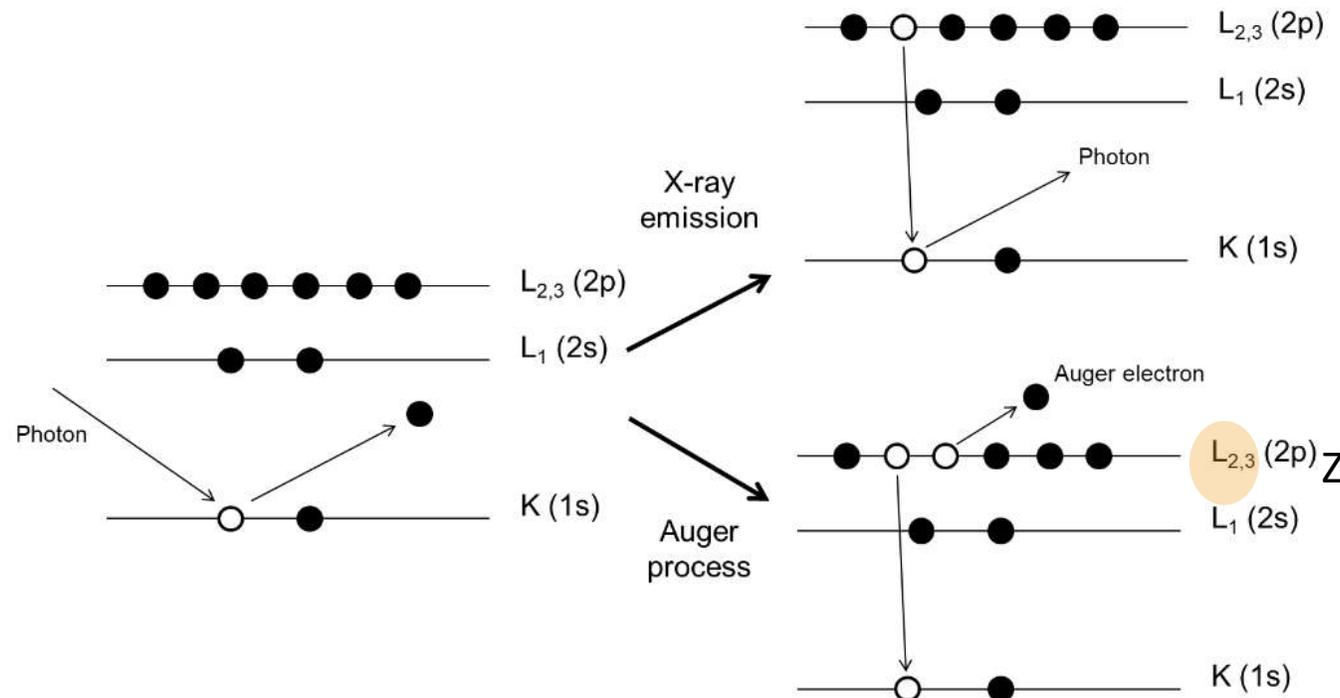
- Both X-ray and Auger mechanisms characteristic of probed atoms

- Auger peaks usually broader and with a more complex structure

- More sensitive to chemistry the core-level

- E_K of Auger electrons independent of $h\nu$: allows to distinguish from core levels by changing the photon energy

- Auger microscopy (few 10 nm) with electron beam excitation

Ti LMV : sensitive to TiO_2 polymorphs and face orientation

Zn LMM
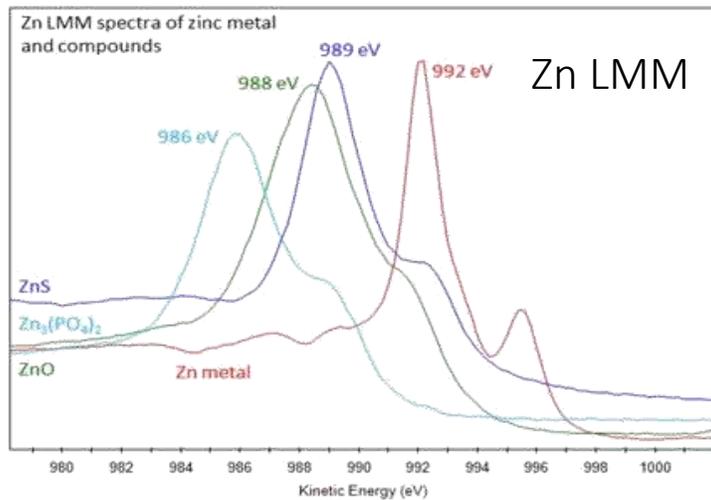
For Zn 2p, $\Delta E_B \simeq 0.2\ eV$
between Zn^{2+} and Zn^0
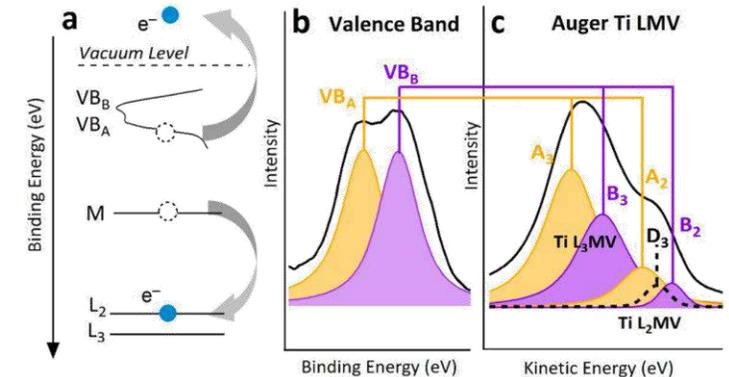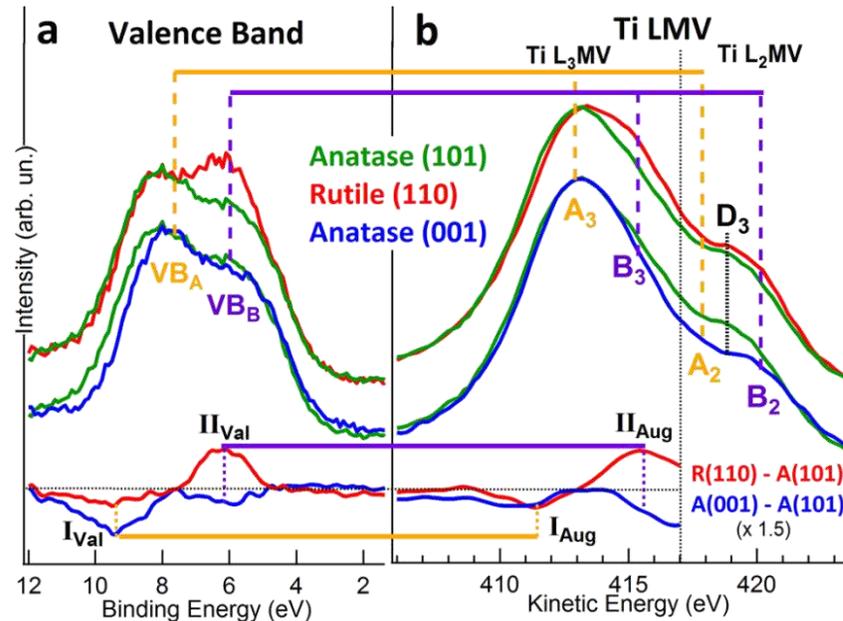
Borghetti et al, Phys. Chem. Lett 7 (2016) 3223

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$$\alpha = E_K(XYZ) - E_K(C) \qquad \alpha' = h\nu + \alpha = E_K(XYZ) + E_B(C)$$

with α, α' the Auger and modified Auger paramters
$E_K(XYZ)$ and $E_K(C)$ kinetic energies of XYZ Auger transition
and of core level C and $E_B(C)$ its the binding energy

- free of charge effect / independent of work function

- Wagner plot ➜ chemistry

- variation of Auger parameter related to relaxation energy
$\Delta\alpha' = \Delta E_K(XYZ) + \Delta E_B(C)$ with $\Delta E_K(XYZ) = \Delta\epsilon + 3\,\Delta R$
and $\Delta E_B(C) = -\Delta\epsilon + \Delta R$ where $\Delta\epsilon$ is the chemical shift (initial state
Effect) and ΔR the relaxation energy around the hole (final state effect)

- silica-based glass
➜ α' depends on local structure and concentration of other cations

Wagner plot of Si
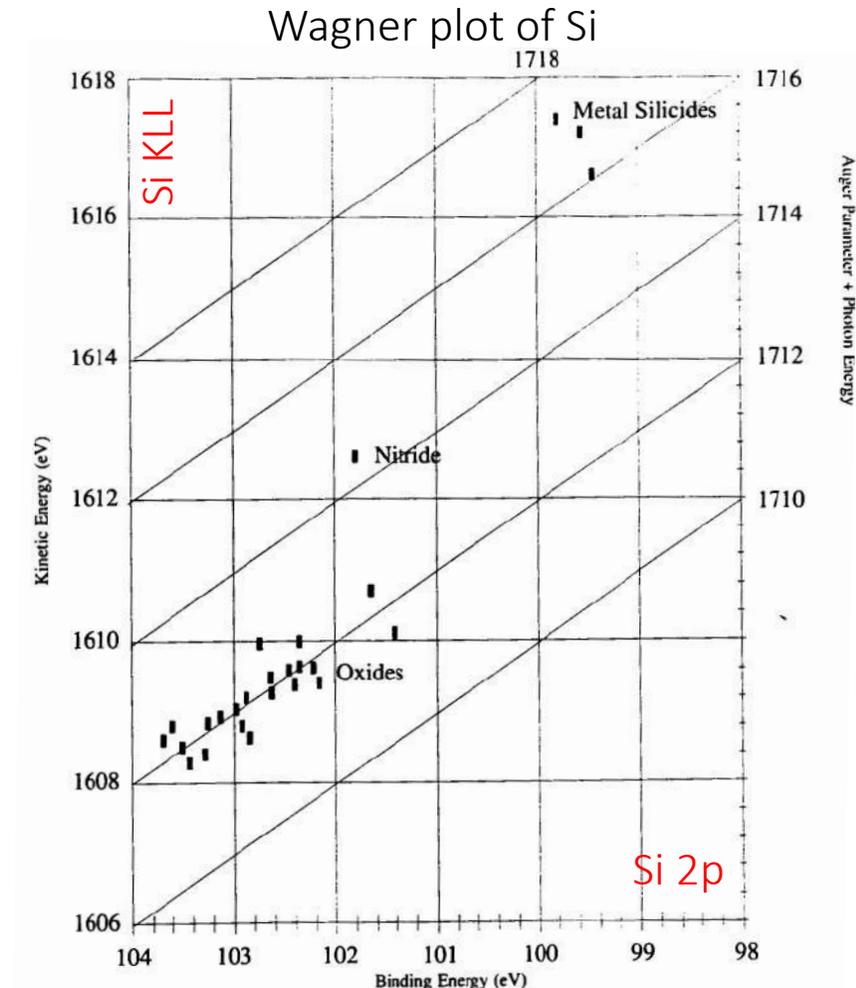
Photoemission : other features and background

- Plasmon, skahe-up, shake-off peaks (photoemission process ≠ sudden process)

- Intrinsic and extrinsic features

- Peaks overlap a continuous background with a step-like structure

  - Calculation of energy losses in the dielectric formalism or EELS measurements

  - The background is continuous since inelastic events are multiple and random

  - Information from deeper layers than elastic peaks

  - Interest of monochromatic sources
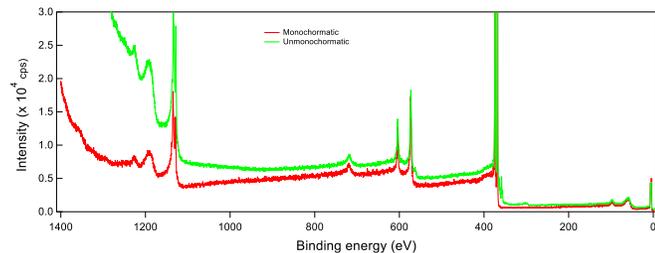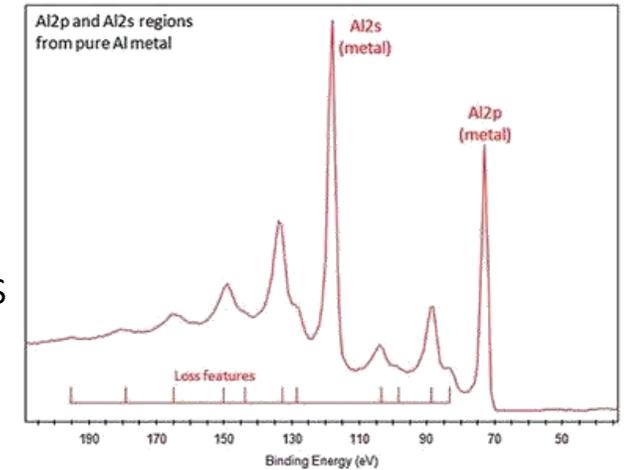
Ag metal

Bremsstrahlung is electromagnetic radiation produced by the deceleration of a charged particle when deflected by another charged particle

- Because of the several features detailed so far, XPS spectra might become quite complex

- Care should be taken when performing the analysis

- A detailed XPS spectrum interpretation often requires a fitting procedure to resolve overlapping different chemical states

- Prior to any fit, a background subtraction is essential to eliminate the inelastic scattering component

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XPS analysis (2): background removal

- Choice of an appropriate background is essential especially when a quantitative analysis is requested

- Various line shapes have been proposed:
  - linear, the simplest method
  - Shirley
  - Tougaard

Shirley

- Shirley: iterative method, background intensity at a given binding energy is proportional to the elastic peak area at lower binding energies

- Tougaard: assumes the existence of an inelastic scattering cross section based on dielectric theory which describes the probability for an electron to suffer inelastic scattering during its travel through the solid as a function of its kinetic energy

S. Tougaard, J. Vac. Sci. & Technol. A, 39 (2020) 011

XPS analysis (3): line shape

- Different factors affect peak line shapes:
    - The excitation source line shape (lab source, synchrotron)
    - The finite lifetime of the core-hole
    - Thermal broadening
    - Surface potential inhomogeneities
    - Surface charging
    - Analyser resolution

- To model peak line shapes, Voigt functions are often used.

- A Voigt function $V(E)$ is the convolution of a Lorentzian $L(E)$ function, arising from the finite core-hole lifetime and energy width of the photon source, and a Gaussian $G(E)$ function, accounting for the instrumental response and the other broadening sources

XPS analysis (4): line shape

$$V(E) = A \int_{-\infty}^{+\infty} L(E')G(E - E')dE'$$

where $L(E) = \dfrac{1}{\pi \gamma_L} \dfrac{\gamma_L}{(E-E_0)^2 + \gamma_L^2}$ and $G(E) = \sqrt{\dfrac{ln2}{\pi}} \dfrac{1}{\gamma_G} \exp\left(-\dfrac{E^2}{\gamma_G^2}\right)$

- γ_L and γ_G are the FWHM, E_0 is the peak position and the A peak area.

- Often a linear combination of the two curves is used.

- Electron-hole pair creations have to be accounted for when a metal sample. It introduces a high E_b asymmetry. A Doniach-Sunjic line shape is then used:

- $DS(E, \alpha) = A \dfrac{\cos\left[\pi\frac{\alpha}{2}(1-\alpha)\tan^{-1}\left(\frac{E-E_0}{\gamma_{DS}}\right)\right]}{\left[(E-E_0)^2 + \gamma_{DS}^2\right]^{\frac{1-\alpha}{2}}}$

α : asymmetry parameter, γ_{DS} related to the FWHM.
when $\alpha = 0$ a Lorentzian function is obtained

- Fractured sample
- Chemical shift of about 2 eV between BO/NBO due to the more electropositive Na
- Negative chemical shift with Na_2O content
- Broader BO FWHM

Nesbitt, et al. J. Non. Cryst. Solids 357 (2011) 170

- Electronegativity argument on Si 2p (inital state effect) ➡ $E_B(Q_4) > E_B(Q_3) > E_B(Q_2)$
- Problem of resolution and Si 2p spin-orbit splitting
- Similar estimates with NMR

Nesbitt,et al. J. Non. Cryst. Solids 357 (2011) 170

Swayer et al. J. Non. Cryst. Solids 358 (2012) 290

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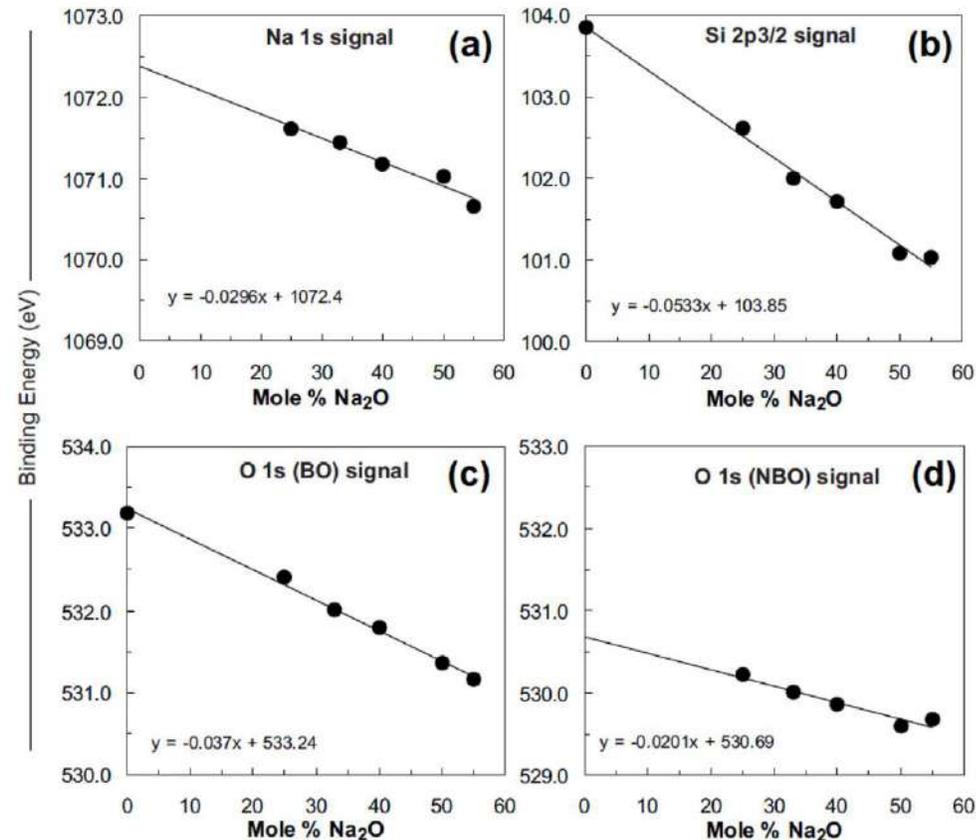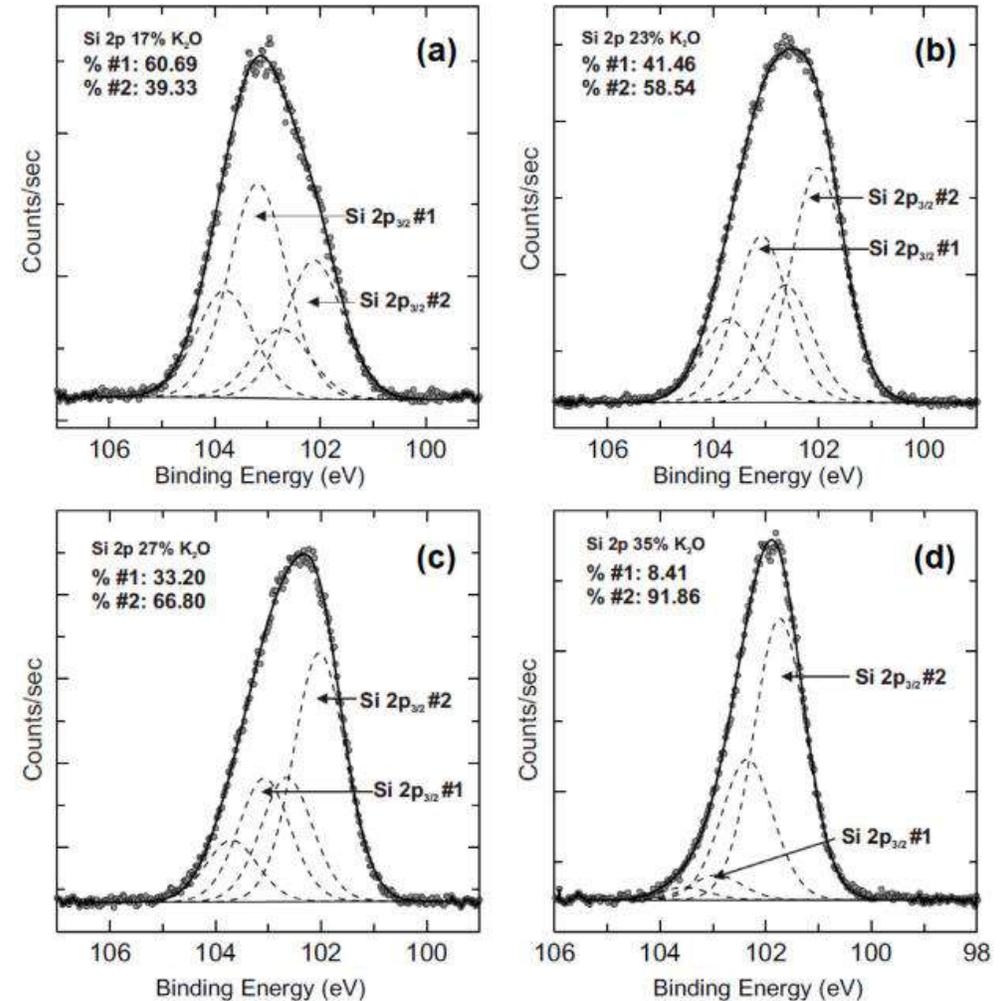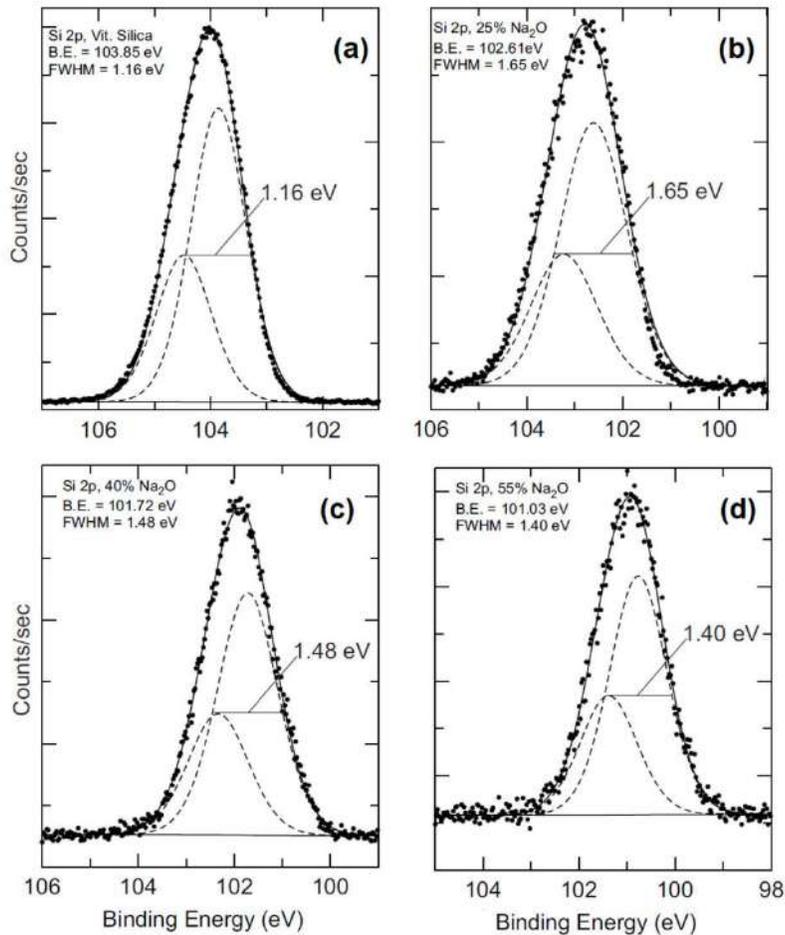
Photoemission in alkaline glass (3) : beam damage

- X-ray or secondary electron induced beam damage
- Change in BO/NBO ratio and mobility of alkaline
- Specific measurement strategies: different positions, cooling, time dependence

Sharma et al., Surf. Inter. Anal. 31 (2001) 369

- OH on fractured glass difficult to detect; shift to higher E_B (~0.6eV)
- Leaching of glass ➔ hydratation, network hydrolysis and ion exchange; depend on pH, Q_n content and alkaline type; precipitation and recrystallisation of carbonates
- Weathering ➔ complex problem (SO_x, NO_x, CO_2)
- Interpretation ? Peak fitting ?
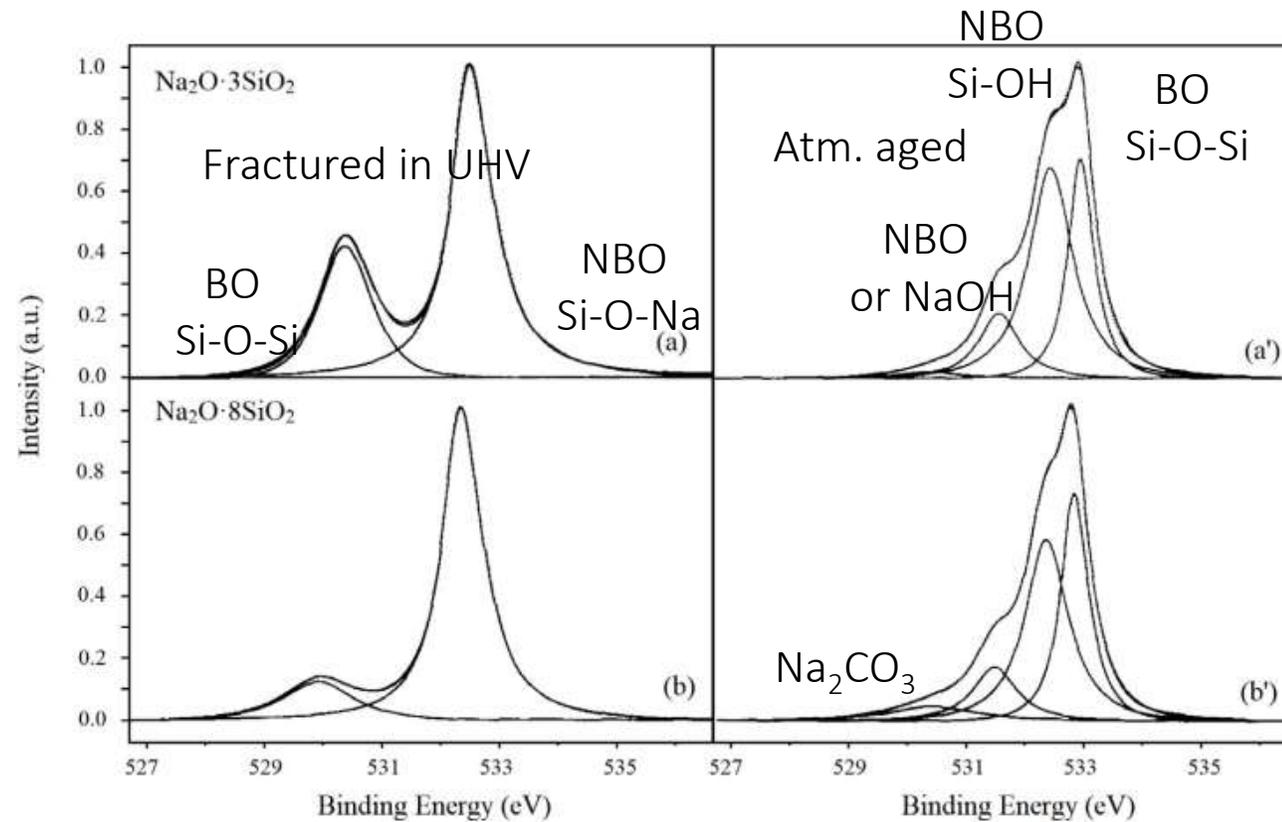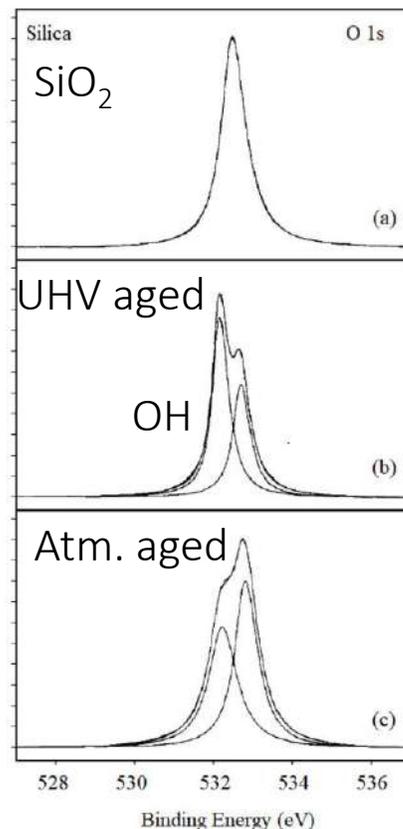
Deconvoluted spectra

XPS probe
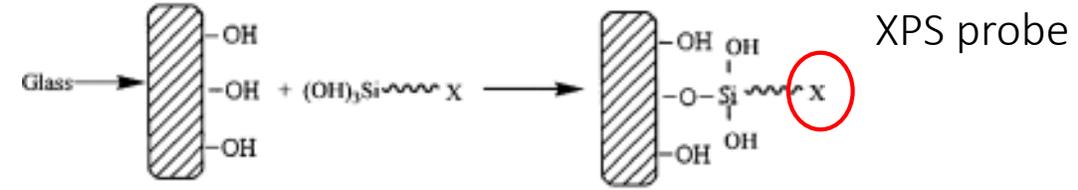
- Evolution of water contact angle of float glass
- Hydrophobicity of glass induced by C-species due to silanol Si-OH density (not Sn-OH)
- Quantification of surface OH difficult by IR spectroscopy at oxide surfaces
- Surface OH density from chemical labelling (silane grafting) / Few OH.nm^{-2}
- Site accessibility ?

Float air
Float Sn
Pure SiO$_2$
boroaluminosilcate

Takeda et l, J. Non Cryst. Sol 249 (1999 41

33
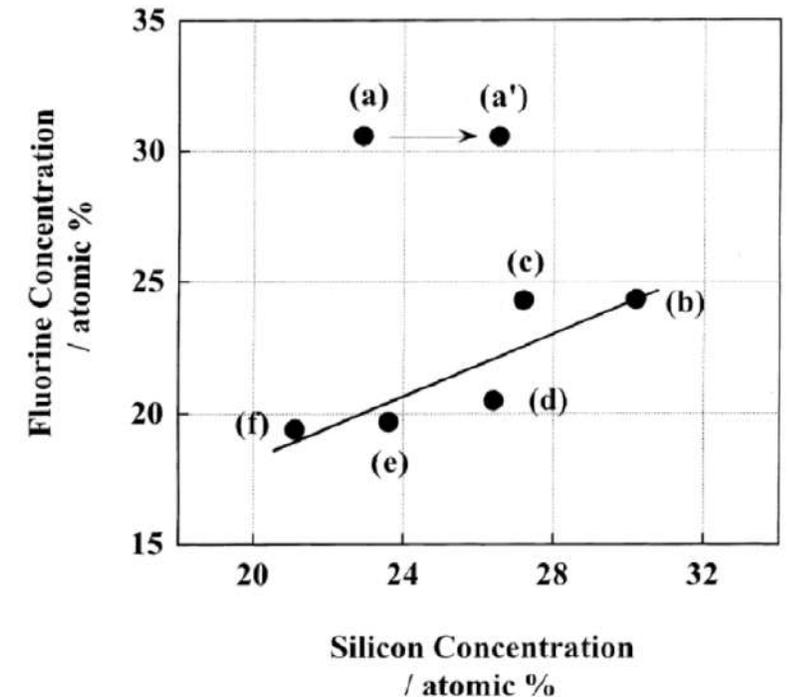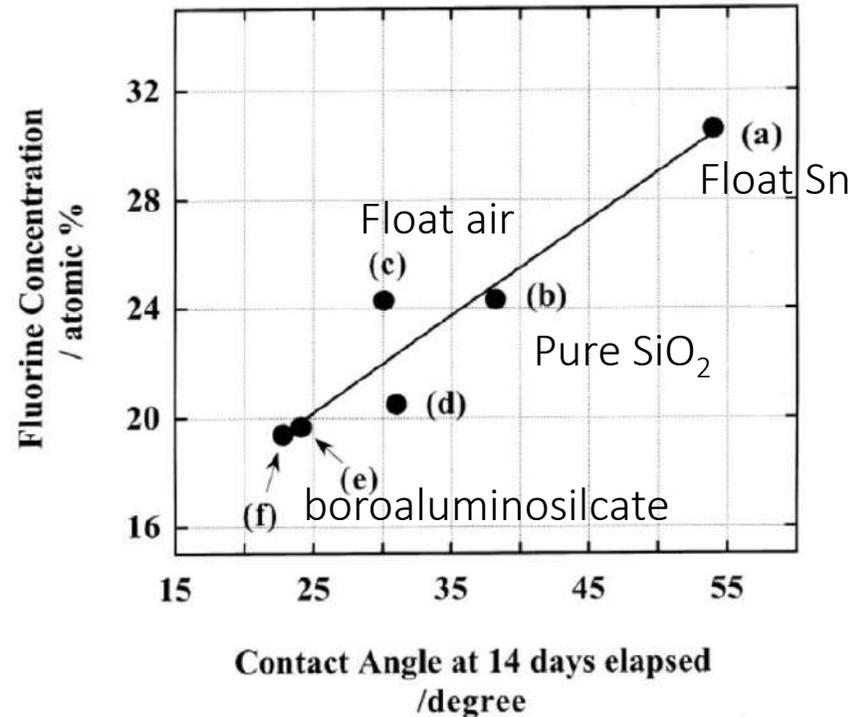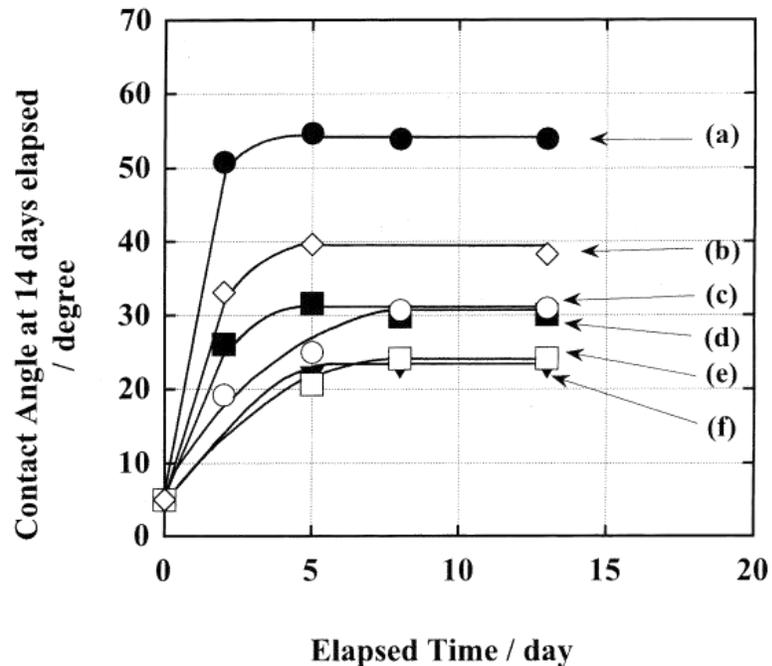
$$I(E_K) \propto F\, A\, D\, \Omega\, T(E_K)\, \sigma(h\nu) \exp\left[-\frac{z}{\lambda(E_K)\cos(\Theta)}\right] n(z)dz$$

- $I(E_K)$: elastic peak intensity for layer of thickness dz at depth z
- F : photon flux
- A : analysed area
- D : detector efficiency
- Ω : solid angle of collection
- $T(E_K)$: transmission function of the analyser
- $\sigma(h\nu)$: photoionisation cross section at photon energy $h\nu$
- $\lambda(E_K)$: inelastic mean free path at E_K
- $n(z)$: element concentration at depth z

- Integration from 0 to ∞ with constant concentration n_A
- ➔ peak area $I_A(E_{K,A}) \propto T(E_{K,A})\, \sigma_A(h\nu)\lambda(E_{K,A})\cos(\Theta)n_A$
- Quantification from ratio of peak areas for a compound $A_{1-x}B_x$
- ➔ $\dfrac{I_B(E_{K,A})}{I_A(E_{K,A})} = \dfrac{x}{1-x}\dfrac{T(E_{K,B})}{T(E_{K,a})}\dfrac{\sigma_B(h\nu)}{\sigma_A(h\nu)}\dfrac{\lambda(E_{K,B})}{\lambda(E_{K,A})}$ ➔ composition
- Film thickness

θ

n(z)   z   dz

Tabulated calculated $\sigma(h\nu)$

Si[14]

Si 2p

Si 2s

2p 2s

Si 3s   3s

Si 2p

3px

Cross Section (Mb)

Photon Energy (eV)
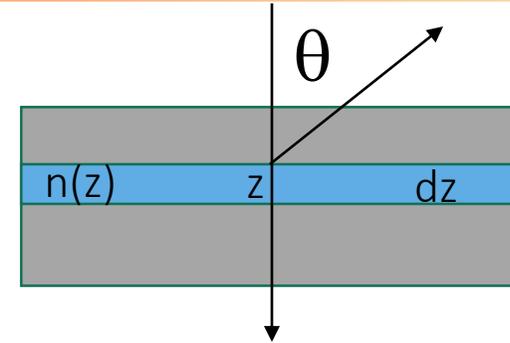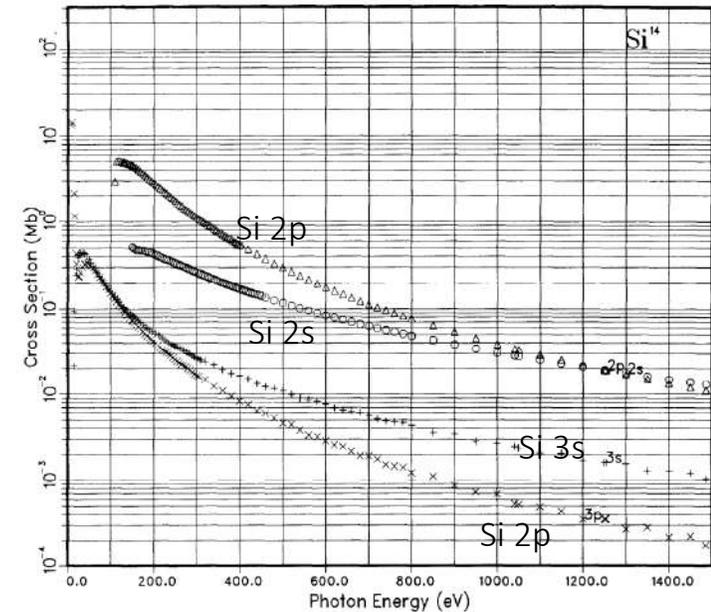
Yeh, J. & Lindau, I.
Atomic subshell photoionization cross sections and assymetry parameters: 1l<Z<300
At. Data Nucl. Data Tables, **1985**, *32*, 1-155

- Quantification of frozen glass surface (≠ crushed glass)
- Role of relative sensitivity factors and contamination (water)
- Glass fractured/melted/acid leached : Composition and speciation of O in BO, NBO and OH ?
- ➔ constraints of conservation and charge balance

Alumino-silicate glass
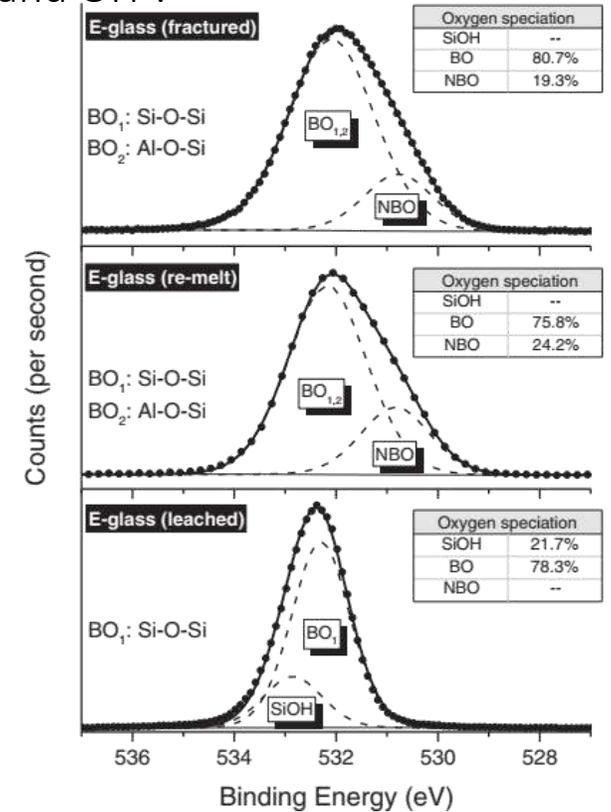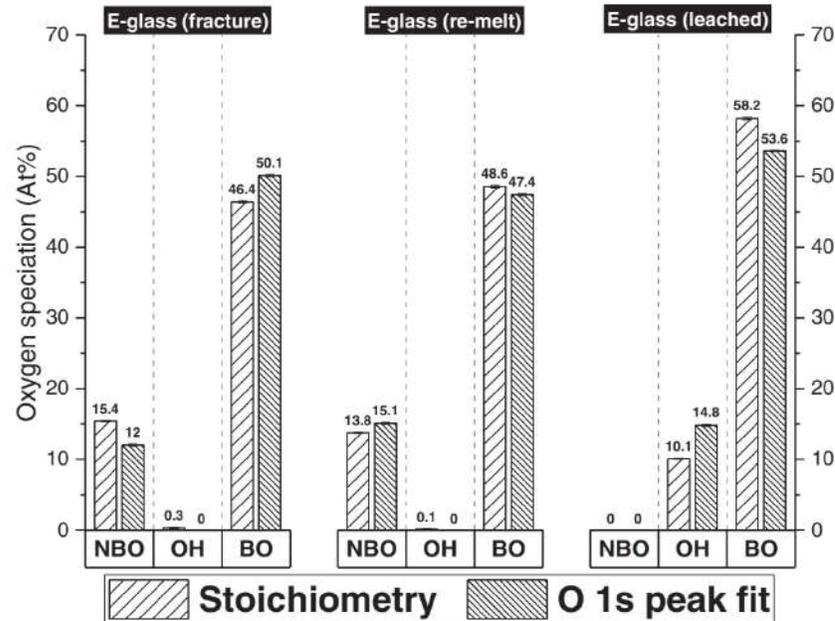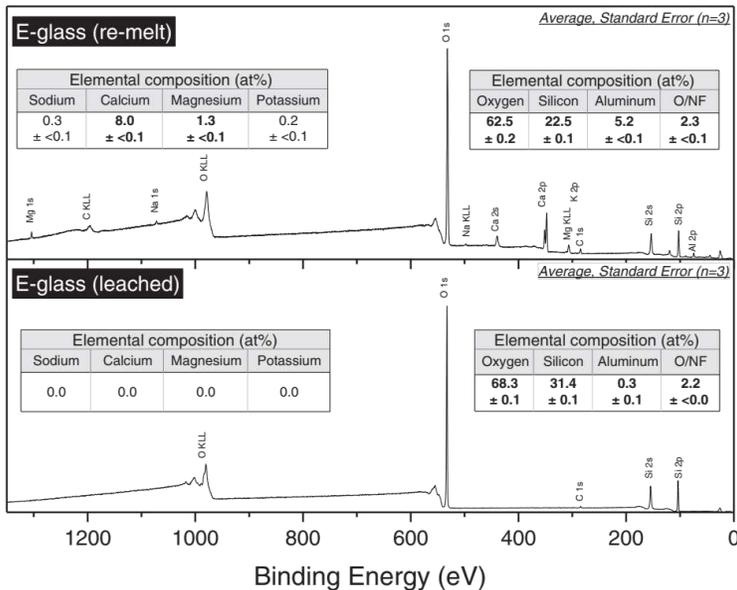
Banerjee et al., J. Non. Cryst. Sol. 450 (2016) 185
Banerjee et al., J. Am. Ceram. Soc. 101 (2018) 644

➔ Repolymerization upon leaching

- Few measurements in the literature (pb of cross sections in XPS) vs calculations
- Poorly dispersive lower and higher valence band in SiO_2
- Evolution upon hybridation with Na 3s for soda-lime glass

Nesbitt et al, Surf. Inter. Anal 49 (2017) 1298
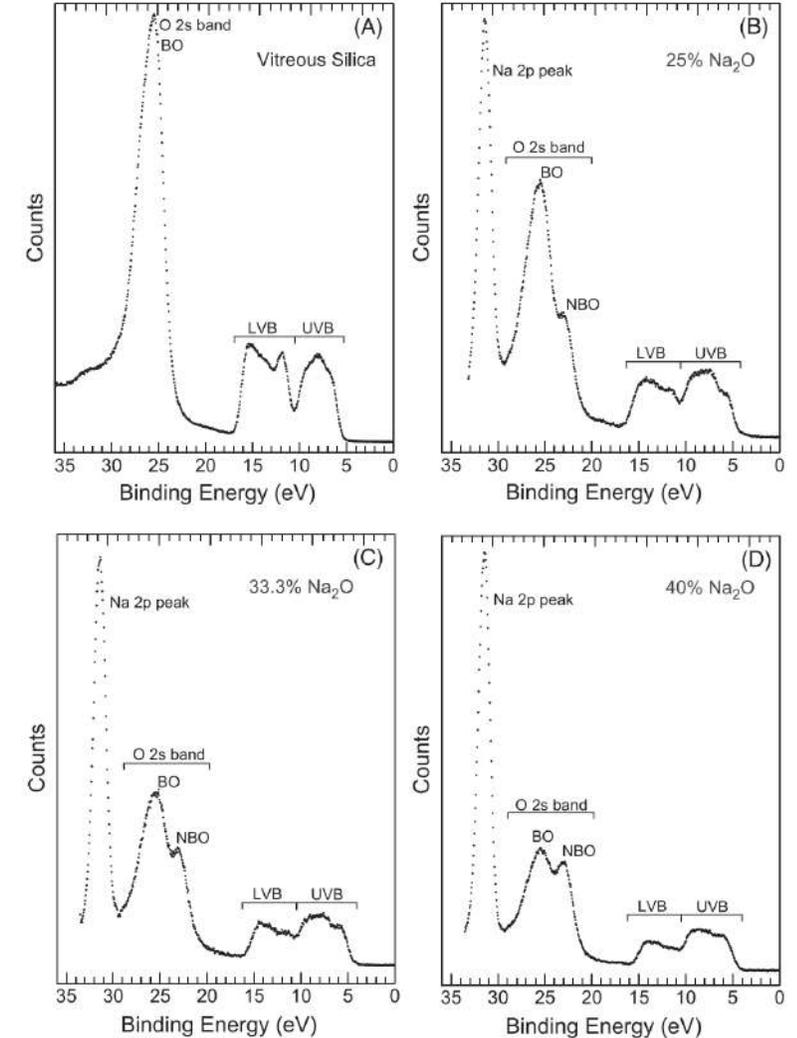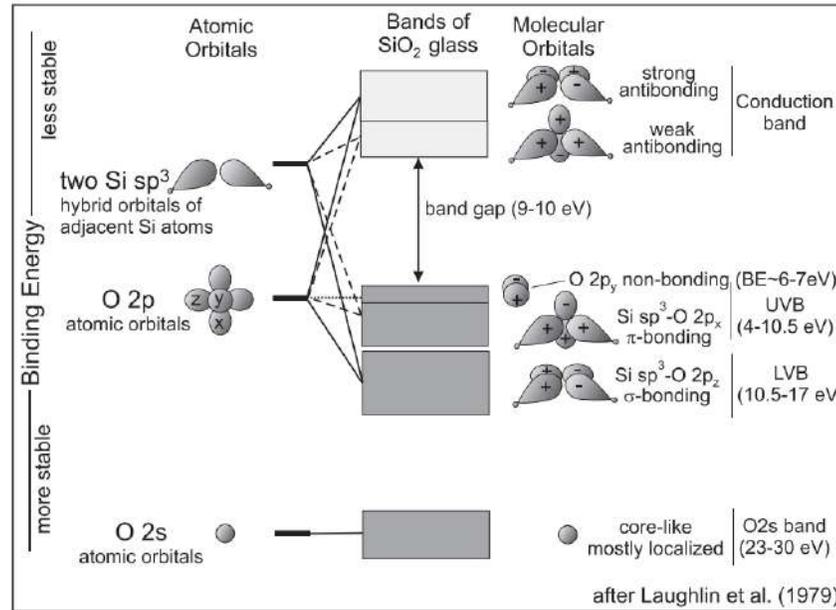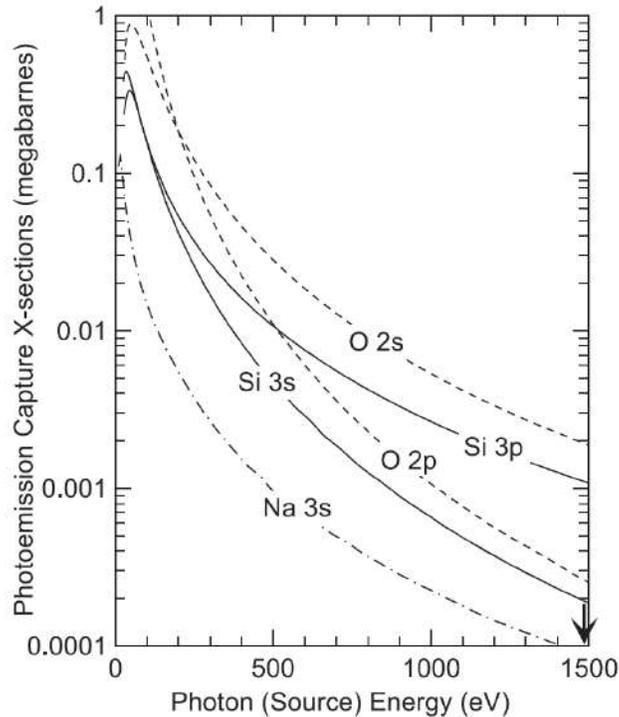
Depth profiling with conventional XPS

Angle resolved XPS

- Escape depth $\lambda \cos(\theta)$ ➜ sampling over a few nm
- Angle resolving lens and 2D detector;
  no coupling between analysed area and sample position;
  no problem of charge effect
- Modelling of the exponential damping signal
- But homogeneous and flat sample (roughness= shadowing);
possible photodiffraction effects
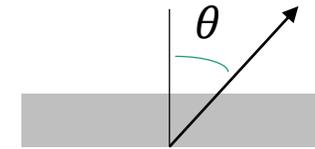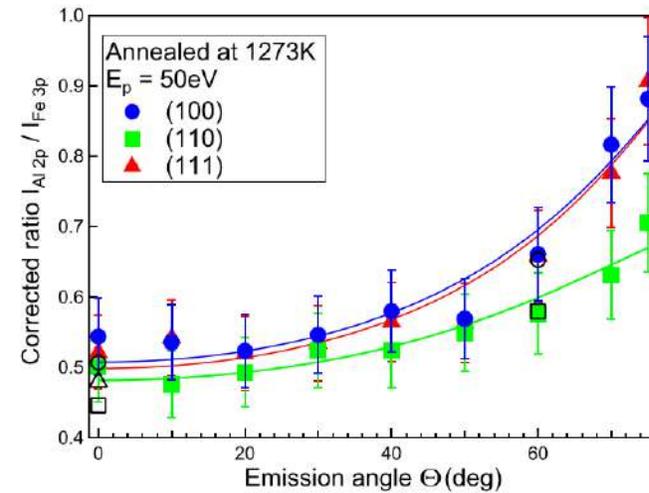
Segregation at $Fe_{0.85}Al_{0.15}$ surface

$A_{1-x(z)} B_{x(z)}$
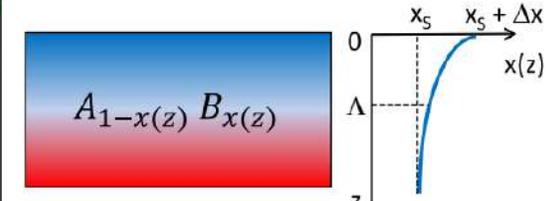
Dai et al, Appl. Surf. Sci 492 (2019) 886

Profilometry by sputtering

- Depth profile by sequential sputtering/analysis ➜ calibration for thickness
- Artefacts of preferential sputtering of light elements, atomic mixing,
implantation, redeposition, diffusion under electric field
- ➜ change of composition, chemistry, stress
- Neutral gas ion beam (Ar^+, 1keV) ➜ difficult on glasses
- Gas cluster ion beams ➜ ~1000 atoms/cluster; a few eV per atom; less damage
- C60 sputtering ➜ accurate diffusion profiles

Soda-lime silica glass
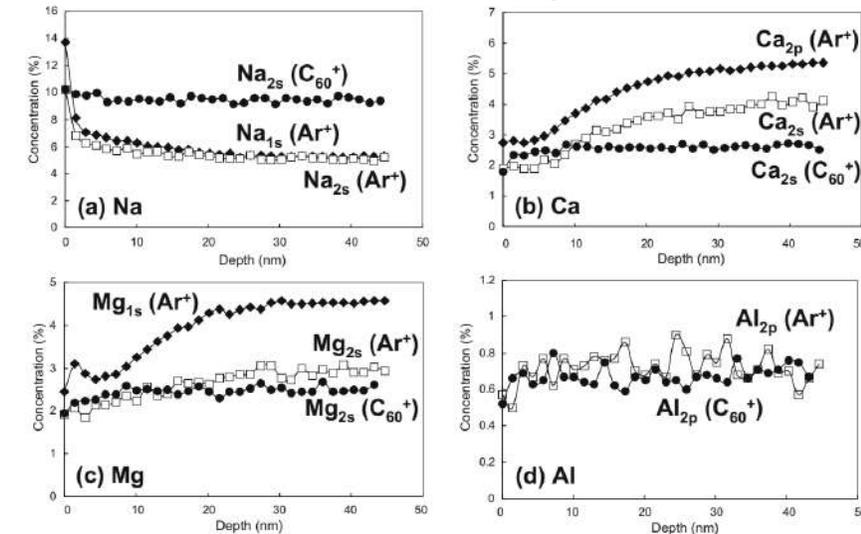
Yamamoto et al, J. Non. Cryst. Sol. 356 (2010) 14, Surf. Inter Anal. 44 (2012) 931

- Synchrotron or Al (1486.6eV) /Cr(5414.7eV)/Ga(9251.8eV) Kα laboratory sources
- Bulk sensitivity through increased inelastic mean free path compared to XPS(Al Kα)
- No sputtering damage as with profiling; charging avoided by conductive overlayer
- Deeper E_B core levels / shift Auger lines
- But lower photoionisation cross sections
- Applications: buried interfaces, band alignment, batteries, *operando* analysis on devices

Mo	5	nm
Ti	3.5	nm

ZnO

Si
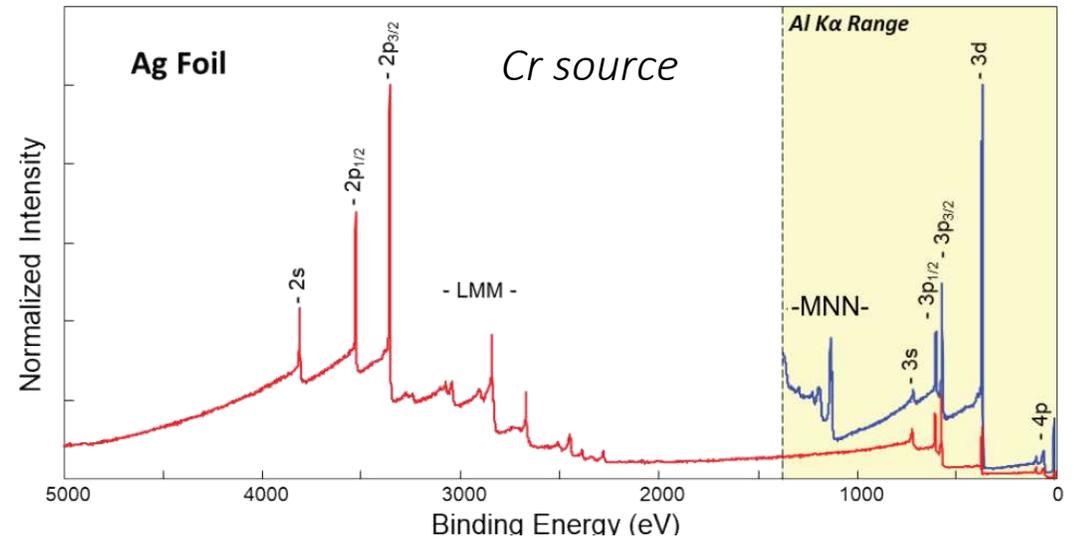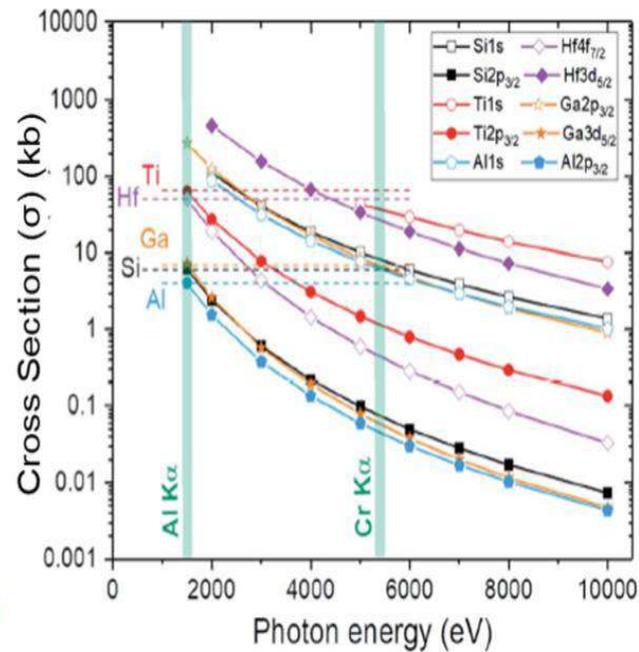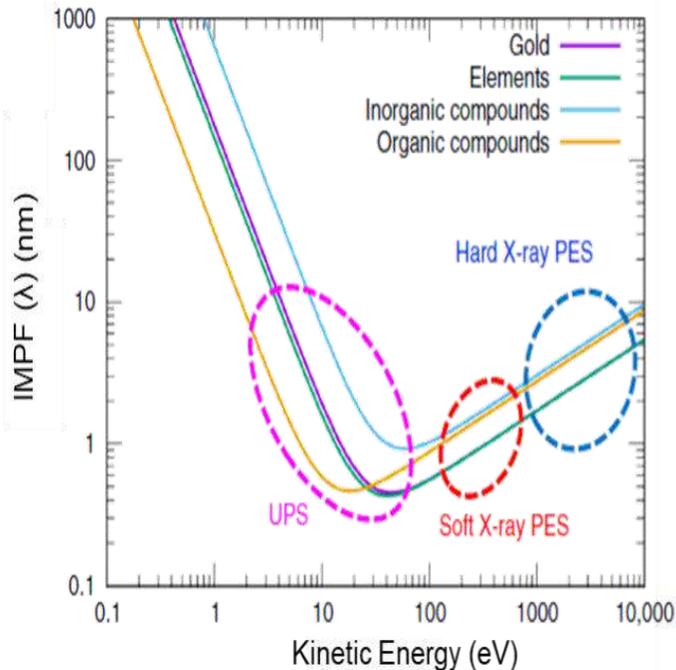
- Model system of buffer layers used in low-emissive coatings on glass
- Interfacial reaction between Ti and ZnO upon annealing

Ti 2p
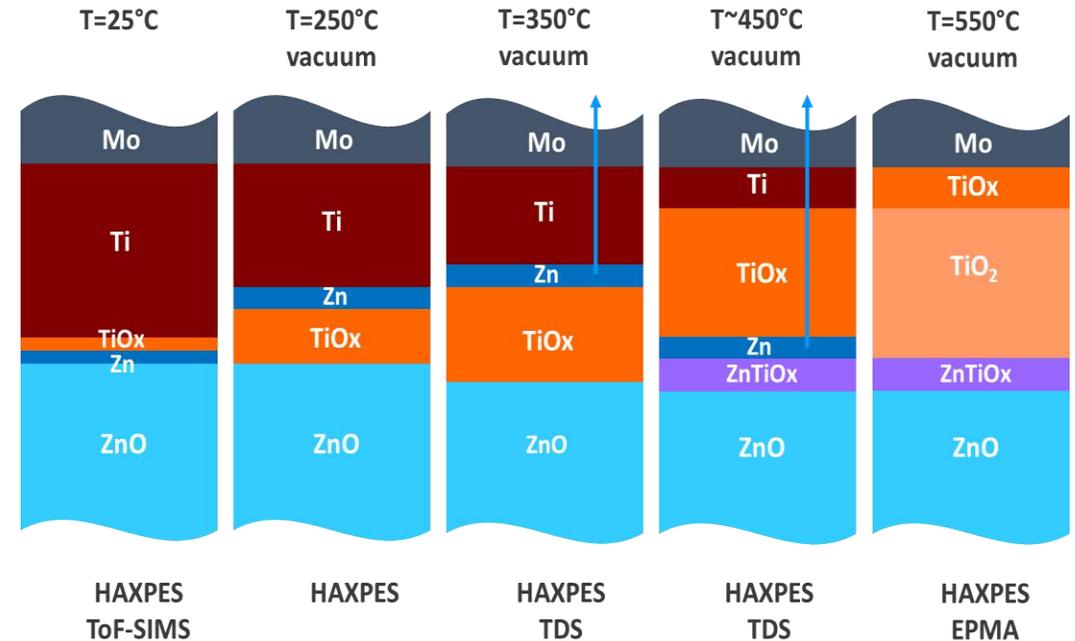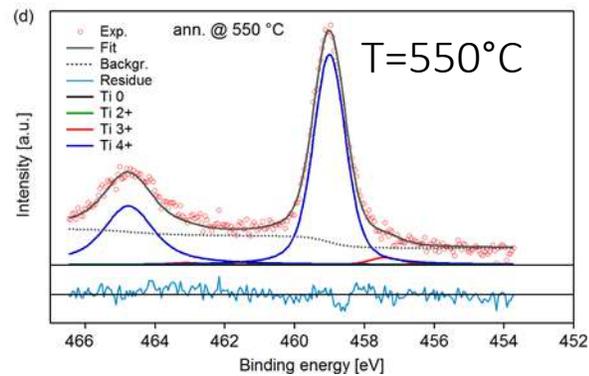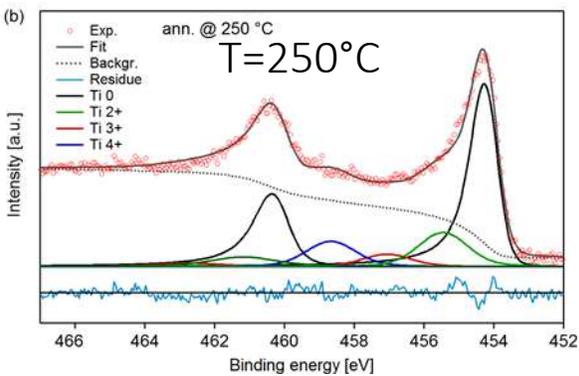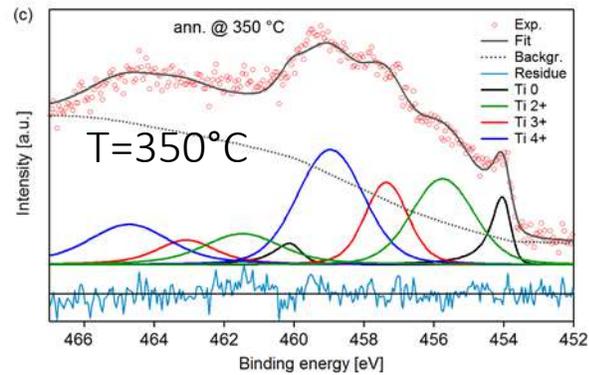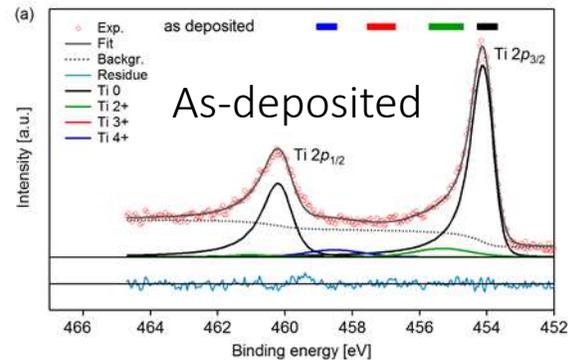
- Very few results in the literature !
- HAXPES@$h\nu = 5953.4\ eV$ on Bi-based glassed
- Charging avoid by amorphous conductive C layer (8.5nm)
- Coloration related to Bi[(0)] precipitate

Bi 4f
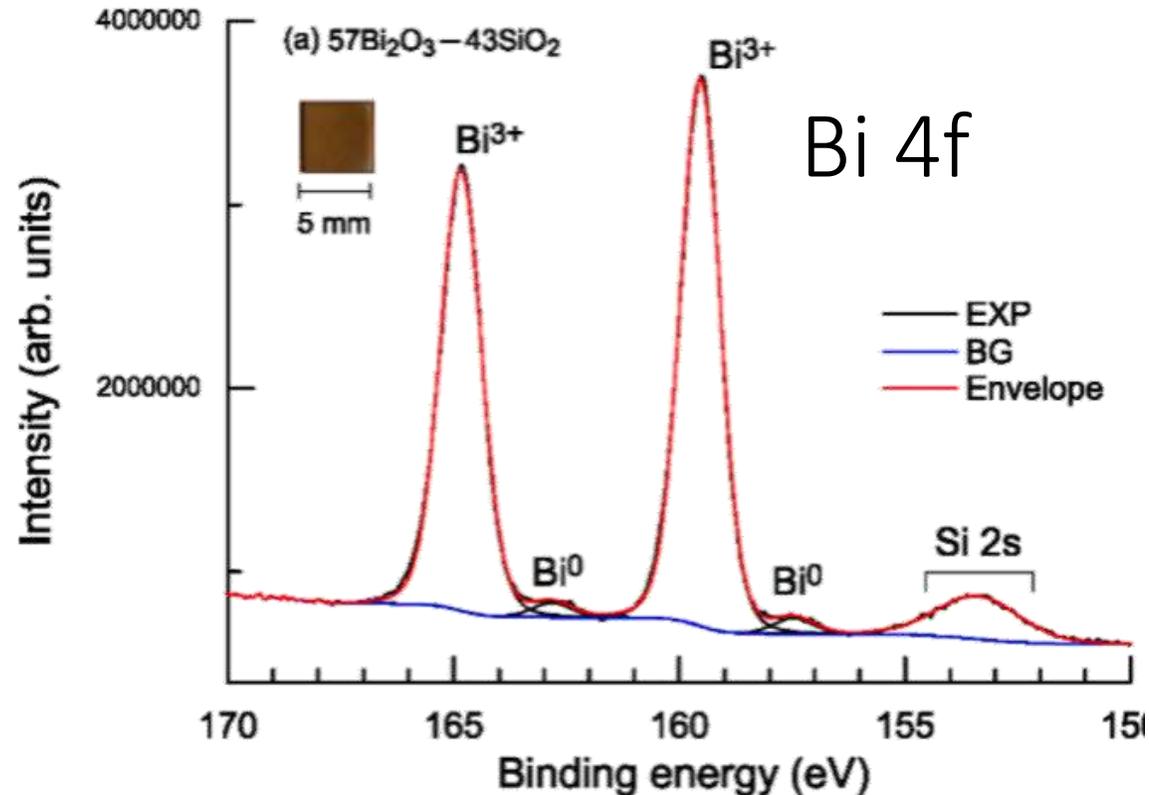
- Absorption spectrum = variation of the absorption coefficient $\mu(E)$ as a function of the photon energy $E = h\nu$ (Beert-Lambert law)

- $\mu(E)$ discontinuities: absorption threshold associated with the excitation of an electron from a particular core level to an empty or free state
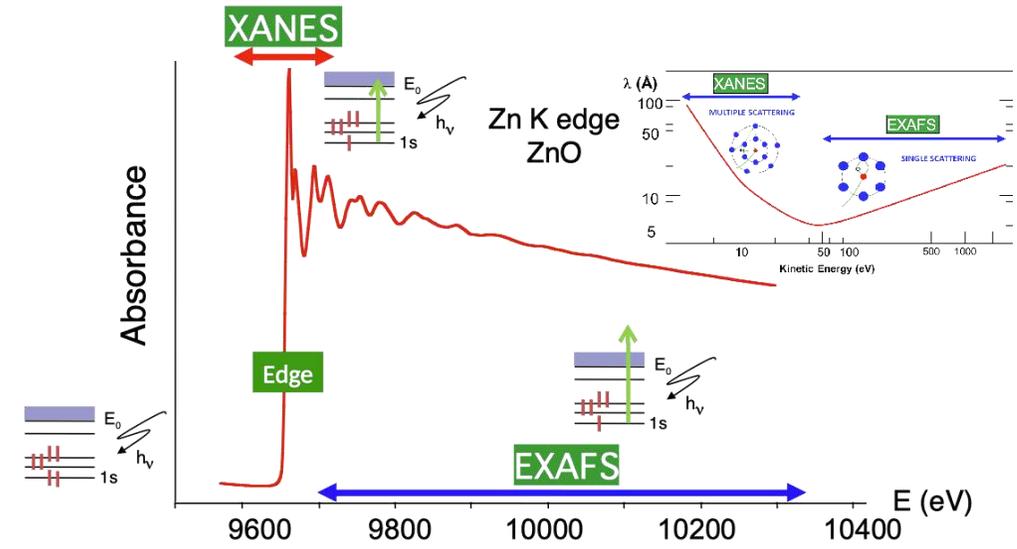
- Below ~50 eV after the absorption threshold is the X-ray Absorption Near Edge Structures (XANES)➔ bound state

- Above ~50 eV is the domain of Extended X-ray Absorption Fine Structures (EXAFS) ➔ excitation in the free electron state

- Element selective analysis tool suited for the study of the chemical state and local atomic structure in ordered or disordered materials; perfectly studied for probing local order in glasses

- Spectroscopic notation K(n=1), L (n=2), M (n=3), N(n=4), , .. edges of elements

- Link to the X-ray emission spectroscopy

- XAS requires synchrotron radiation i.e. electromagnetic radiation emitted when a charge moving at relativistic speed in a storage ring follows a curved trajectory

- Light emitted in a continuous spectrum from infrared to hard x-rays in a very narrow cone tangential to the electron orbit; very large brilliance

- Strongly collimated in the forward direction and strongly polarised in the plane of the orbit

- Storage ring ; basic components (dipole magnets, undulators, radiofrequency cavities)

- Beamline optics adapted to energy range and technique (mirror, Bragg monochromators); sample environment

XAS (3) : measurement and analysis

- Beamline optimised for a given energy range
- Modes of measurements : transmission, X-ray fluorescence and total electron yield + flux normalization
- Probing depth from a few μm down to a few hundreds of nm
- Possibility of change of polarisation, focalisation (μm²), quick scan, different environments
- Extraction of modulation $\chi(E) = [\mu(E) - \mu_0(E)]/\mu_0(E)$ compared to

free atom $\mu_0(E)$, conversion in free electron k-space $k = \left[\frac{2m}{\hbar^2}(h\upsilon - E_0)\right]^{\frac{1}{2}}$

Followed by Fourier transform

LUCIA@SOLEIL

- Involves electronic transitions from deep energy levels to empty states in the bottom of the conduction band (unoccupied states); complementary to photoemission

- Mainly electric dipolar transitions $\Delta l = \pm 1$, $\Delta j = \pm 1$, $\Delta s = 0$
($s \rightarrow p$, $p \rightarrow s,d$, $d \rightarrow p,f$, $f \rightarrow d,g$)

- Average free path of the electron is large and will be sensitive to an atomic environment exceeding the first neighbours

- Interpreted in terms of the medium-range order of a material (3Å-15Å)

- Complex multiple scattering of the wave emitted by the probed atom backscattered by all of these neighbours

- Chemical information

- Comparison with standards with similar environment and/or complex ab initio simulations of $\mu(E)$ (FDMNES)
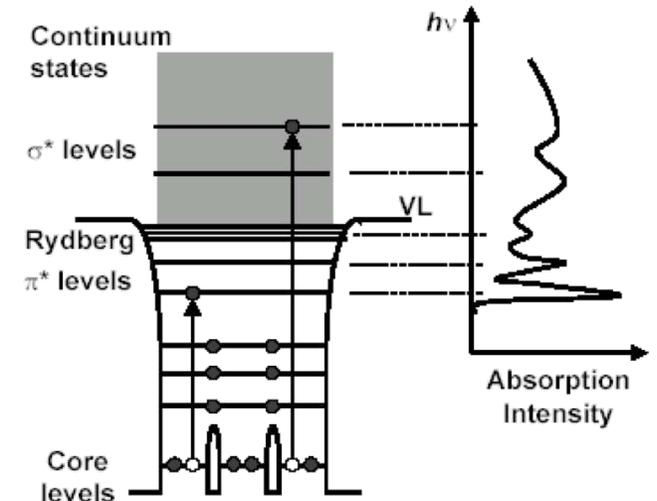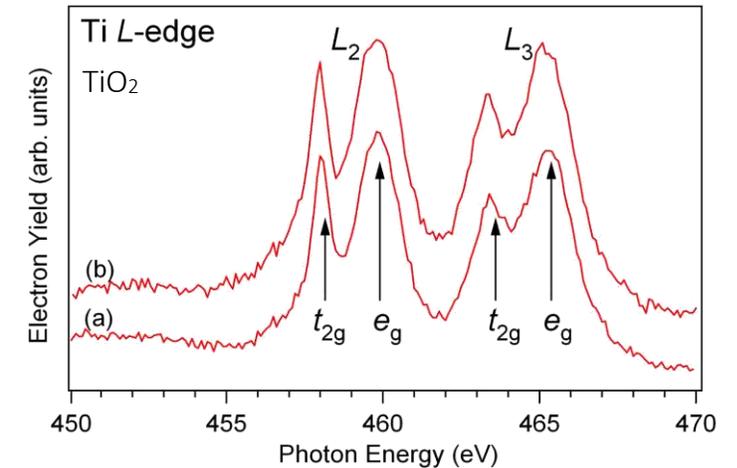
- AZO used to encapsulated Ag in low-emissive/anti-solar coating on glass
- Transparent conductive oxide
- Film deposited by magnetron sputtering
- Position and evolution of Al-dopant upon annealing ?

After air annealing @ 800°C: precipitation of spinel phase and not alumina

$ZnAl_2O_4$

As-deposited : Al_{Zn} substitution

O. Kerivel, PhD Thesis (2023)
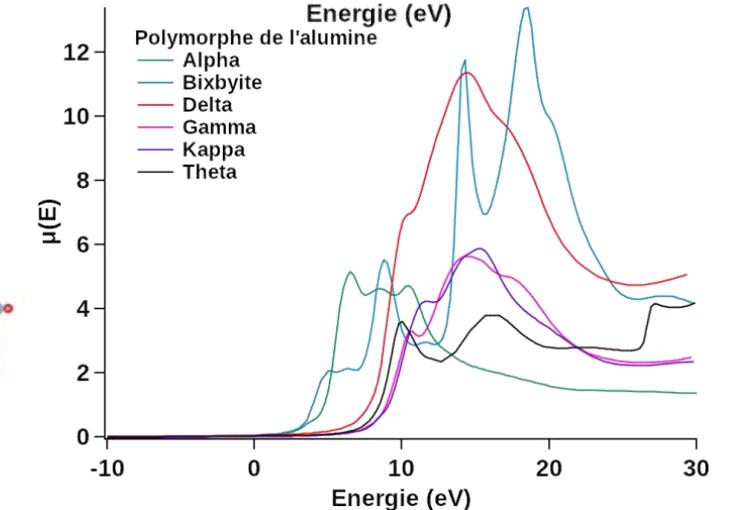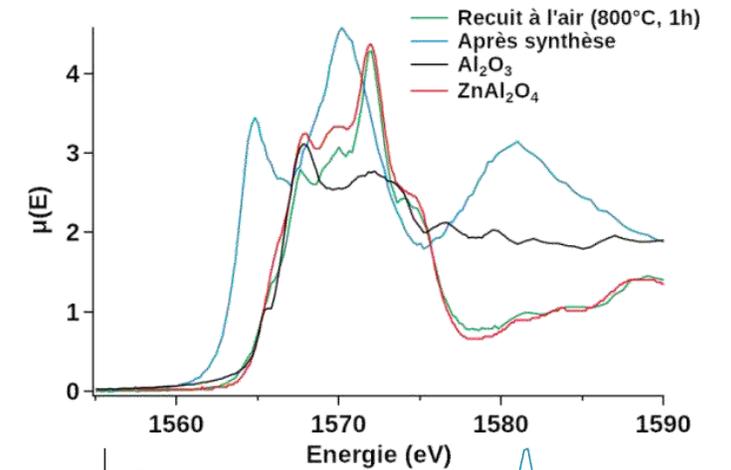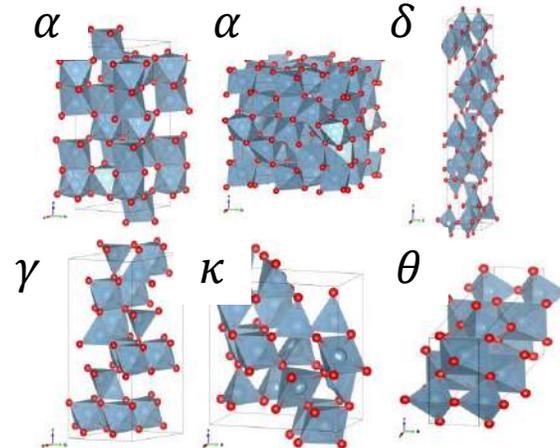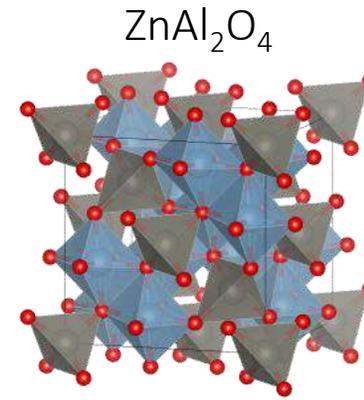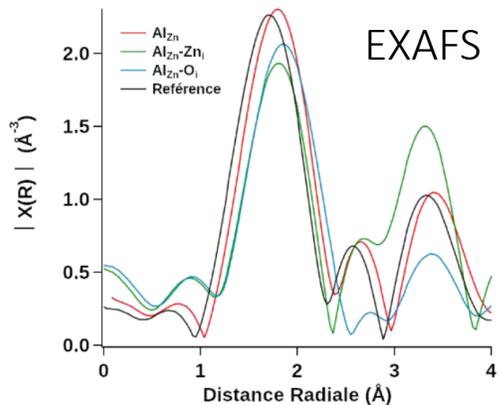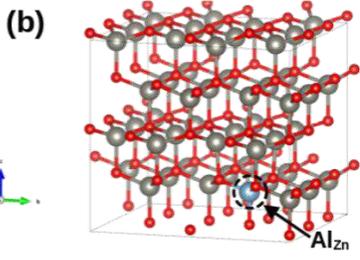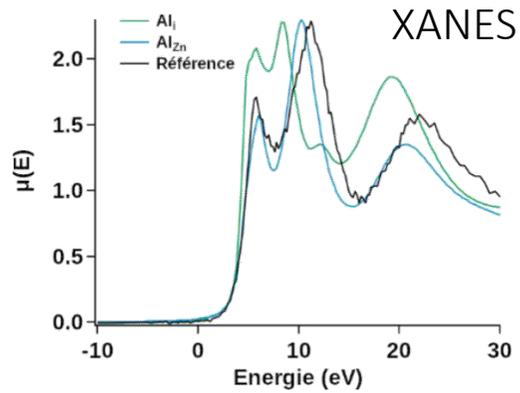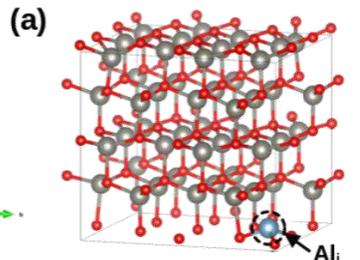
- Profile and oxidation states of Sn, S(0.3wt%), Fe (0.1wt%) at float glass surface
- Difference between air/Sn faces due to reducing atmosphere
- µ-XAS/fluorescence at K-edges of elements (LUCIA) + EPMA

XANES
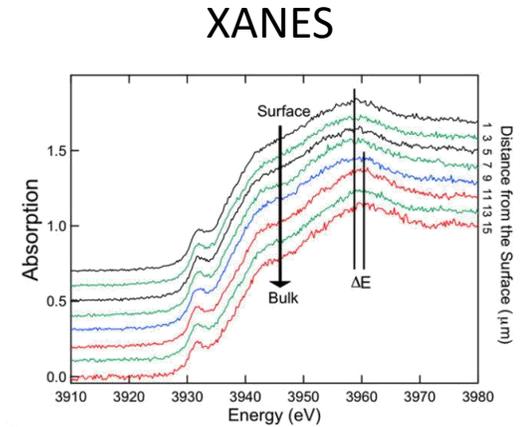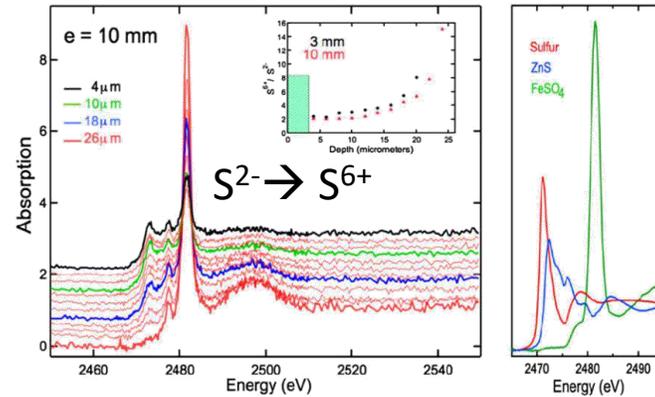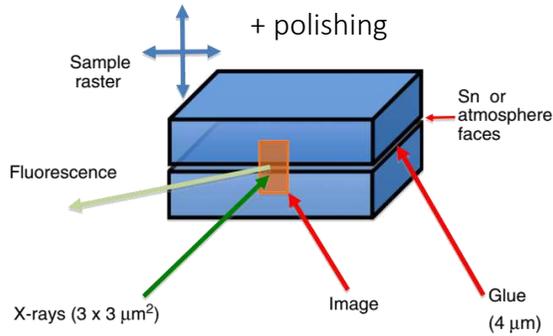
Fluorescence map (2 Sn faces)
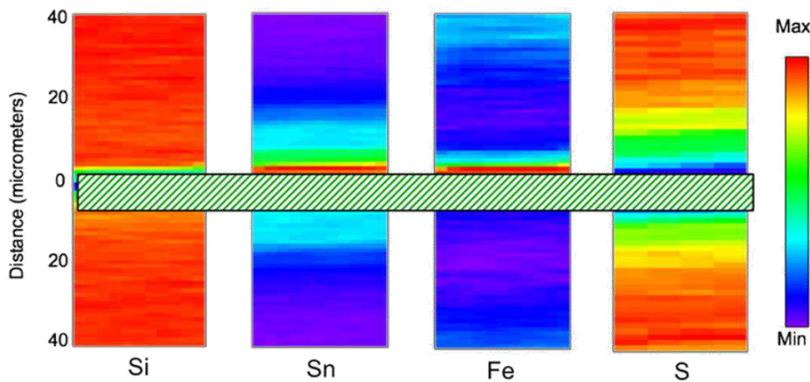
Flank et al., J. Non Cryst. Sol. 357 (2011) 3200

$S^{2-} \rightarrow S^{6+}$

Open (XAS) / EPMA (filled)

$4Sn^{2+} + S^{6+} \rightarrow 4Sn^{4+} + S^{2-}$ (not iron)
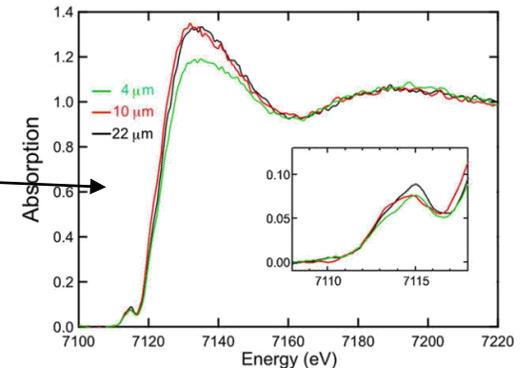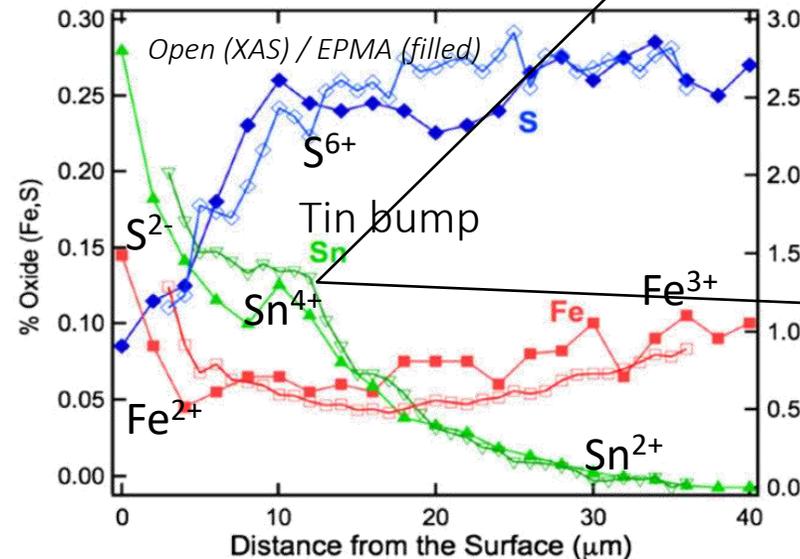
Extended X-ray Absorption Fine Structure (1) : basis

- EXAFS oscillations : constructive and destructive interferences between the outgoing part of the photoelectron wavefunction (free state) and the part of it backscattered by neighbouring atoms.
- Possible to characterise the environment of the probed atom (nature, number of neighbours and distance) ; mainly first and second shell as λ is minimal at E=50-100 eV

- The EXAFS formula (k-wavevector)

$$\chi(k) = \sum_i \frac{N_i A_i(k)}{kR_i^2} e^{-\frac{2R_i}{\lambda}} e^{-2\sigma_i^2 k^2} \sin[2kR_i + \phi_i(k)].$$

- $A_{i(k)}, \phi_i(k)$ amplitude and phase at scattering on atom i
- N_i number of scatterer at distance R_i
- σ_i Debye-Waller
- λ inelastic mean free path
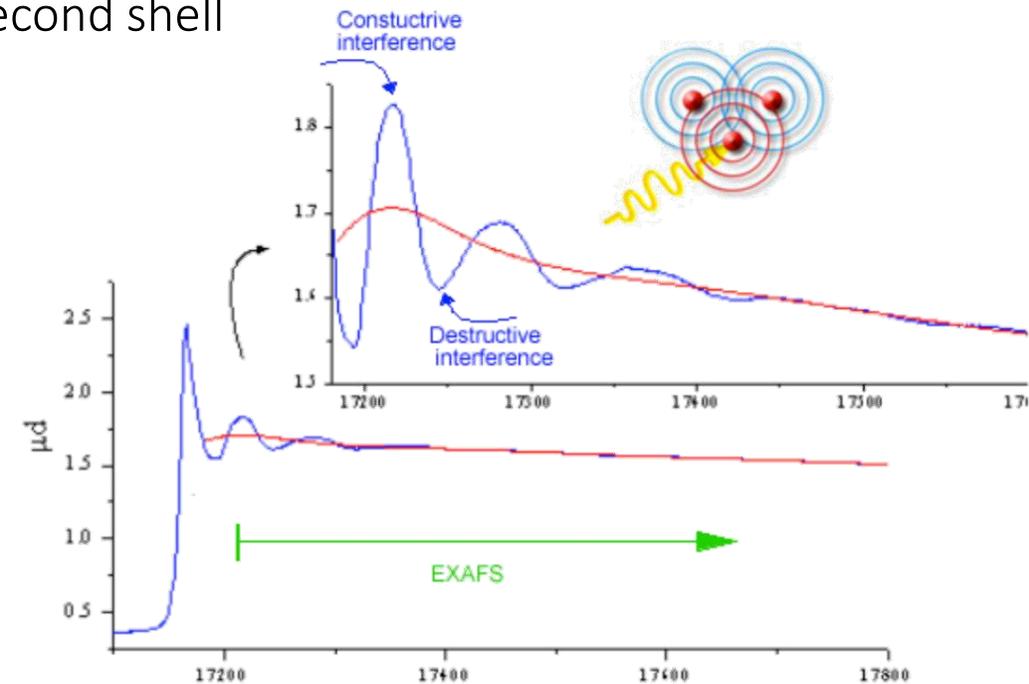
- Signal modelling with multiple scattering events and measured /calculated phases ➔ N_i $(\pm 1); R_i(\pm 0.02\text{Å})$
- Perfectly suited for dopants or amorphous materials

- Deposition under ultra-high vacuum of Na on SiO2(6nm)/Si
- Local medium/range around Na from Na K-edge (TEY) ? Ordering ?

XPS O 1s

NBO

glass

BO
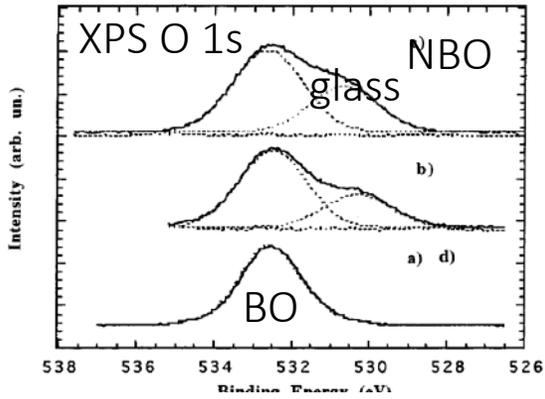
Reversible depolymerisation

XAS Na-K

T<220K ➜ metal

Warming @300K

Deposition@300K
➜ dissolution
Ionic Na⁺

Na-O

Concentration
10,30,36 at%
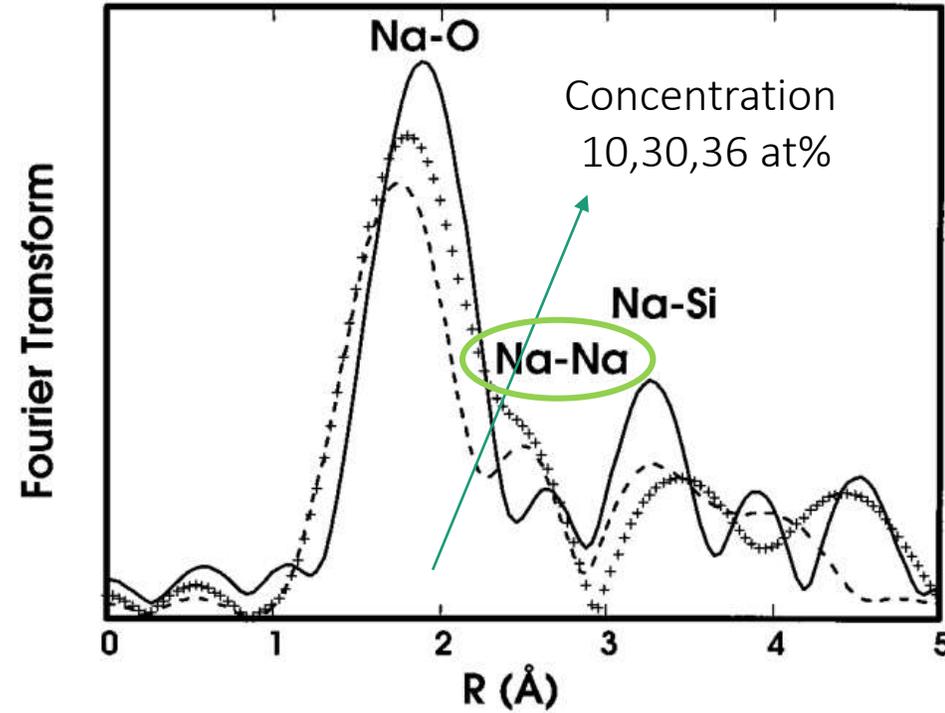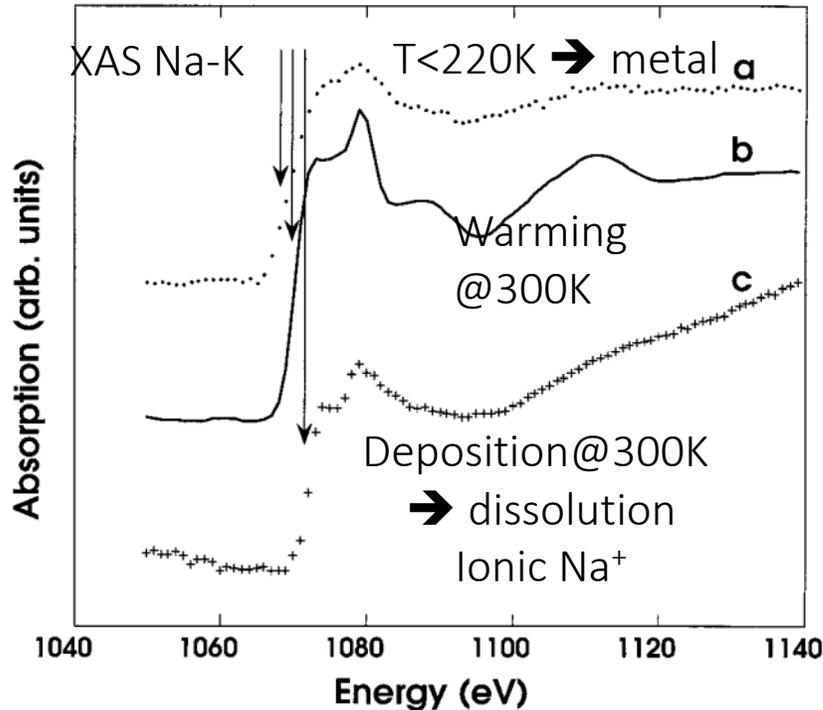
Na-Si

Na-Na

Defined stereochemical order around Na independent of concentration similar to SiO$_2$-Na$_2$O glass

$$d(Na - O) = 2.3\text{Å}, d(Na - Na) = 3\text{ Å}, d(Na - Si) = 3.8\text{Å}$$

Ordered silica tetrahedra (Na-O-Si not random) similar to crystalline Na$_2$SiO$_3$

Link to the modified random network model

J. Jupille et al, J. Am. Sceram. Soc. 85 (2002) 1041
G.N. Greaves, J. Non Cryst. Sol 71 (1985) 203

X-ray diffraction in a nutshell

- Thompson scattering = X-ray matter interaction (beyond edge) ($\lambda \approx 1.54\text{Å}$ Cu Kα)➔ polarisation of electronic cloud ➔ dipole radiation ➔ interference effects

- Scattered intensity described in reciprocal space : $I(\boldsymbol{q}) = \left|\int \rho(\boldsymbol{r})\exp(i\boldsymbol{q}.\boldsymbol{r})\, d^3r\right|^2$ with scattering vector $\boldsymbol{q} = \mathbf{k_f} - \mathbf{k_i}$ [$(\mathbf{k_f}, \mathbf{k_i})$ scattered and incident wave vectors] that spans reciprocal space (RS); $\rho(r)$ electronic density

- Elastic scattering $|\mathbf{k_f}| = |\boldsymbol{k_i}| = \frac{2\pi}{\lambda}$ ➔ Ewald sphere construction

- $\rho(r)$ depends on the organisation of matter !!

Perfectly ordered crystal

translation symmetries ➔ structure factor ➔ reciprocal lattice vectors ➔ Laue condition or Bragg law ➔unit cell content ➔ form factor ➔ Bragg peak intensities ➔ nature and atomic positions

Real materials

microstructural information in Bragg peak shape (ex: thin films: grain size, mosaicity, micro and macro strain)

Amorphous materials

No-long range order ➔ peak broadening with q ➔ diffuse scattering ➔ pair distribution function
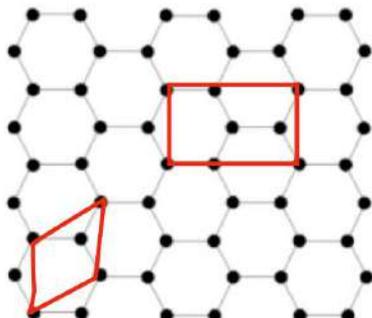
Ordered: crystal   ....   Amorphous : glass
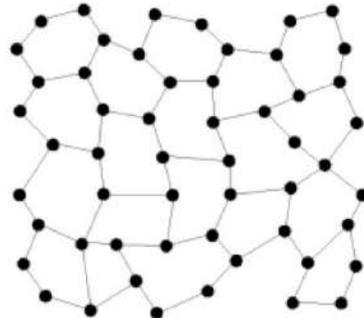
Max Von Laue   *Bragg, father and son*

A few words about X-ray atomic pair distribution function

- Interesting for nano-sized or amorphous
- Classical powder diffraction but measurements with high-energy X-ray (synchrotron/lab Mo Ka/2D detector)

up to large angle angle ➔ large q-range (up to 30Å^{-1}) $q = \frac{4\pi}{\lambda}\sin(\theta)$

- Bragg+diffuse = total scattering ➔ correction by atomic form factor $|\langle F(q)\rangle|^2$ (good statistics; Compton scattering) ➔

Fourier transform of structure factor of $S(q)$ to get the pair-distribution function $g(r)$

$$g(r) = \frac{2}{\pi}\int_{Q_{min}}^{Q_{max}} q(S(q)-1)\sin(qr)\,dq$$ ➔ statistic of interactomic distances

- analogy with SAXS; neutron vs X-ray; anomalous; comparison with atomistic simulations

Cormier, Neutron and X-ray diffraction of glass, Springer (209)
Billinge, Phil Trans. A 377 (2019) 20180413
Fischer, H.; Barnes, A. & Salmon, P.,Rep. Prog. Phys. 69 (2005) 233
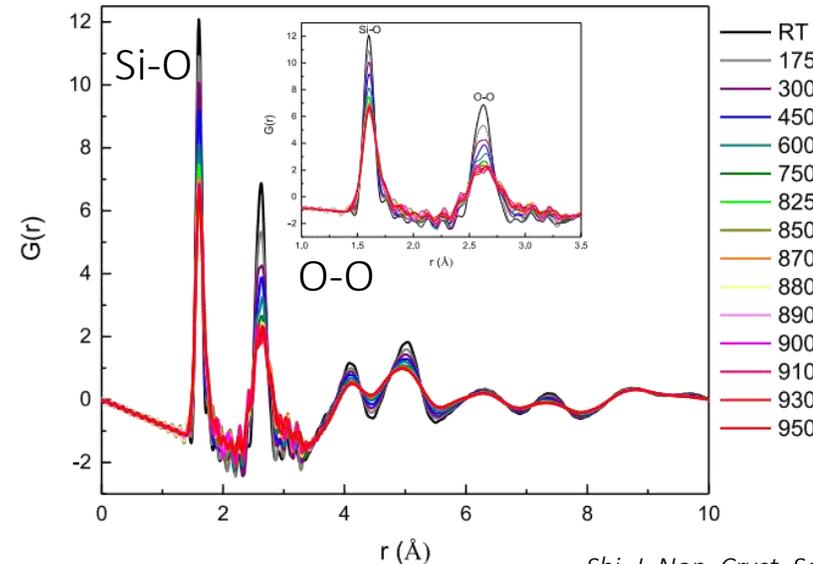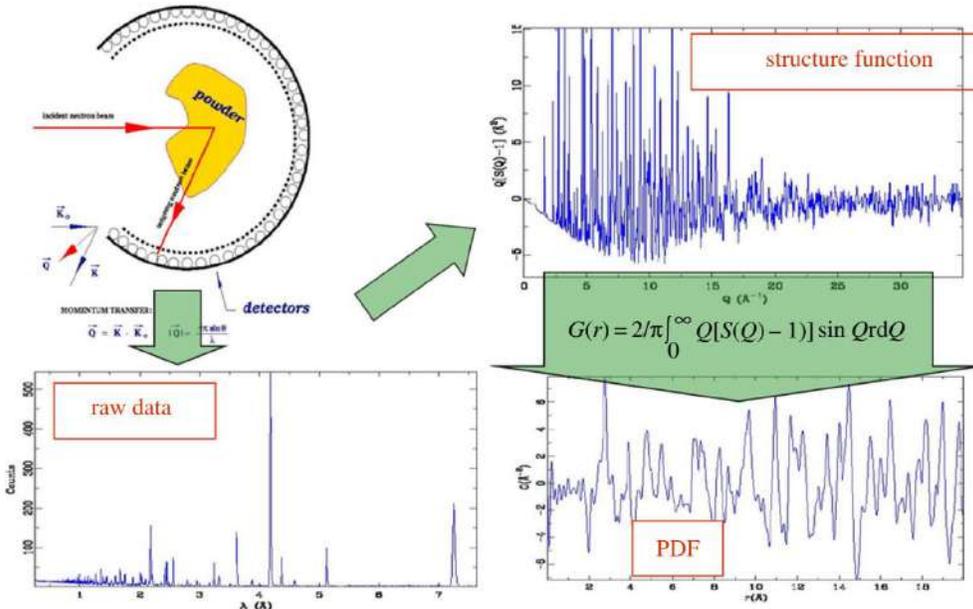
An example :
silica below Tg
Neutron

Shi, J. Non. Cryst. Sol. 528 (2020) 119760

XRD : scattering geometries for surface and thin films

Ewald construction

Laue condition $\boldsymbol{q} = \boldsymbol{G_{hkl}}$

$\Leftrightarrow$ Bragg law $2d_{hkl}\sin(\theta) = n\,\lambda$

$2\pi/\lambda$

2θ

X-ray

$\boldsymbol{k_f}$ $\boldsymbol{q}$ $\boldsymbol{G_{hkl}}$

$\boldsymbol{k_i}$ O

Detector

Reciprocal space

Lab apparatuses + synchrotron
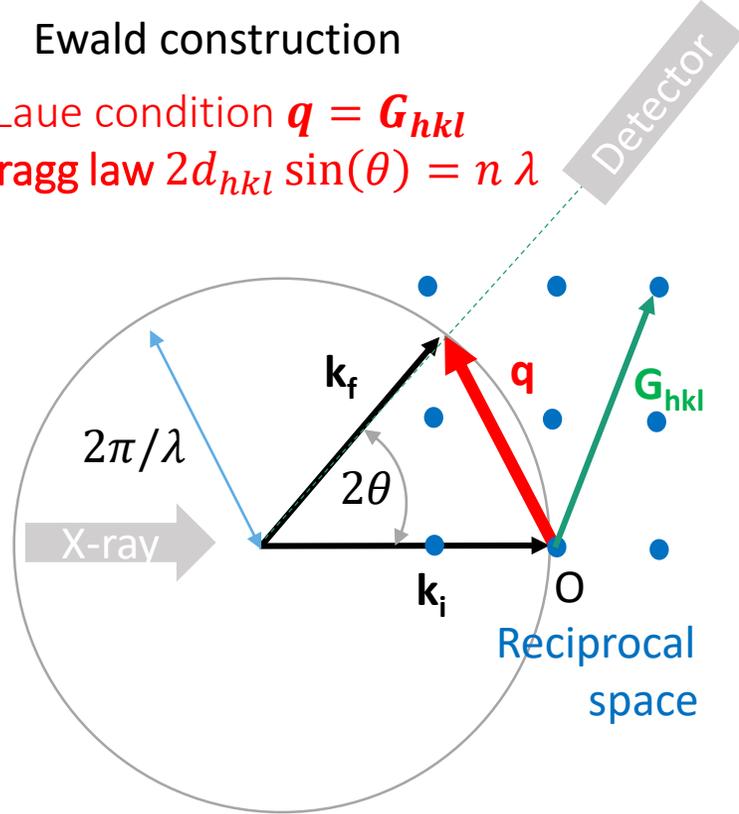
Bragg-Brentano $\theta - 2\theta$ ➜ $q_\perp$ = lattice plane parallel to surface
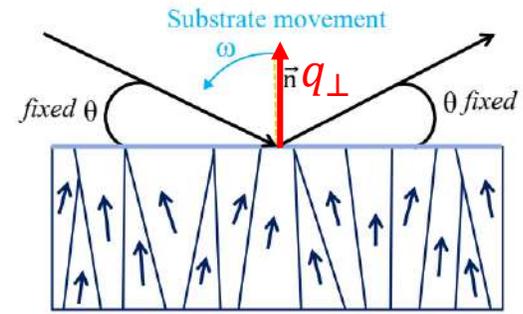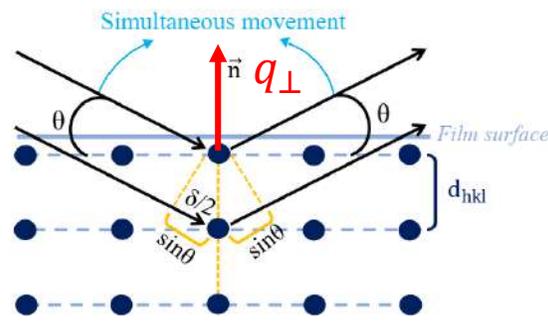
Grazing-incidence diffraction (GID)
➜ $q_\parallel$ = lattice planes perpendicular to surface
GISAXS
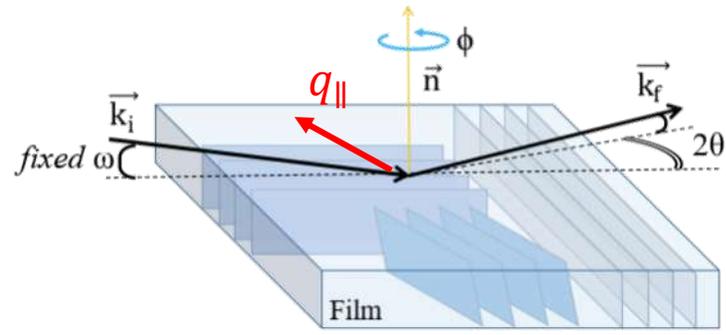
Pole figure
➜ cross section of RS at q=ct
➜ orientation of a given lattice plane

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X-ray reflectivity

- X-ray reflectivity = Bragg-Brentano but at small 2θ (few deg) ➔ $\frac{1}{q_\perp} = \frac{\lambda}{4\pi\theta}$ ➔ nm distances ➔ $F(q) \approx Z \approx ct$

- Kinematic approximation ➔ $I(q_\perp) = \left| \int \rho(z) \exp(i q_\perp z)\, dz \right|^2 = \frac{1}{q^2} \left| \int \frac{\partial \rho}{\partial z}(z) \exp(i q_\perp z)\, dz \right|$ ➔ sensitivity to gradient

- Total external reflection below critical angle $\alpha_c \propto \sqrt{\rho}$ (0.1-0.3°) ➔ evanescent wave over $\Lambda_c = \frac{\lambda}{4\pi\alpha_c} \approx 10$ nm

- Thin films with sharp interfaces ➔ Kiessig fringes of interference

- Analysis with matrix/Parratt formalisms for multilayers ➔ density, thickness and roughness of layers

a)

c)
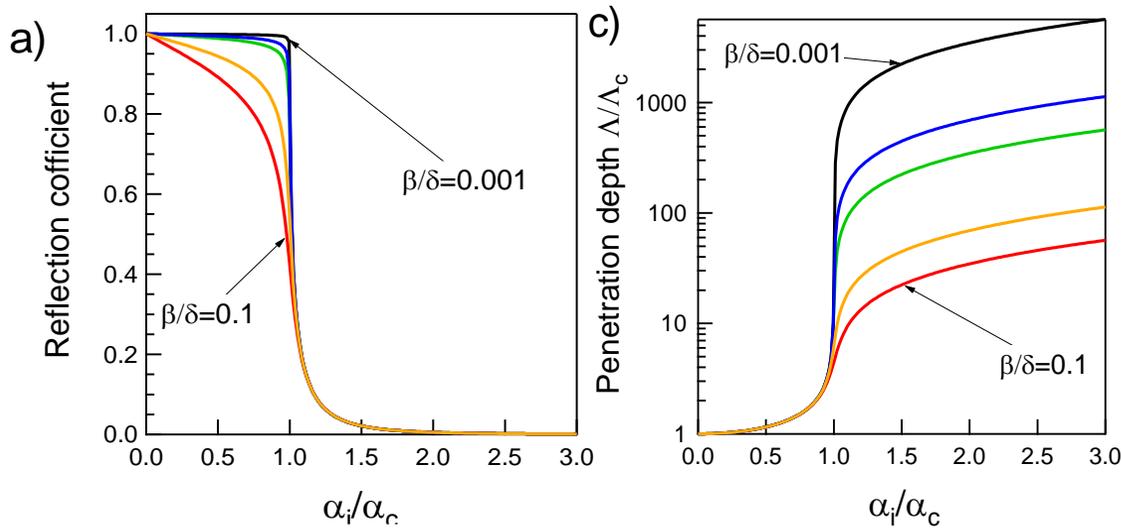
➔ Limited probed depth in grazing incidence diffraction
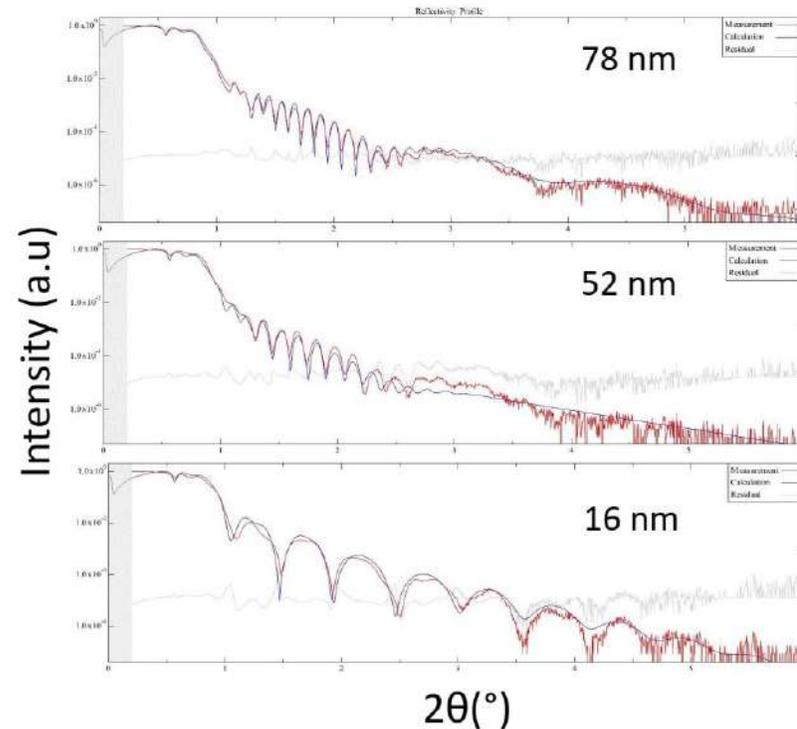
Multilayers on glass

| SiN 30 nm |
| ZnO 5 nm |
| Ag |
| ZnO 5 nm |
| SiN 20 nm |
| Glass |
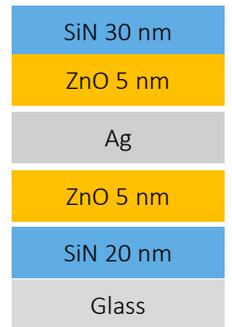
Ageing under air of soda-lime float glass and fused silica
Cleaning with water
Fit of thickness t, roughness σ and density ρ

Longer ageing
Hydrated/carbonated layer
due to alkali exchange with H
Nothing under vacuum
Identical in water
Much less dense layer

Flat surface
$\neq \alpha_c \Rightarrow \rho_{glass} > \rho_{silica}$
$\sigma_{silica} > \sigma_{glass} = 0.2 - 0.3$nm

48 h ageing
Not an increase of σ slighlty
less dense layer $t \simeq 3\,nm$
Nothing on silica

Grimal et al, J. Non Cryst. Sold 196 (1996) 128
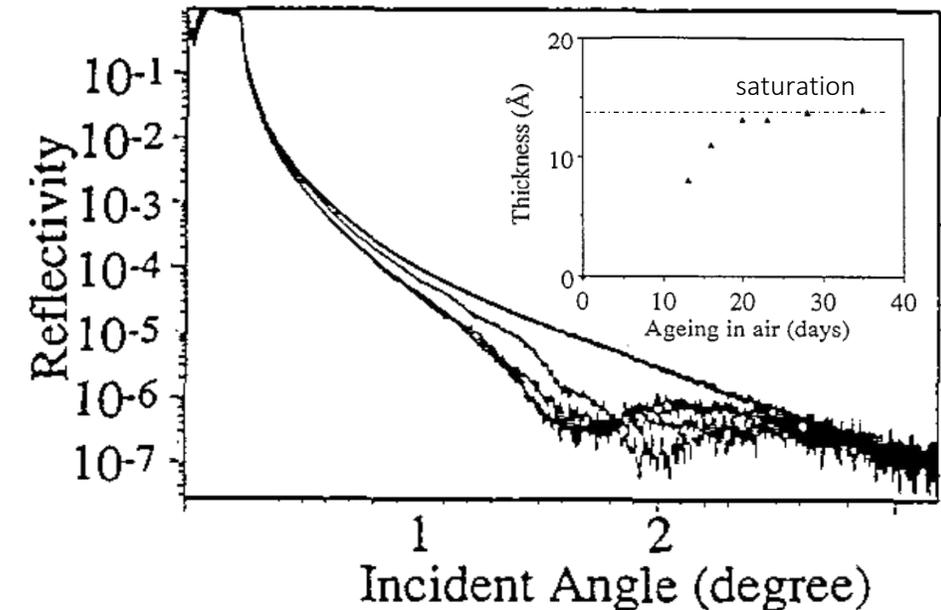
Grazing-Incidence Small-Angle X-ray Scattering
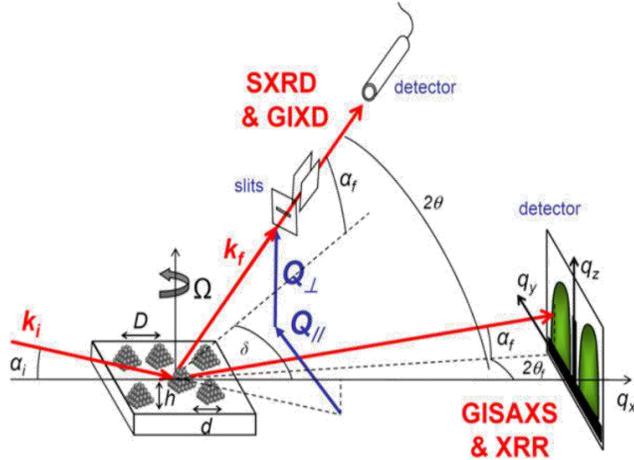
- Probe the origin of reciprocal space
- Small-angles (few degs) ➡ nanometric distance

$$q = k_f - k_i = \frac{2\pi}{\lambda}\begin{bmatrix} \cos(\alpha_f)\cos(2\theta_f) - \cos(\alpha_{fi}) \\ \cos(\alpha_f)\sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{bmatrix} \simeq \frac{2\pi}{\lambda}\begin{bmatrix} 0 \\ 2\theta_f \\ \alpha_f + \alpha_i \end{bmatrix}$$

- Scattering by electronic contrast and roughness
- Control of penetration depth with incident angle : surface/bulk
- Very grazing α_i, α_f multiple scattering effect (Yoneda peak)
- Synchrotron + 2D detector ➡ real-time analysis
- Application: film growth, mesoporous films, polymer films, implantation/ionic exchange, and phase precipitation/separation, glass alteration, ...
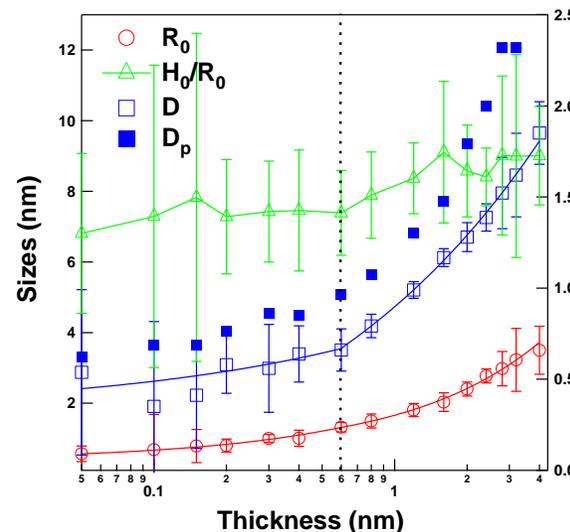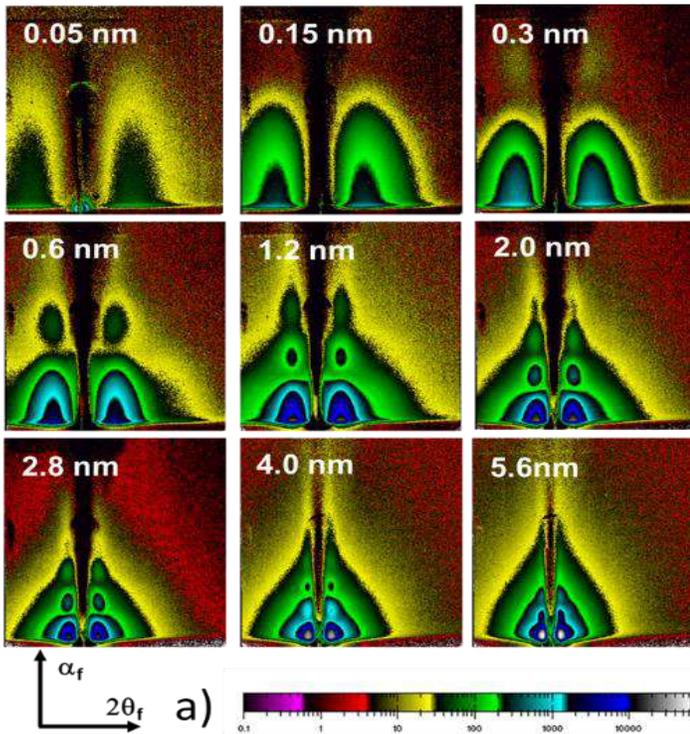
Deposition of Au/TiO$_2$(110)
➡ 3D growth of nanoaprticles
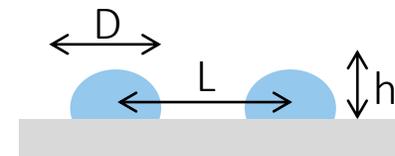
Renaud et al, Surf. Sci. Rep 64 (2009) 255

Film microstructure from Bragg peak shape

Example of Bragg-Brentano (similar analysis in GID)

Peak position ➔ lattice parameter ➔ macrostrain (also $\sin^2(\Psi)$ method)

Peak broadening ➔ convolution of size, microstrain and mosaicity effects ➔ analysis of Willamson-Hall

Ag(10nm)/ZnO(0001)
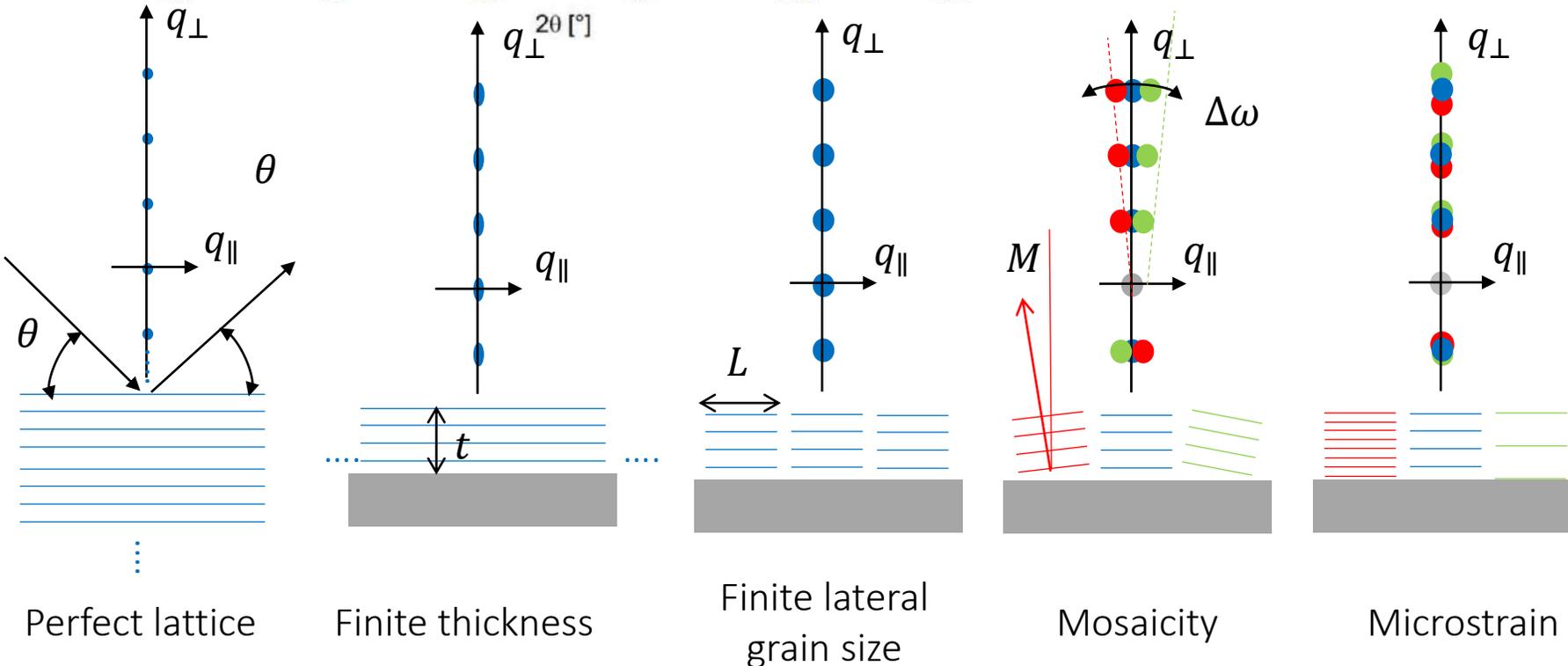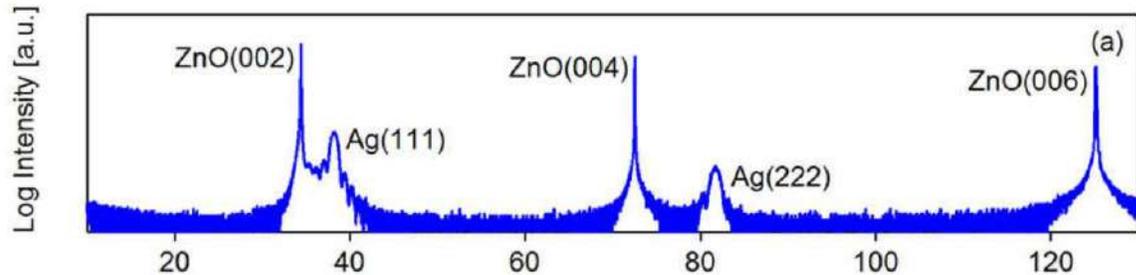
Measurement of peak width of several orders of diffraction

$$\Delta q_\perp^2 = \left(\frac{2\pi}{t}\right)^2 + q_\perp^2 \left(\frac{\Delta a}{a}\right)^2$$

$$\Delta q_\parallel^2 = q_\perp^2 \Delta\omega^2 = \left(\frac{2\pi}{L}\right)^2 + q_\perp^2 M^2$$

Otherwise coherent domain size from Scherrer law

$$t = \frac{2\pi}{\Delta q_\perp} = \frac{K\lambda}{\Delta\theta \cos\theta}$$

Perfect lattice | Finite thickness | Finite lateral grain size | Mosaicity | Microstrain

55

Grazing-Incidence Diffraction

- Surface crystallogaphy ➔ relaxation and recontruction of bare/covered surfaces from crystal trunction rods
- Reduced the probed depth by using grazing incidence and emergence $\alpha_i = \alpha_f \simeq 0.1 - 0.5°$
- Scattering wave vector in plane $\boldsymbol{q} = \boldsymbol{q}_\parallel$ ➔ diffraction by lattice planes perpendicular to the surface
- Analysis of in plane epitaxy, texture, grain size, mosaicity, strain etc…

Ag/ZnO(0001) epitaxy ?
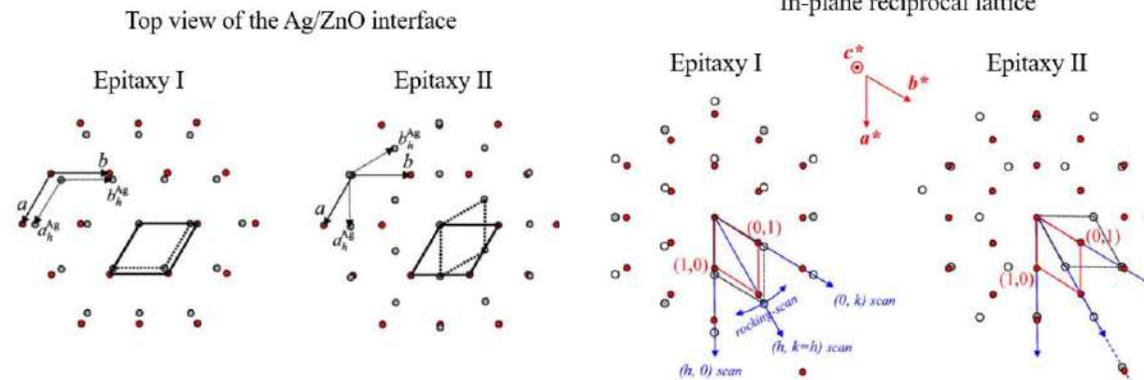
Ph. F. Corbella (2022), V. Haspot
Jedrecy et al, Phys. Rev. B 72 (2005) 045430, 72 (2005) 195404
Benedetii, et al, J. Phys. Chem. C 124 (2020) 6130

Polycristalline layers

Bragg-Brentano $\theta - 2\theta$
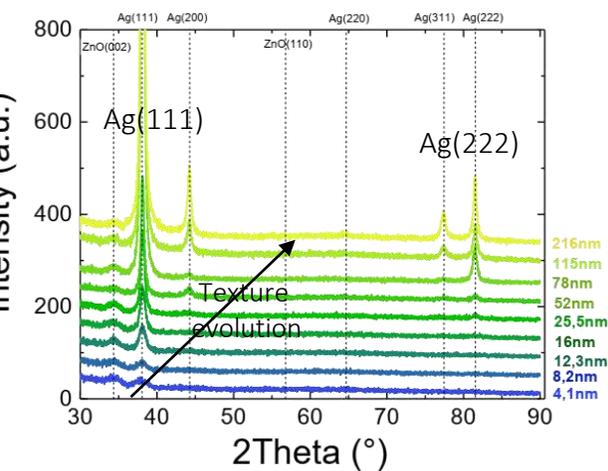
GID
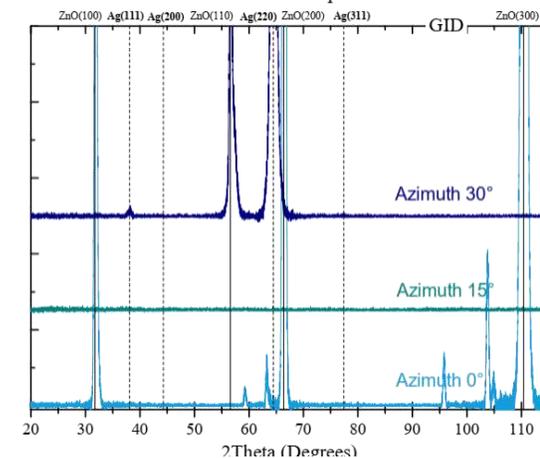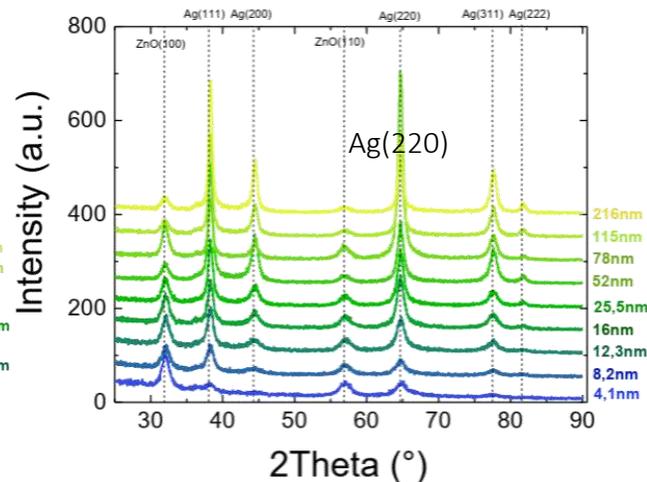
Single crystal substrate

56

Film crystalline texture and pole figure

- Pole figure = spherical cross section of reciprocal space
- Convention of stereographic projection
- Direct visualisation of film texture
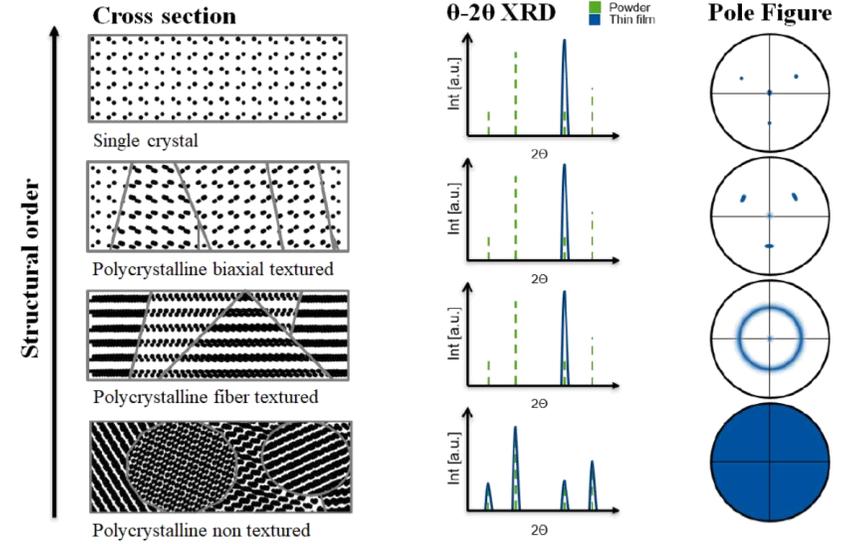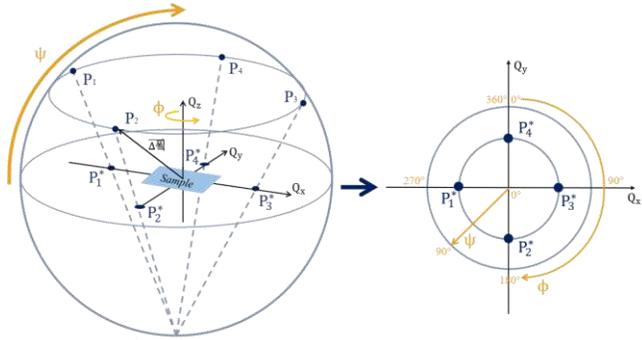
Ag(111)/ZnO(0001) hexagone/hexagone !

Pole figure Ag(111)

Glass-based stacks

ZnO-single crystal-based stacks

Ag/SiN_x (amorphous)

Ag/ZnO-polycristalline textured

Ag/ZnO(0001) As-received

Ag/ZnO(0001 sputtered/annealed

Color map: 111, 200, 220

Linear-intensity (arb. units)

$(\bar{1}11)$

$(11\bar{1})$

(111)

$(11\bar{1})$

$(1\bar{1}1)$

| SiN 30 nm |
| ZnO 5 nm |
| Ag 12 nm |
| ZnO 5 nm |
| SiN 20 nm |
| Glass |

| SiN 30 nm |
| ZnO 5 nm |
| Ag 12nm |
| ZnO(0001)-O |

PhD thesis F. Corbella (2022)

+ twin stacking ABC/BCA

57
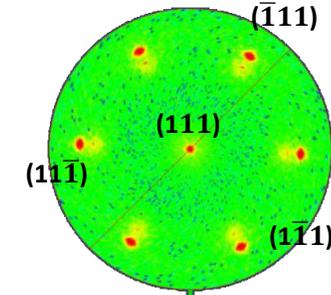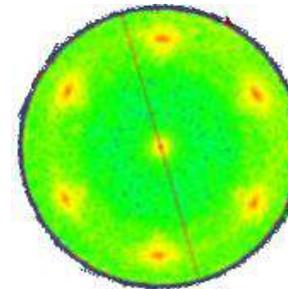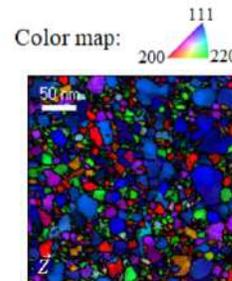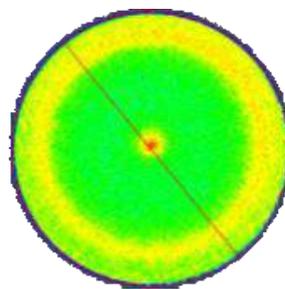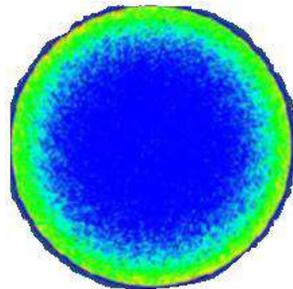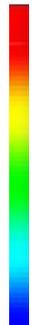
Optical spectroscopies and dielectric function

- UV/Vis/NIR but not vibrational spectroscopies (Raman/IR)
- Key quantity = material dielectric function

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) = [n(\omega) + ik(\omega)]^2$$

➜ band gap, defect states, exciton, interband transitions, conductivity
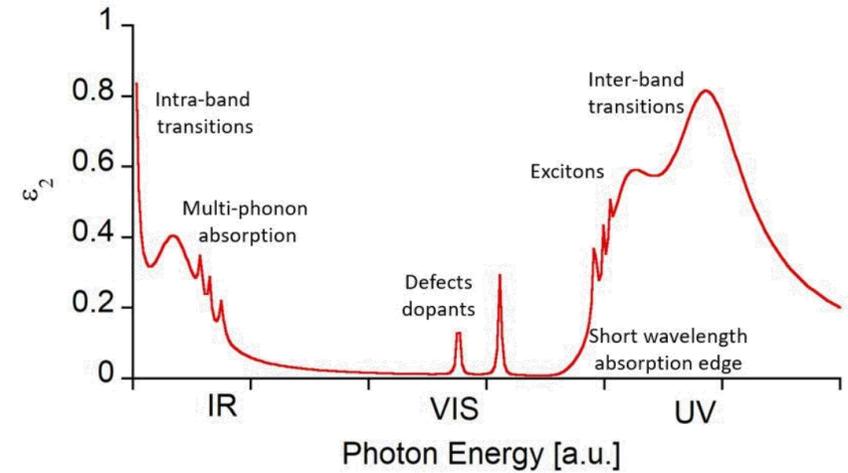
- Reflection R /transmission T /absorption A ➜ Fresnel coefficients in energy $R + T + A = 1$
- 2 eigen polarisation states s, p; reflection amplitude ➜ $r_s = \dfrac{n_i \cos(\theta_i) - n_t \cos(\theta_t)}{n_i \cos(\theta_i) + n_t \cos(\theta_t)}$, r_p

$$= \dfrac{n_t \cos(\theta_i) - n_i \cos(\theta_t)}{n_t \cos(\theta_i) + n_i \cos(\theta_t)}$$

- Spectroscopic ellipsometry ➜ change of light polarizarion state upon non-normal reflection

➜ $\dfrac{r_p}{r_s} = \tan(\Phi)\, e^{i\Delta}$

- Determination of film thickness (nm to μm; transparent), roughness and $\epsilon(\omega)$ (ex stress state)
- Modelling based on matrix formalism (interference effects) with assumption on $\epsilon(\omega)$ or on Kramers-Kronig transform
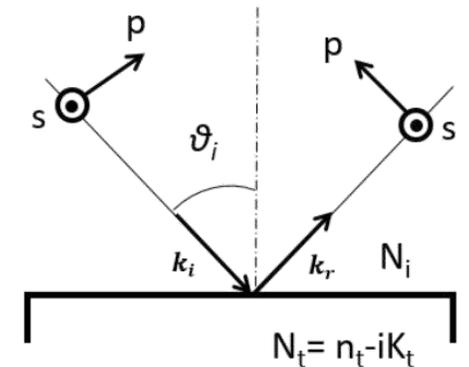
Oates, T. et al., Prog. Surf. Sci. 86 (2011) 328

Optical response of film stacks: Ag-based coatings

Engineering of transmission/reflection in reinforced insulation glass

Drude model

Metal

Si $\lambda < \lambda_p$

$\lambda_p = 2\pi c / \omega_p$

$\omega_p^2 = 4\pi N e^2 / m$

Si $\lambda > \lambda_p$

$Ag\ \lambda_p = 165nm$

Antireflective effect

n_0 $n_1 > n_0$

Dielectric Metal Dielectric

Interference

Fabry-Pérot effect

Transmission

Reflection

Coefficient

Wavelenght (nm)

Glass 4mm
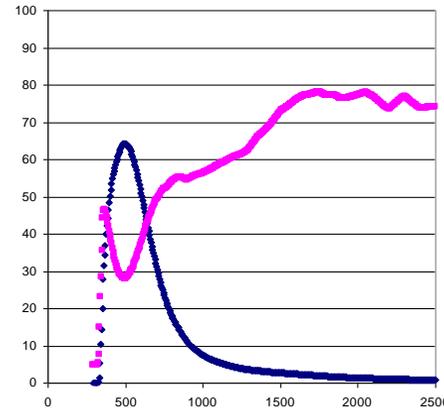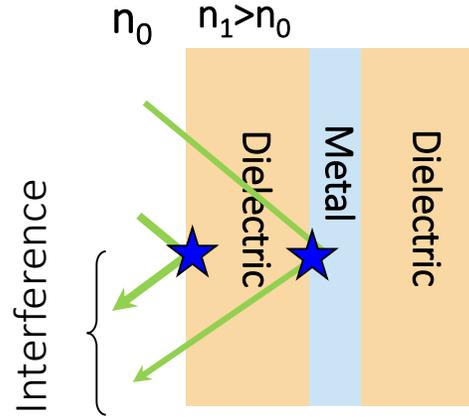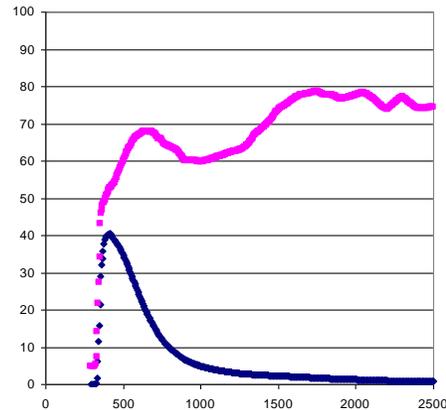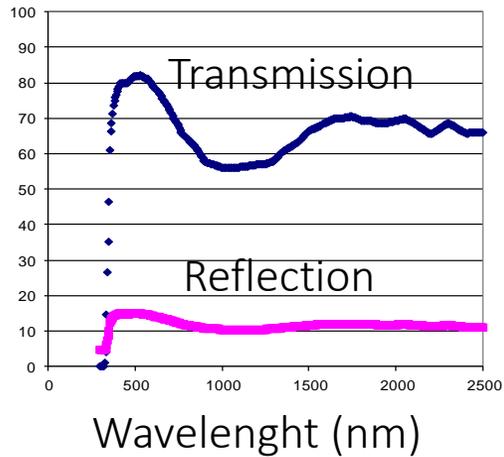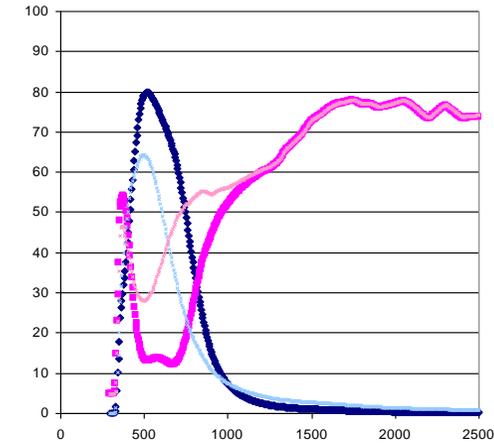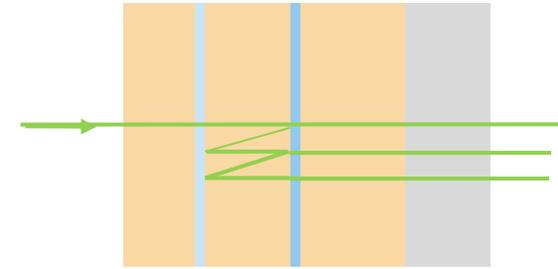
| ZnO (50nm) |
| Ag (20nm) |
| ZnO (50nm) |
| Glass 4mm |

| ZnO (50nm) |
| Ag (20nm) |
| ZnO (50nm) |
| Glass 4mm |

| ZnO (50nm) |
| Ag (10nm) |
| ZnO (100nm) |
| Ag (10 nm) |
| ZnO (50nm) |
| Glass 4mm |

SDRS: monitoring growth by plasmonics

- Surface Differential Reflectivity Spectroscopy (SDRS) ➔ relative variation of UV-vis reflectivity upon deposition
- *In situ* and real-time monitoring of film growth
- Metal nanoparticles ➔ excitation of plasmon resonances ➔ sensitivity to size and shape ➔ wetting ?
- Dielectric modelling

Ag sputtering growth on SiO_2

R. Lazzari et al, J. Phys. Chem. C 118 (2014) 7032, ACS Appl. Nano. Mater. 3 (2020) 1257
PhD thesis R. Zapata (2023)

60
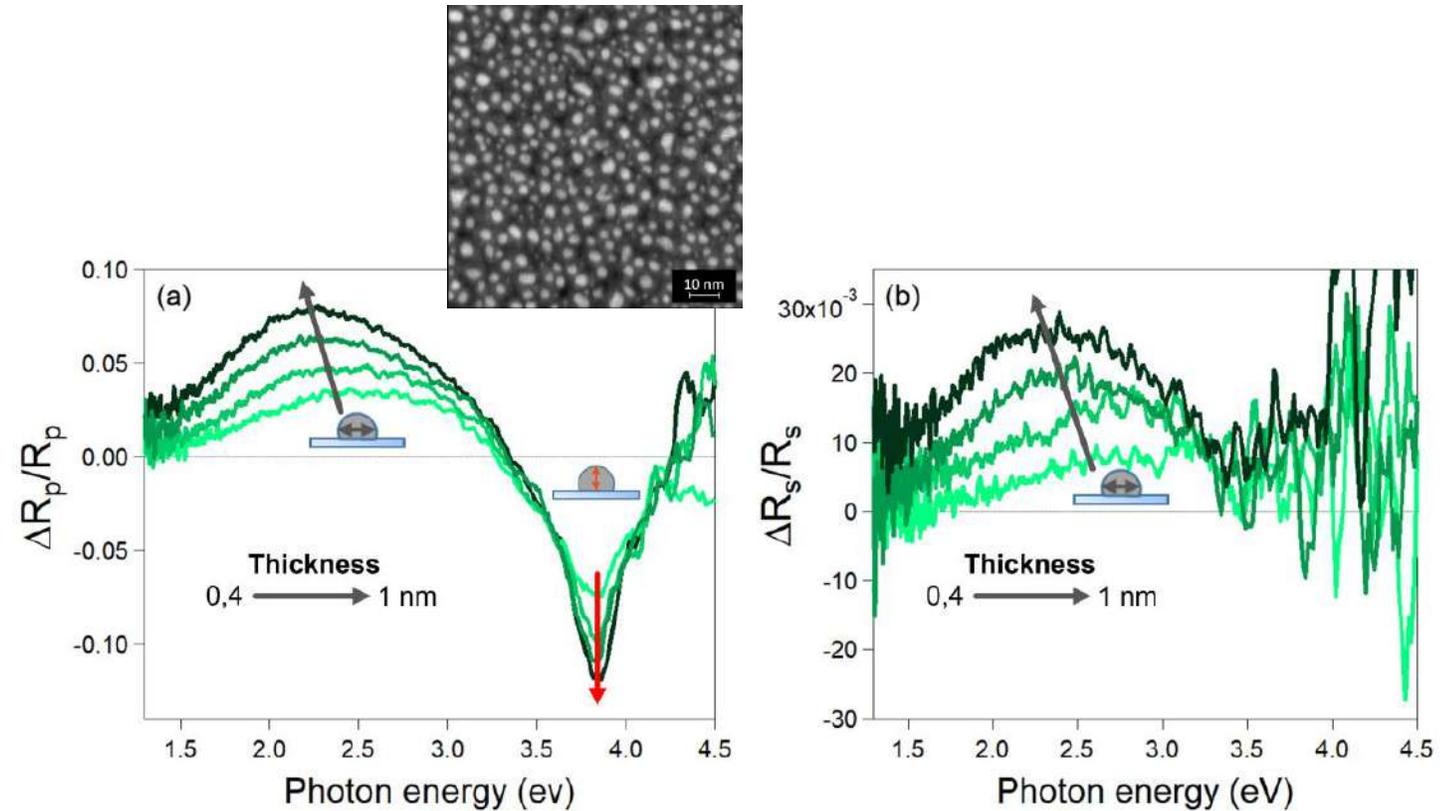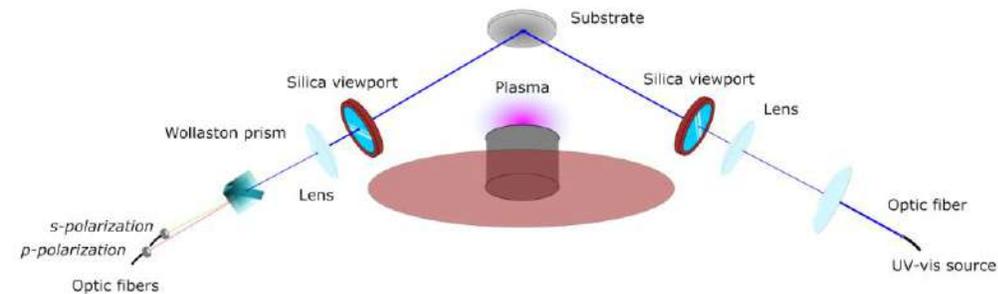
2D silica films : a model of glass ?

- Different from Si oxidation studied in microelectronics
- Surface science studies of 2D silica on metallic single crystals (Ru(0001), Mo(112), Pt(111)) (oxidation of Si deposit at high-temperature)
- Strongly bonded monolayer
- Weakly bonded bilayer SiO_2 films on Ru(0001) of SiO_4 bonded tetrahedra
- Crystalline and vitreous structures depending on synthesis conditions (cooling rate)
- Thickening ➜ amorphous phase
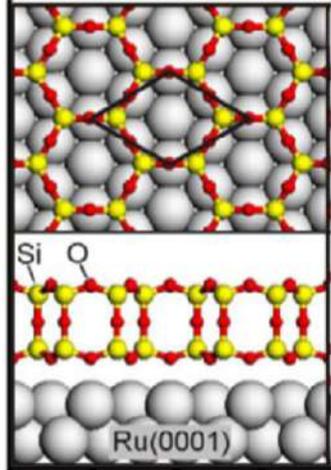
Crystalline phase

STM at different bias
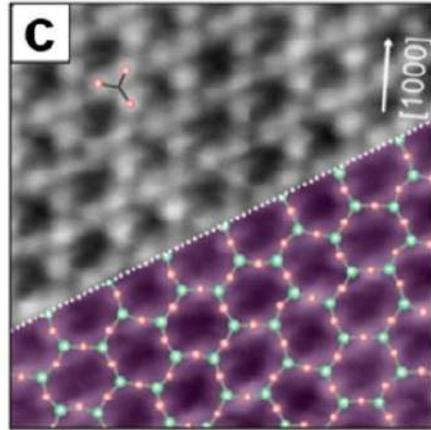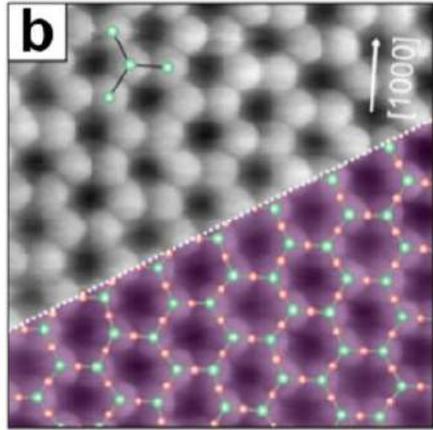
Vitreous phase

Zachariasen model   STM (Si-contrast)   (O-contrast)
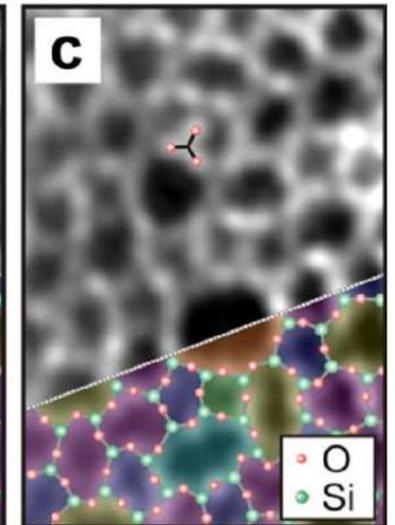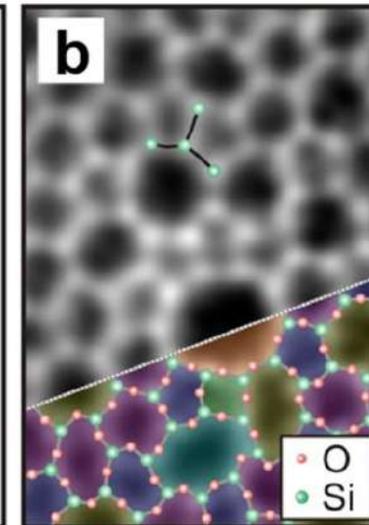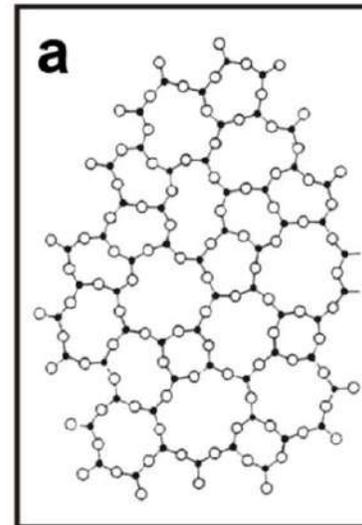
+ XPS, DFT, vibration (IRAS/HREELS), band structure

2D silica films : a model of glass

2ML SiO$_2$/Ru(0001)

Transition between crystalline/amorphous phase

Ring analysis

LEEM ➔ SiO$_4$ tetrahedra rotation
➔ activation enegy related to Stones-Wales defects (5-7-5-7 rings)
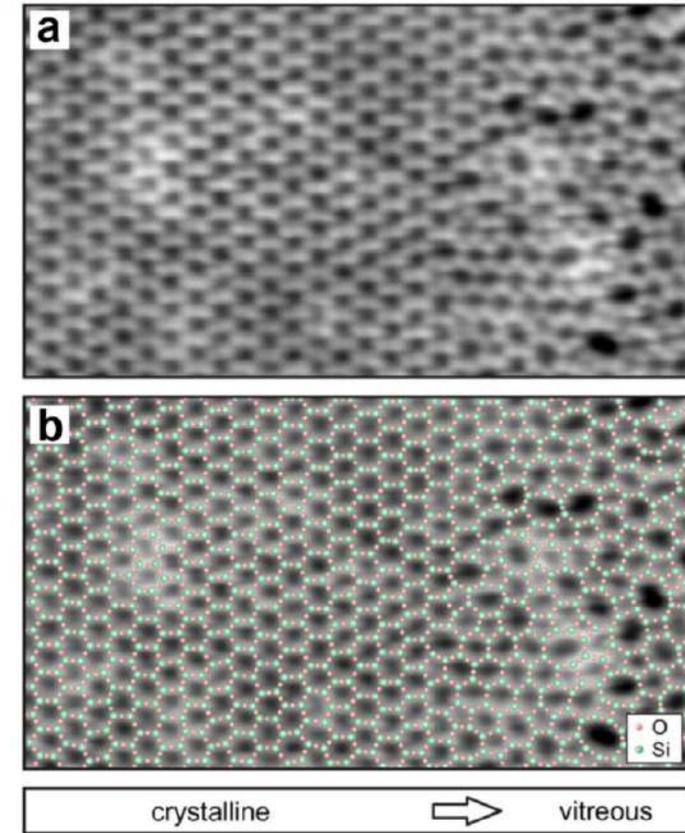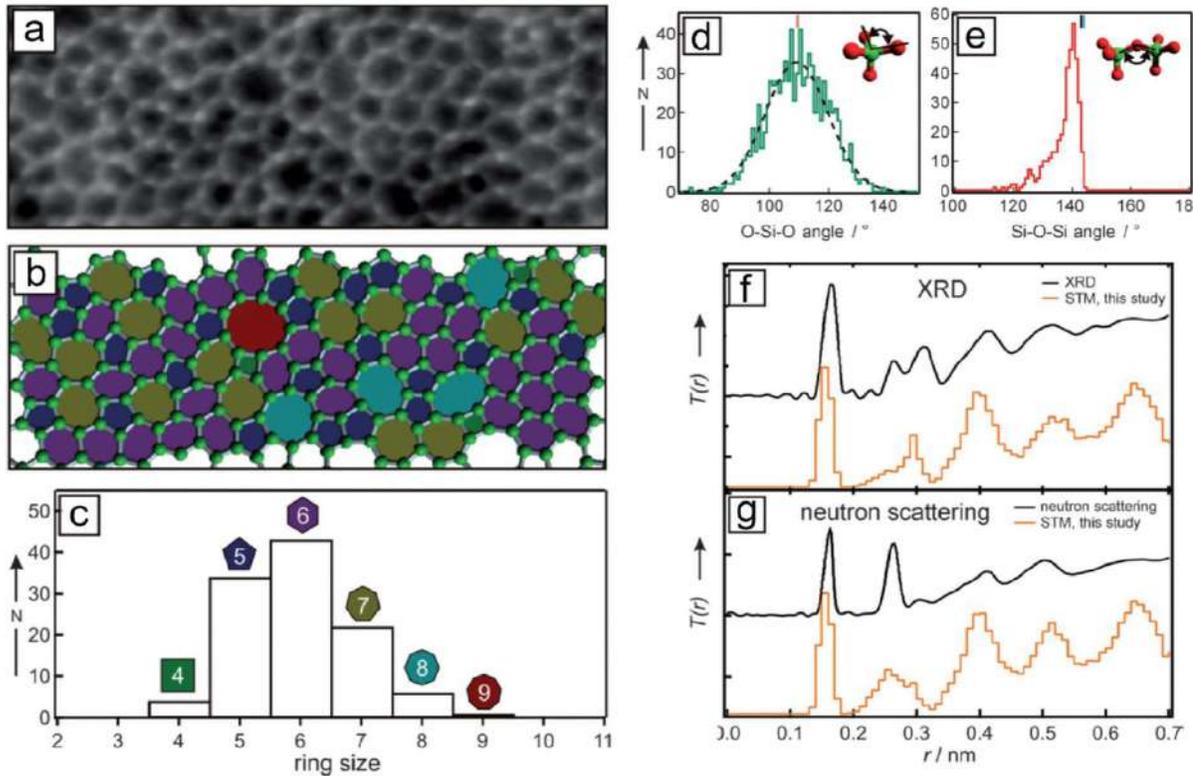
➔ Metal doping/adsorption + hydroxylation
➔ Transfer by peel-off!

Zhong and Freund, Chem. Rev. 122 (2022) 11172

Questions ? Discussions ?

Thank you for your attention