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X-ray Photoelectron Spectroscopy: a powerful characterization tool in material science and biotechnology

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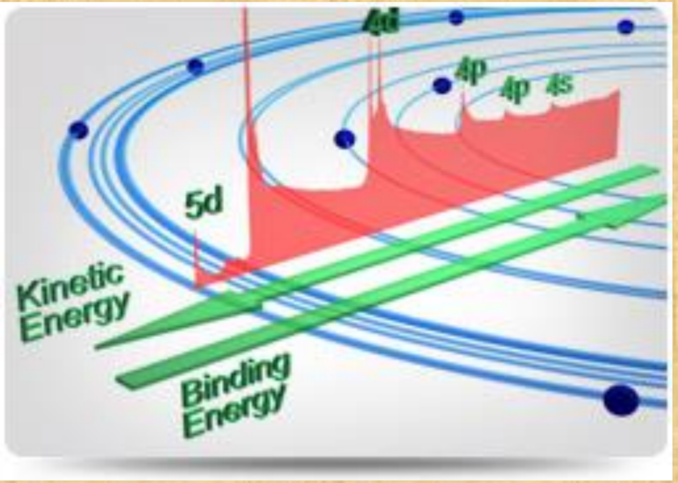

NNUM 2019
7-8 May
DTU, Copenhagen, Danmark

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X-ray Photoelectron Spectroscopy

Introduction

XPS in material science

XPS in biotechnology

What is XPS?

X-ray Photoelectron Spectroscopy (XPS), also known as *Electron Spectroscopy for Chemical Analysis* (ESCA) is a widely used technique to investigate the *chemical composition of surfaces*.

X-ray Photoelectron spectroscopy, based on the photoelectric effect,[1,2] was developed in the mid-1960's by Kai Siegbahn and his research group at the University of Uppsala, Sweden.[3]

1. H. Hertz, Ann. Physik 31,983 (1887).
2. A. Einstein, Ann. Physik 17,132 (1905). 1921 Nobel Prize in Physics.
3. K. Siegbahn, Et. Al.,Nova Acta Regiae Soc.Sci., Ser. IV, Vol. 20 (1967). 1981 Nobel Prize in Physics.

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X-ray Photoelectron Spectroscopy

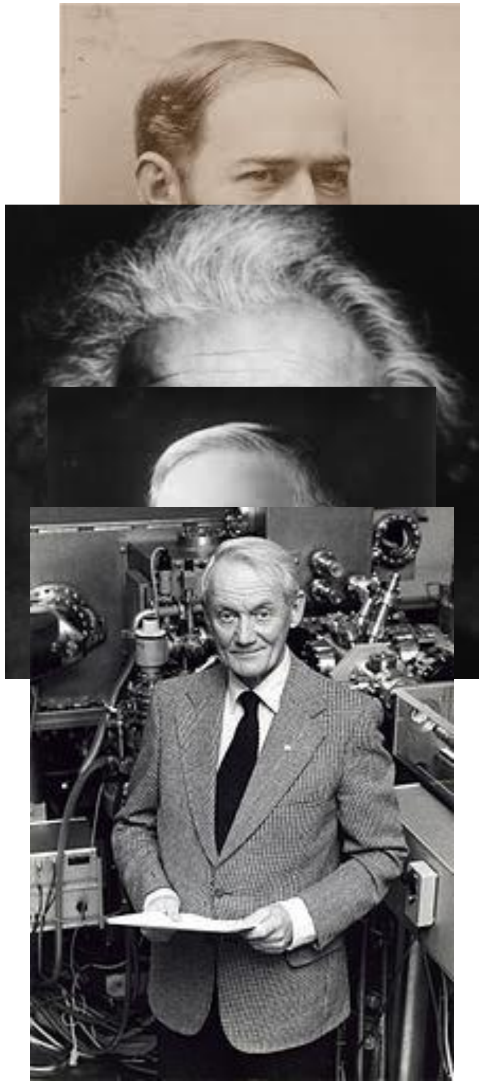
Introduction

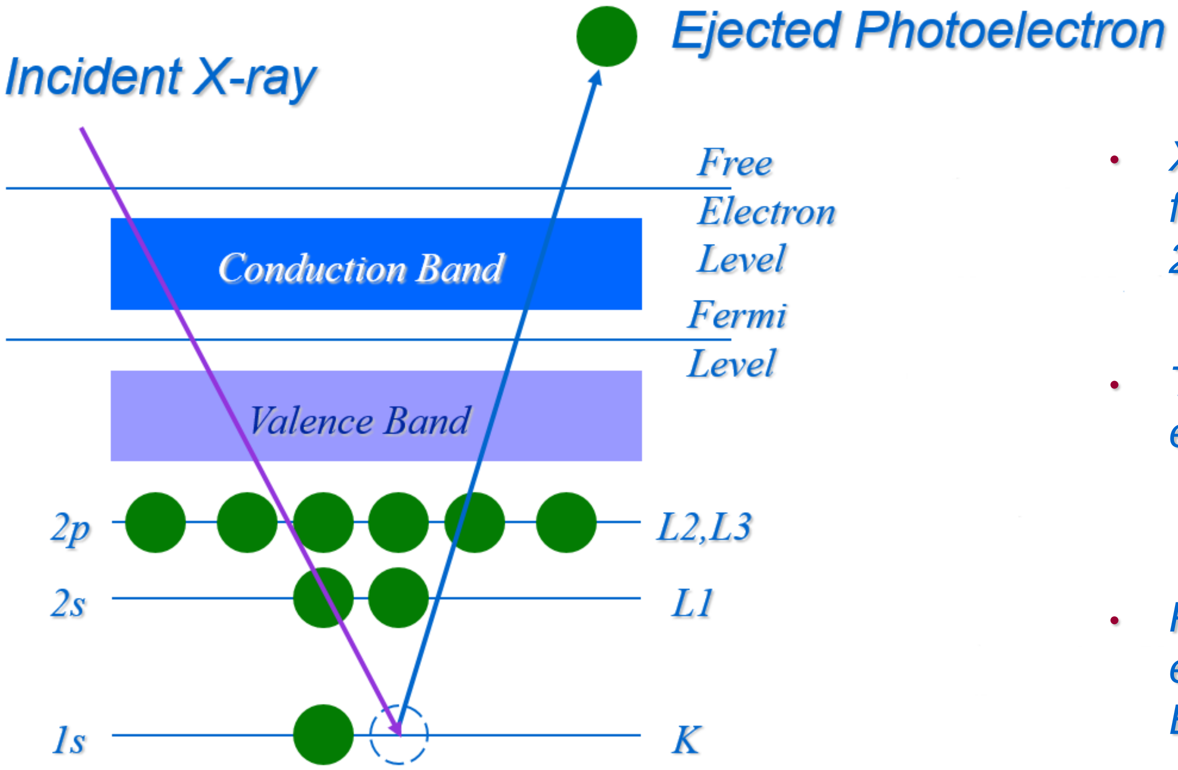
XPS in material science

XPS in biotechnology

History of XPS

- In 1887 Heinrich Hertz observed the emission of electrons
- In 1905 Einstein explained the photoelectric effect and in 1921 he got the Noble prize in physics
- In 1914 Rutherford recognised the kinetic energy of the emmited electron
- In 1930 H.R. Robinson observed the line shift caused by chemical binding
- In 1954 Prof. Kai Siegbahn developed the method of electron spectroscopy for chemical analysis (ESCA) and in 1981 he got the Noble prize in physics
- In 1970 the first commercial XPS machine became available

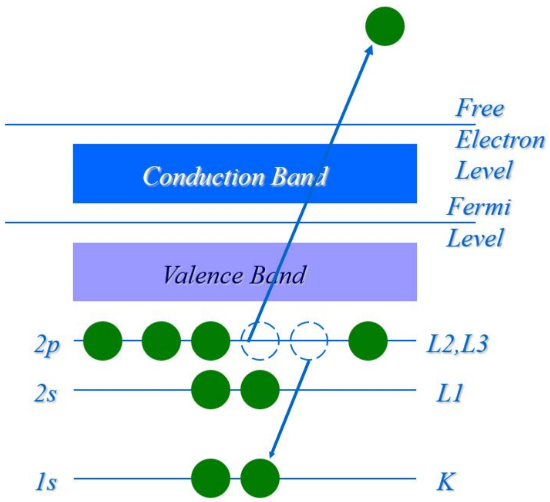




- XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).
- The ejected photoelectron has kinetic energy:

  $KE=hv-(BE+\Phi)$

- Following this process, the atom will release energy by the emission of an Auger Electron.



- XPS measures the kinetic energy of all collected electrons.
- The electron signal includes contributions from both photoelectron and Auger electron lines.

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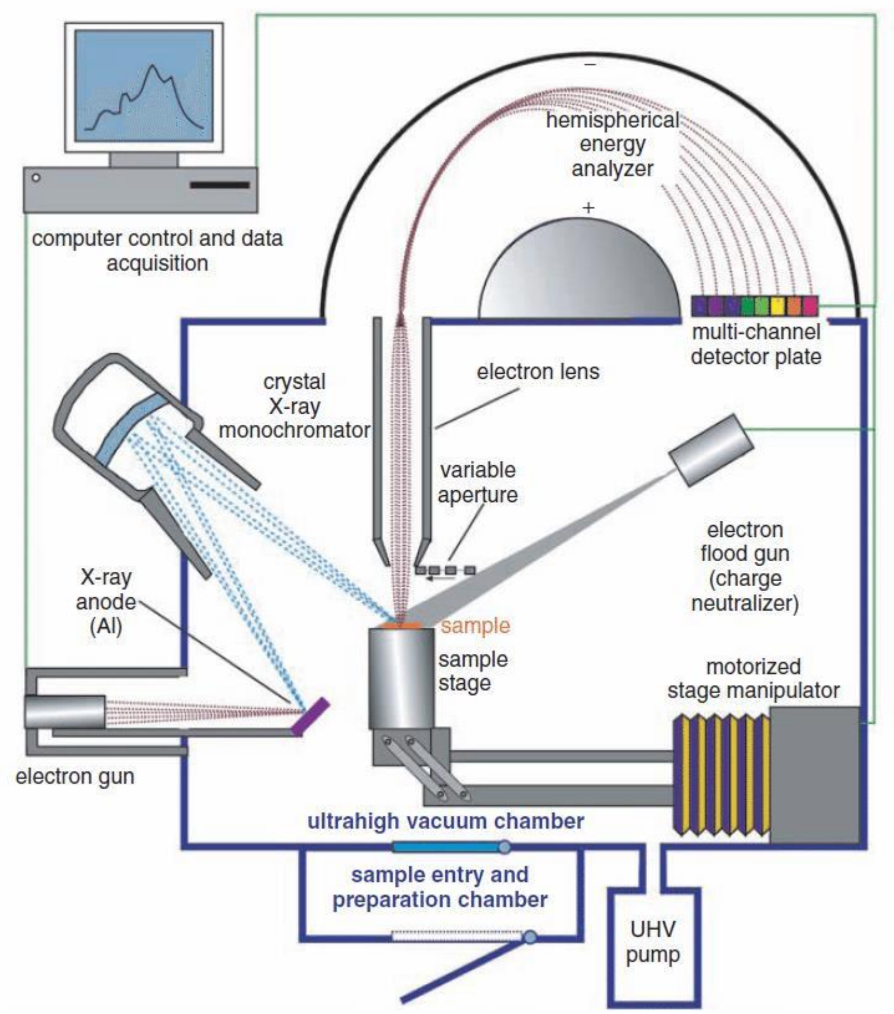
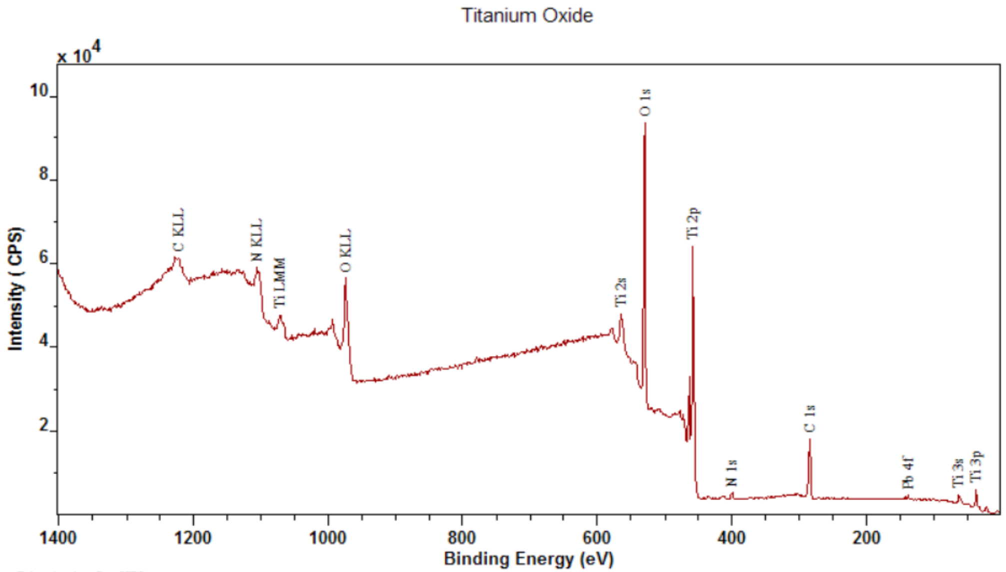
Instrumentation



- *Electron energy analyzer*
- *X-ray source*
- *Ar ion gun*
- *Neutralizer*
- *Vacuum system*
- *Electronic controls*
- *Computer system*
- *……*

- *Ultrahigh vacuum system*
  <10^{-9} Torr (<10^{-7} Pa)
  Detection of electrons
  Avoid surface reactions/contaminations



Understanding Surface Properties Using XPS

1) What does SURFACE mean?

2) How does XPS acquire surface-sensitive data?

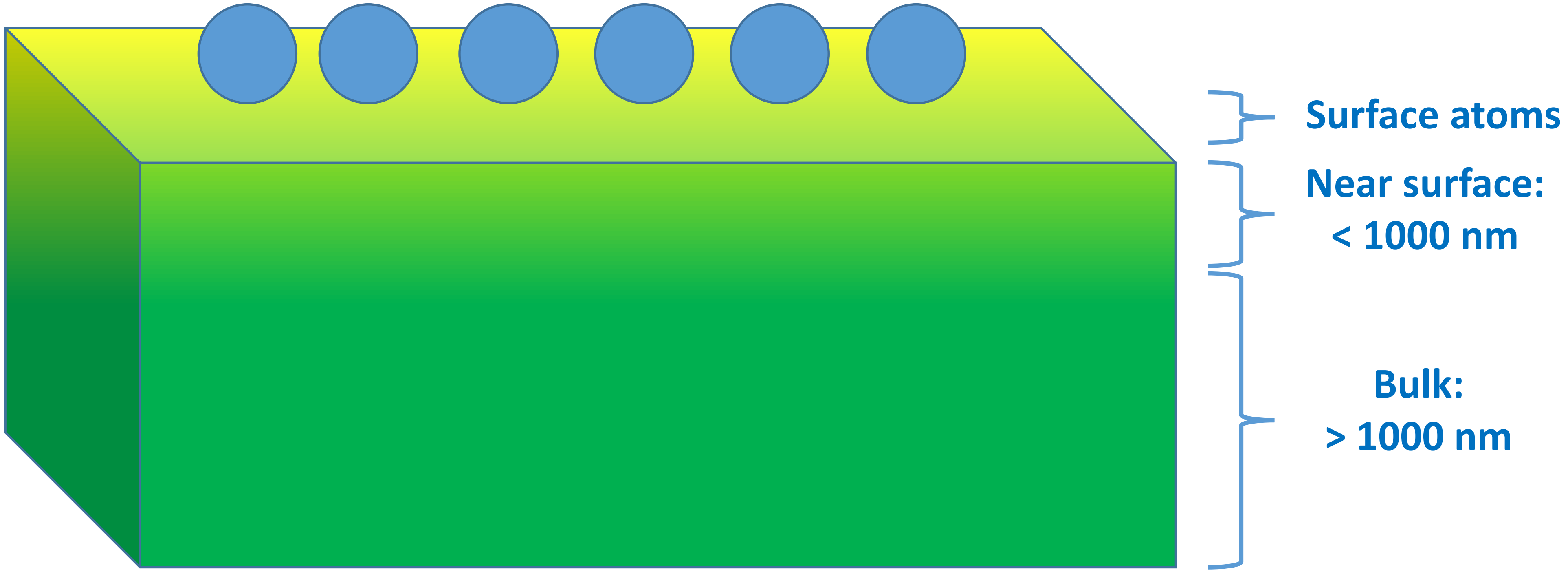
3) Which kind of information we can extract from XPS?

4) What is ion-beam profiling in XPS?

Understanding Surface Properties Using XPS

1) What does SURFACE mean?

The SURFACE contains atoms and molecules on the exterior of an object that can interact with the energy, atoms and molecules from the outside.



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Understanding Surface Properties Using XPS

1) What does SURFACE mean?

SURAFCE properties at different depths:

- **Appereance, Corrosion, Wear:** **> 100 atomic layer**
- **Oxidation, Passivation, Tribolayers:** **> 10 atomic layer**
- **Adhesion, Wetting, Catalysis, Lubrication:** **< 10 atomic layer**

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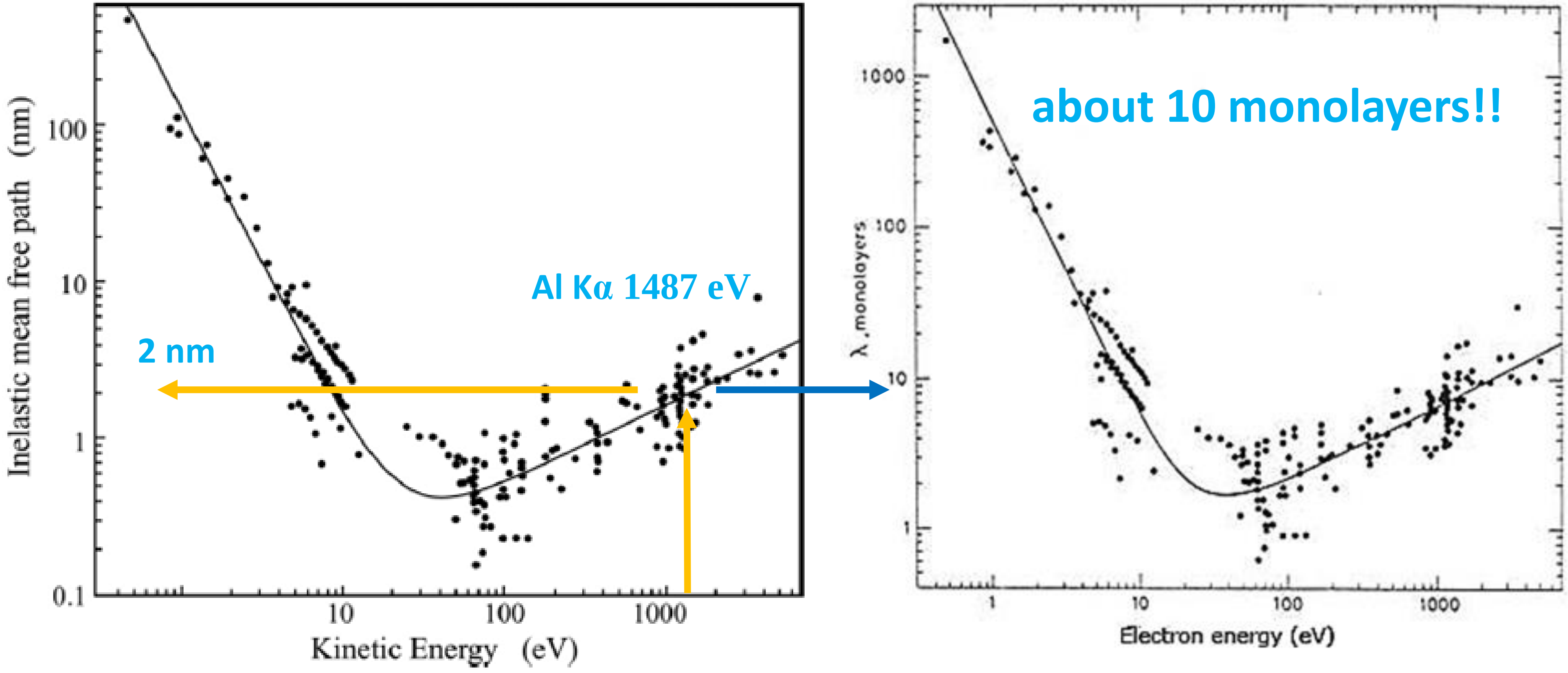
2) How does XPS acquire surface-sensitive data?



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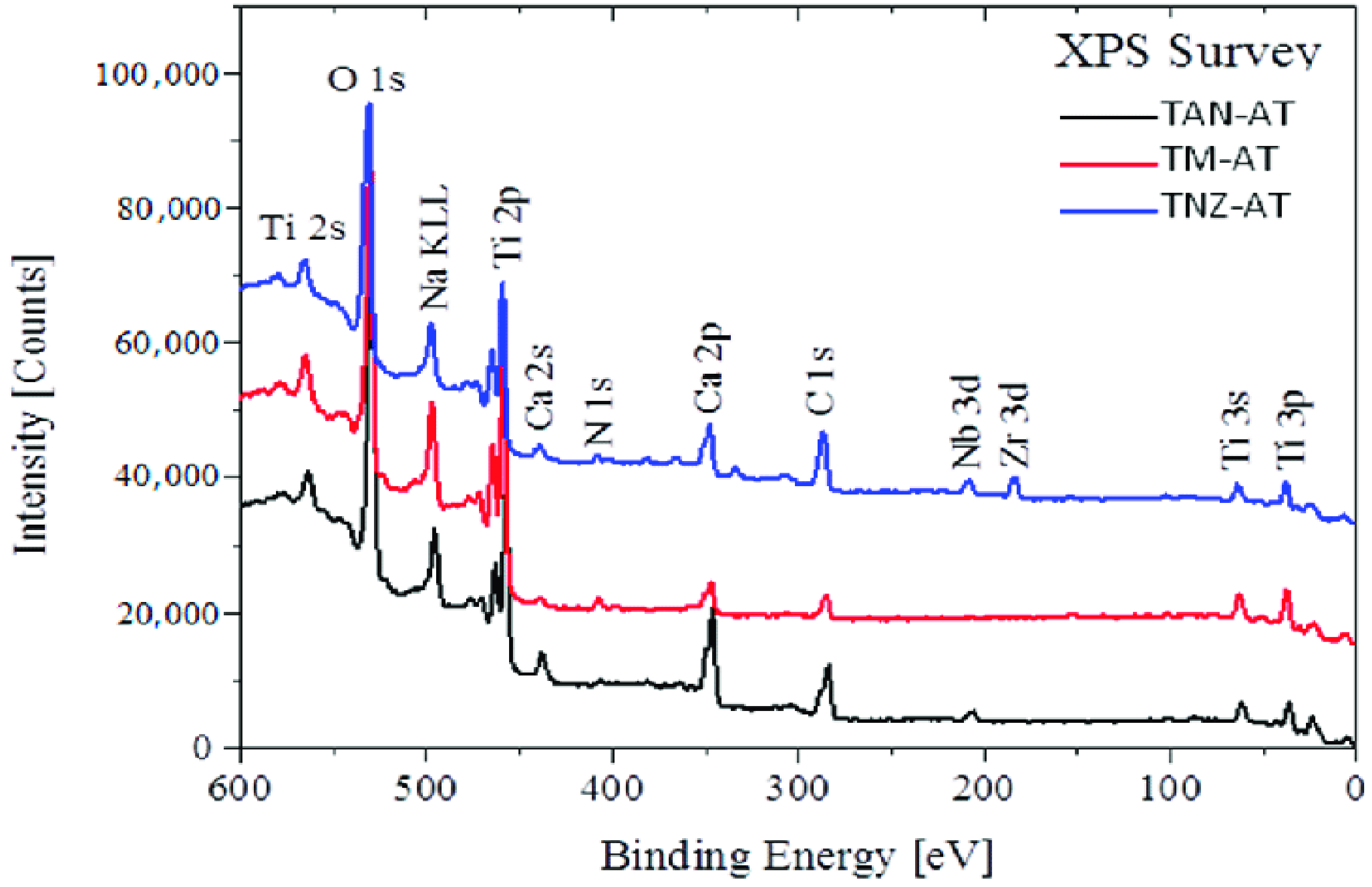
3) Which kind of information we can extract from XPS?

- Elemental data:



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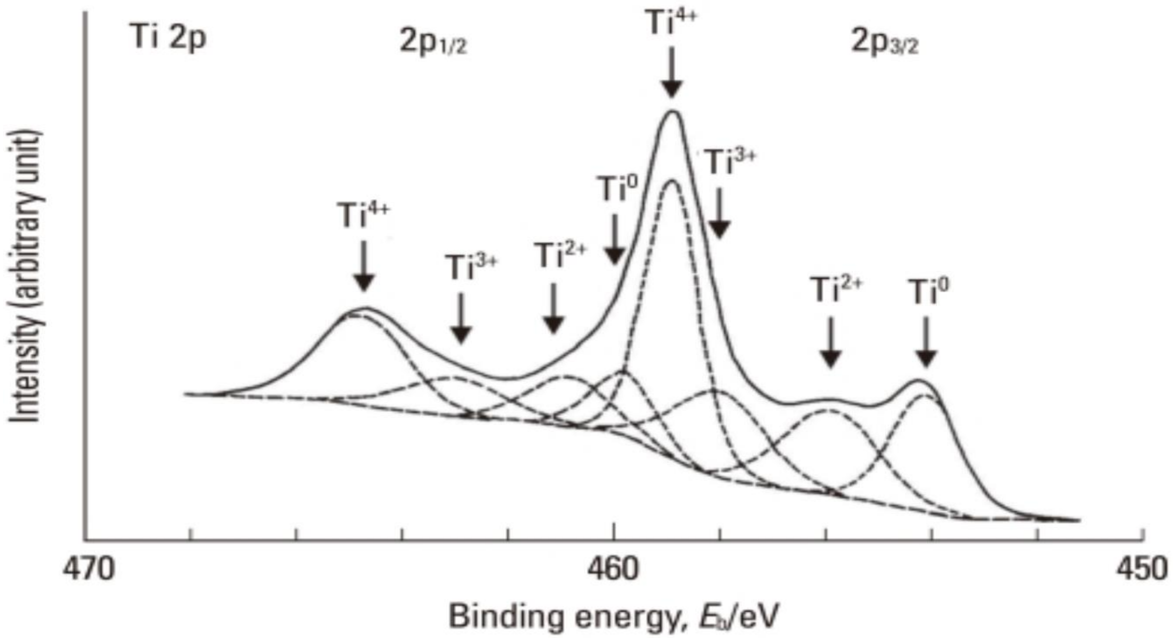
3) Which kind of information we can extract from XPS?

- Chemical state:

BE = hv – KE *binding energy = X-ray photon energy – kinetic energy*

Oxidized element: Fe^{2+} *lower kinetic energy = higher binding energy*

Reduced element: *higher kinetic energy = lower binding energy*



Understanding Surface Properties Using XPS

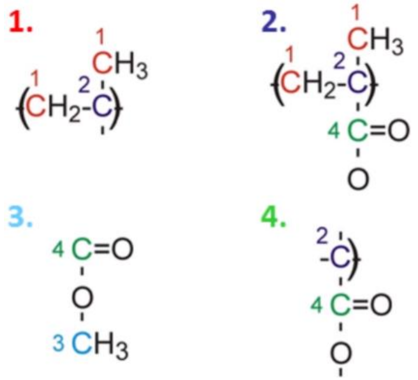
3) Which kind of information we can extract from XPS?

- Chemical state:

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

Electronegativity Increase → Binding energy increase

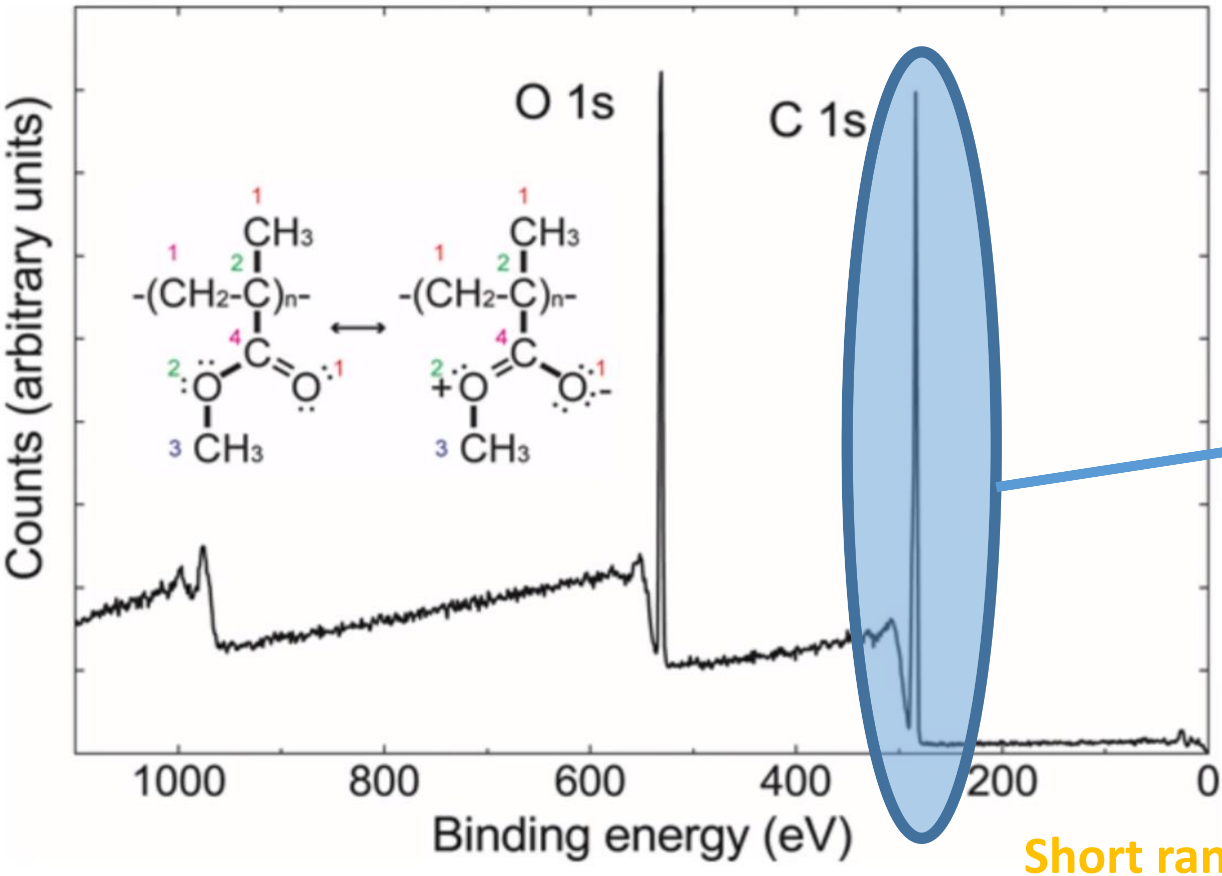
Understanding Surface Properties Using XPS

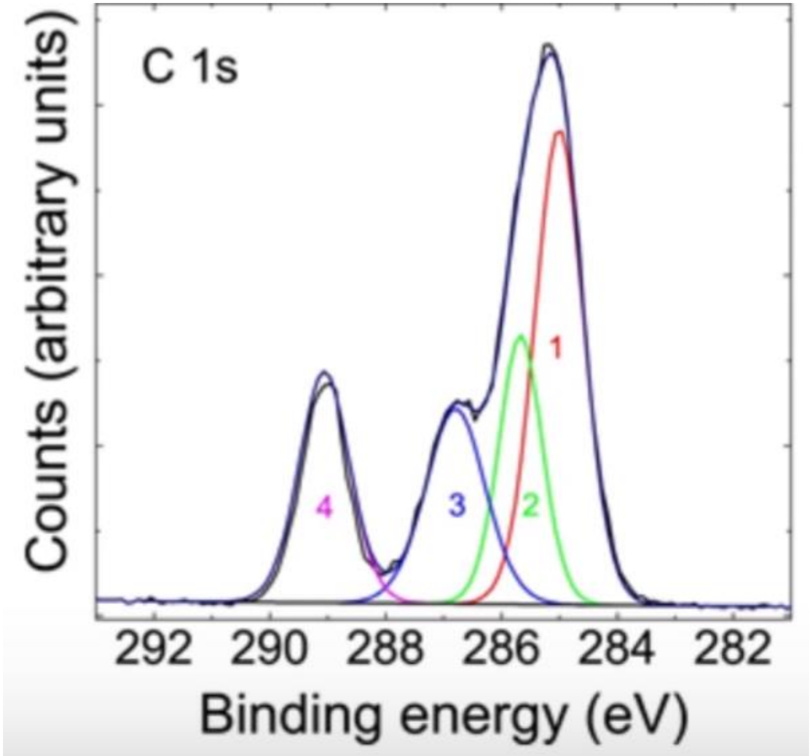


3) Which kind of information we can extract from XPS?

- Chemical state:

XPS of Polymethylmethacrylate





Short ranged sensitivity of XPS to chemical structures!!

R.T. Haarsch, *X ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES)* in *Practical Materials Characterization*, M. Sardela, *Springer Science, New York, 2014.*

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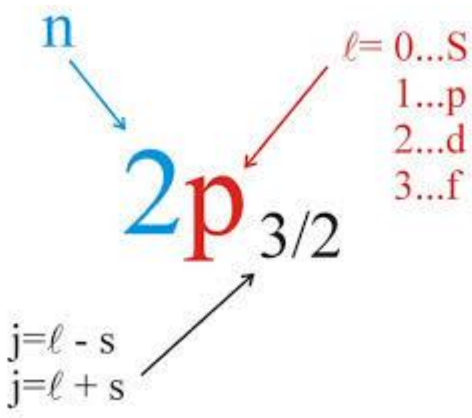
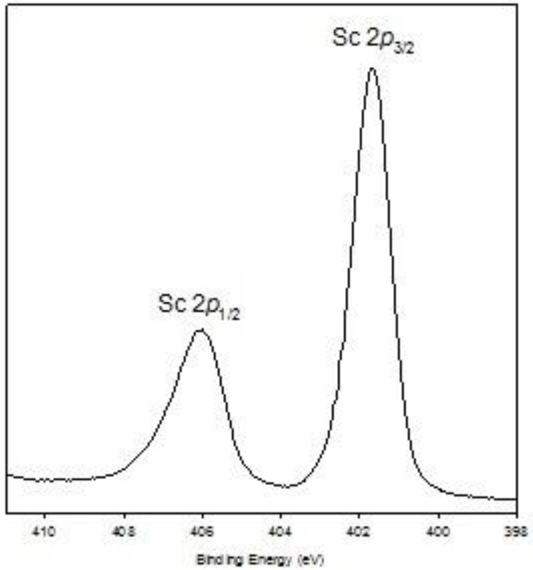
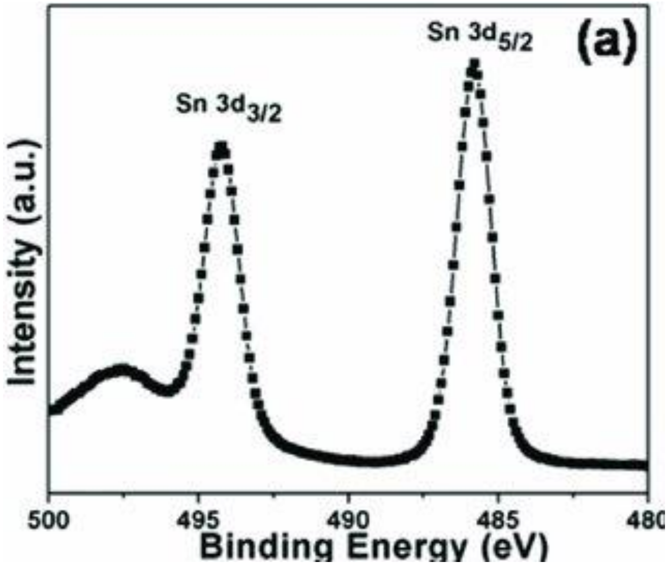
3) Which kind of information we can extract from XPS?

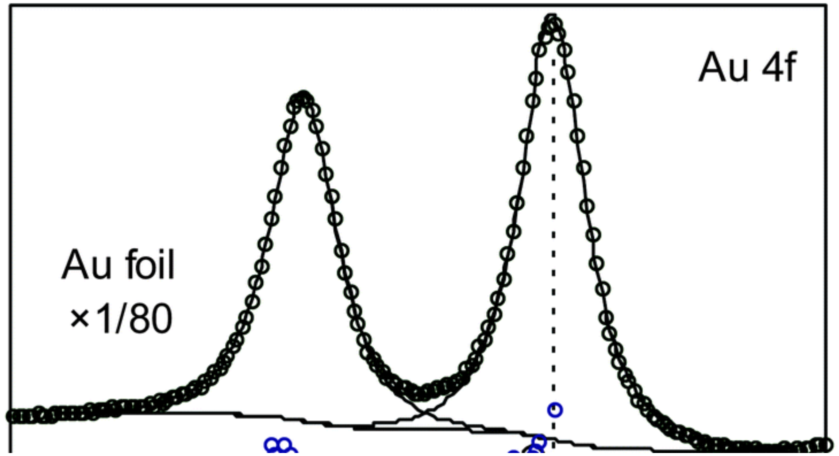
- Spin orbital splitting:

Subshell	*j* values	Area Ratio
s	1/2	n/a
p	1/2 3/2	1:2
d	3/2 5/2	2:3
f	5/2 7/2	3:4









Understanding Surface Properties Using XPS

3) Which kind of information we can extract from XPS?

- Quantitative analysis:

XPS quantitative measurements are as accurate as ± 10%

$$I_i = N_i \sigma_i \lambda_i K$$

I_i = intensity of photoelectron peak of element i

N_i = average atomic concentarion of element i

σ_i = photoelectron cross-section of element i related to the mentioned peak

λ_i = inelastic mean free path of a photoelectron from element i related to the mentioned peak

K = all other factors (assumed to remain constant during the experiment)

Understanding Surface Properties Using XPS

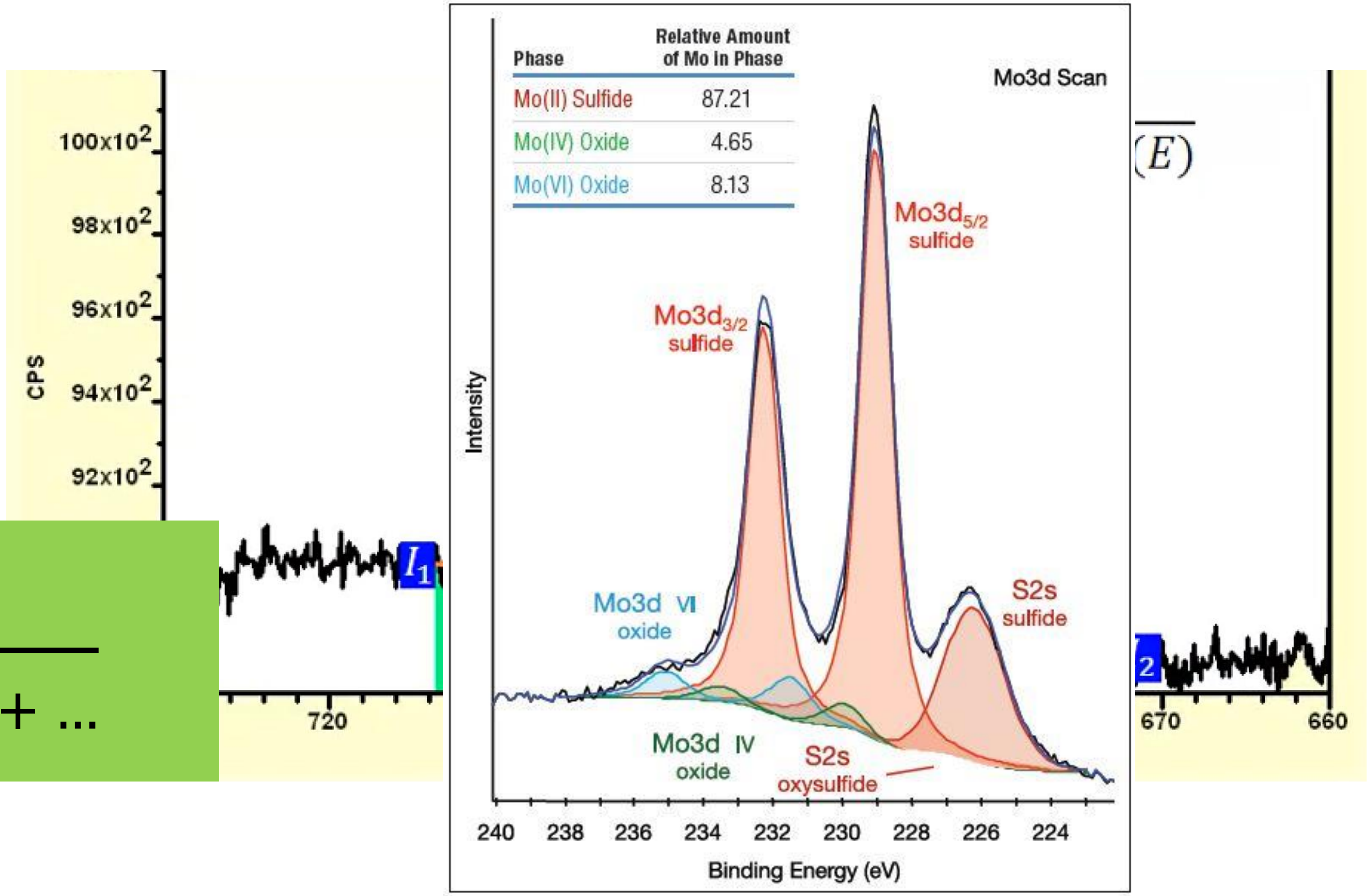
3) Which kind of information we can extract from XPS?

- Quantitative analysis:

$$I_i = N_i\, \sigma_i\, \lambda_i\, K$$

$$C_i = \frac{N_i}{N_i + Nj + Nk + \ldots}$$

$$C_i = \frac{\dfrac{Ai}{\sigma i\, \lambda i}}{\dfrac{Ai}{\sigma i\, \lambda i} + \dfrac{Aj}{\sigma j\, \lambda j} + \dfrac{Ak}{\sigma k\, \lambda k} + \ldots}$$

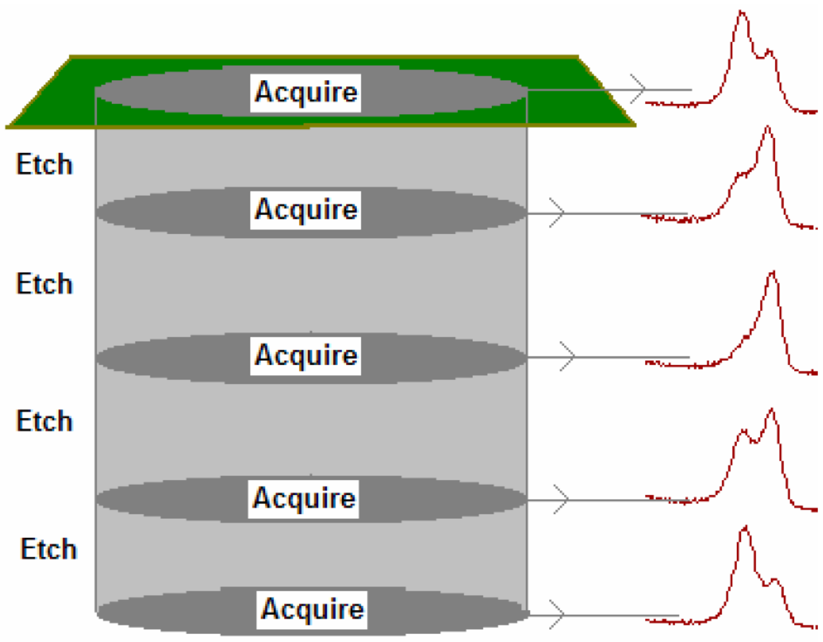


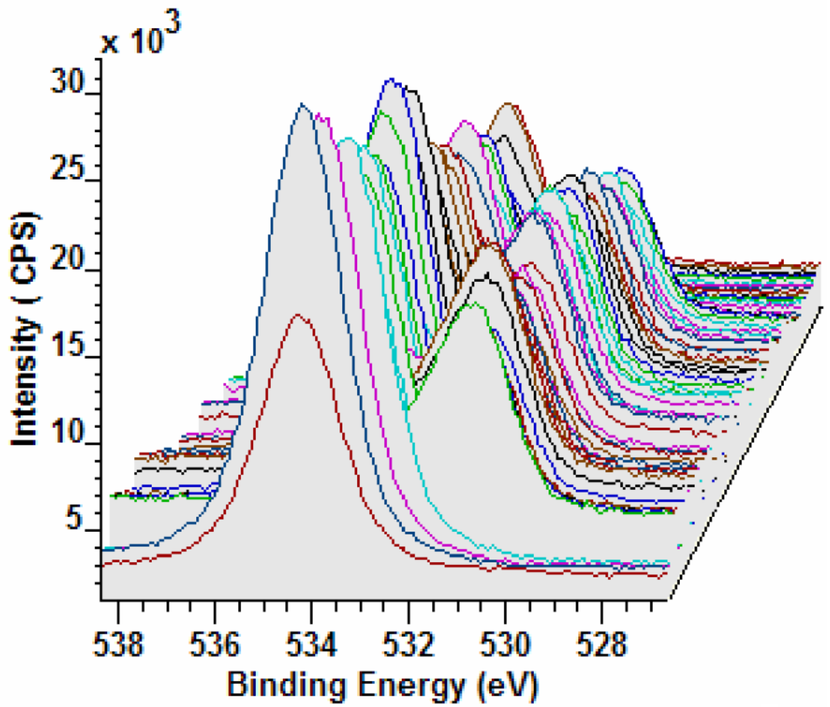
XPS is considered to be a semi-quantitative characterization technique

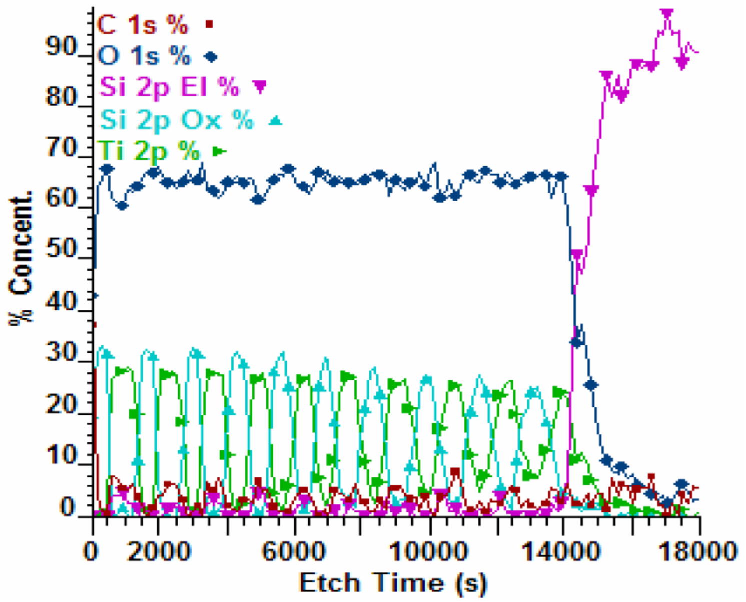
Understanding Surface Properties Using XPS

4) What is ion-beam profiling in XPS?

How to get depth profile with XPS?







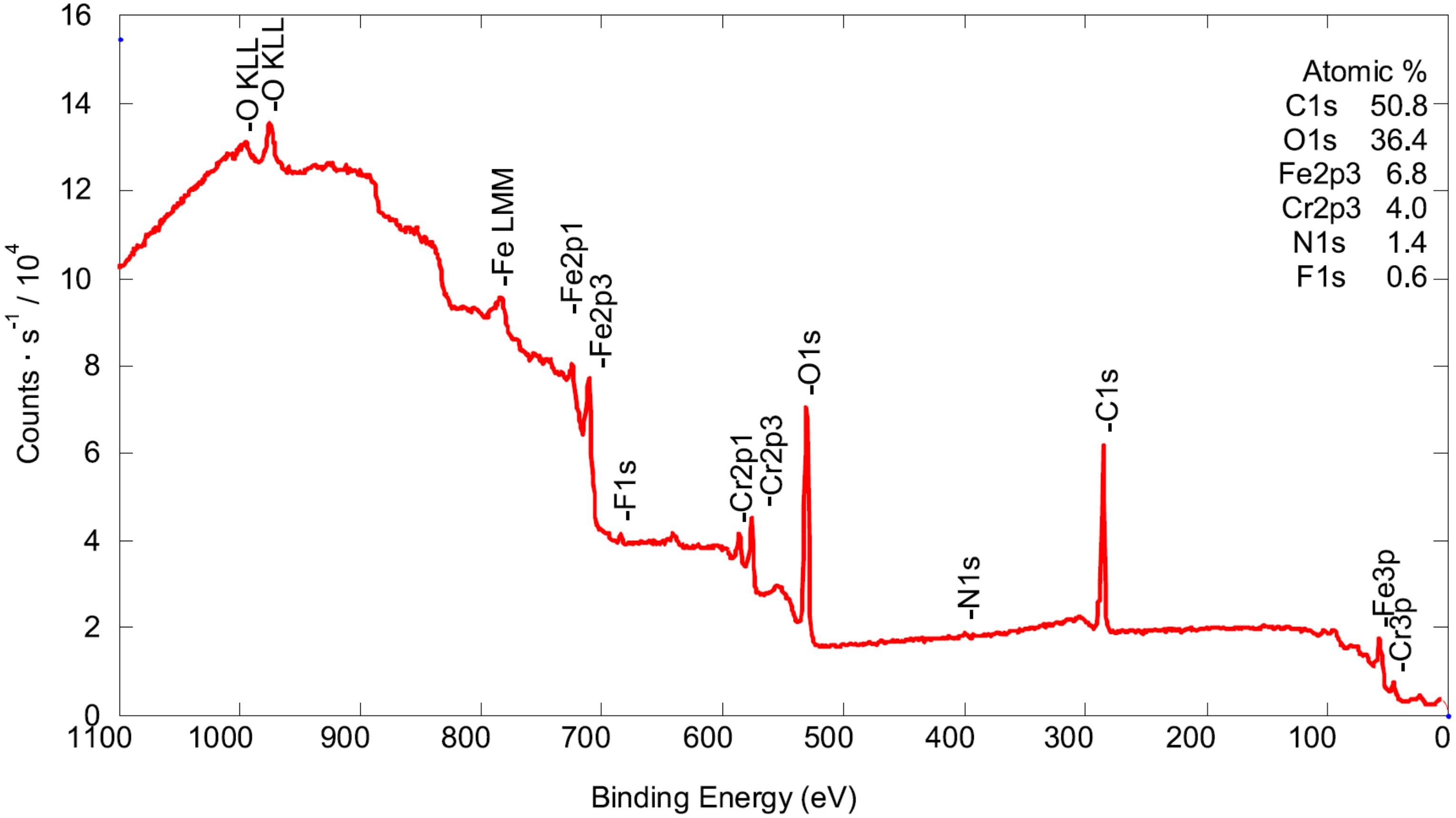
XPS in industrial research

Ussage of XPS in R&D labs of HP Inc.:

Survey spectra:

As received stainless steel parts:

- High amount of carbon
- The polyethylene shipping container is coated by erucamide (a fatty acid slip agent) which transferred to the steel surface
- Contamination layer thickness = 5 nm
- appropriate cleaning process prior to assembly



W.F. Stickle, C.N. Young, *Applying XPS to support industrial research and manufacturing*, J. Electron. Spectrosc. Relat. Phenom. 231 (2019) 50-56.

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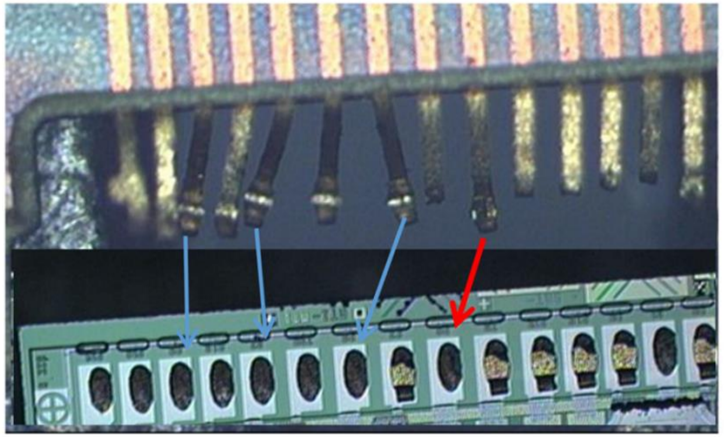
XPS in industrial research

Ussage of XPS in R&D labs of HP Inc.:

Chemical state analysis:

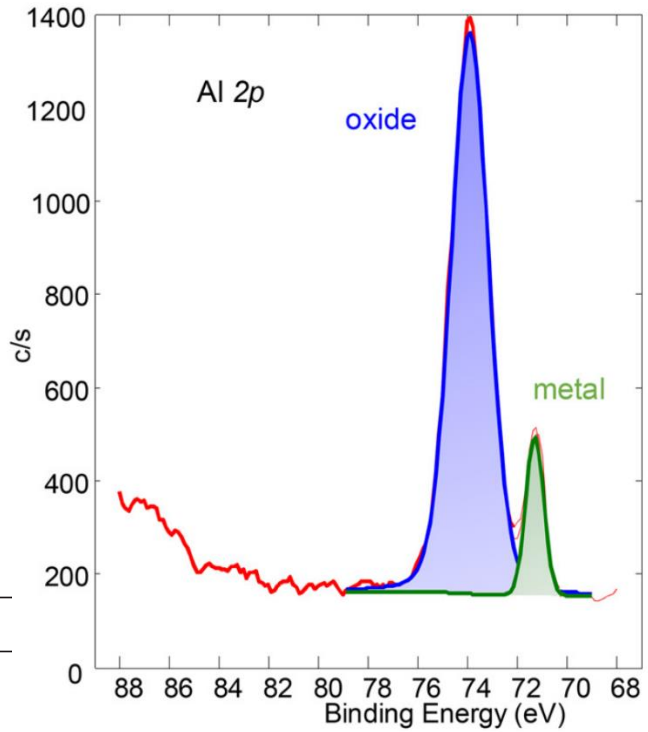
Adjacent bond pads showed different bonding characteristics:

- No difference in the nature of surface phases
- Difference in the thickness of oxide layer
- Different processing conditions of the die which would grow an oxide layer on pad 9.



Surface oxide thickness on aluminum bond pads.

Sample	Oxide (nm)
wafer 4 pad 8	5.6
wafer 4 pad 9	9.5
wafer 4 pad 10	6.5
wafer 18 pad 8	4.7
wafer 18 pad 9	7.8
wafer 18 pad 10	4.6
wafer 22 pad 8	3.7
wafer 22 pad 9	5.6
wafer 22 pad 10	3.9



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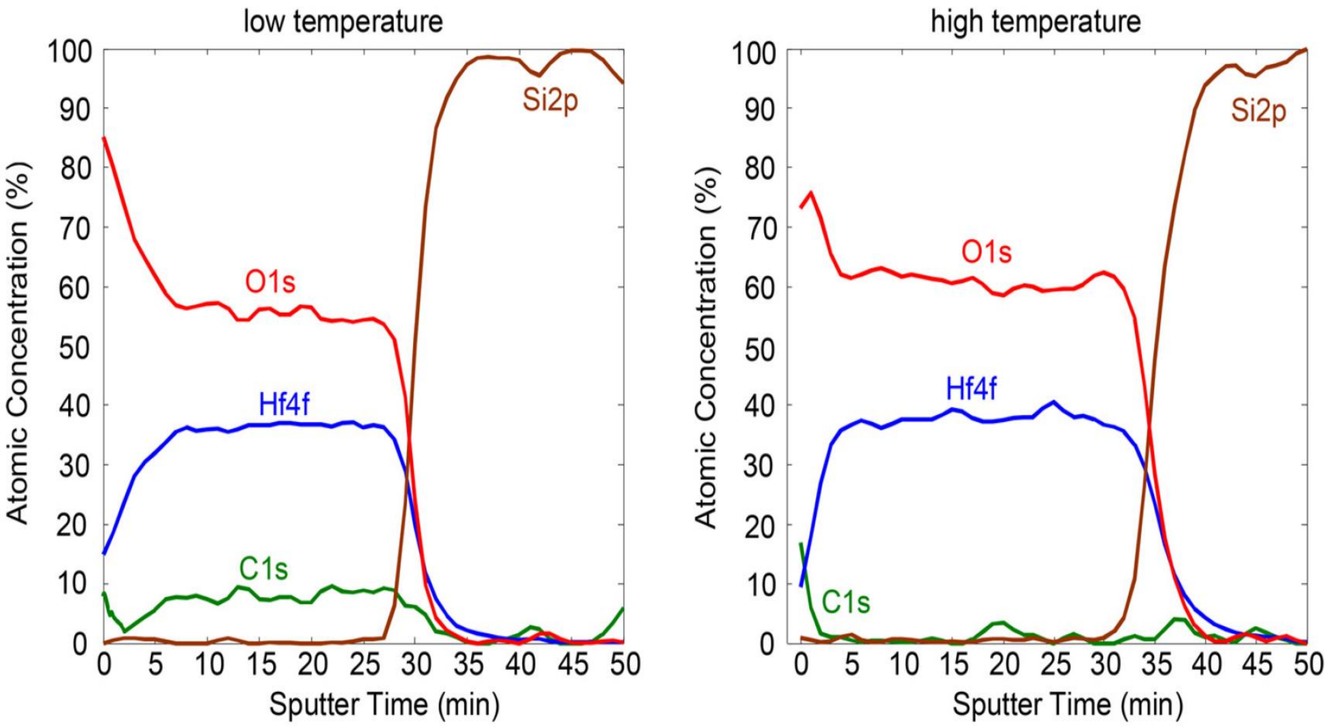
Ussage of XPS in R&D labs of HP Inc.:

Sputter depth profiling:

XPS as support of process control in thin film deposition:

- ALD of HfO_2 thin films
- Difference in carbon content of low temperature and high temperature deposition processes



W.F. Stickle, C.N. Young, *Applying XPS to support industrial research and manufacturing*, J. Electron. Spectrosc. Relat. Phenom. 231 (2019) 50-56.

XPS in battery material characterization

Redox flow batteries (RFB):

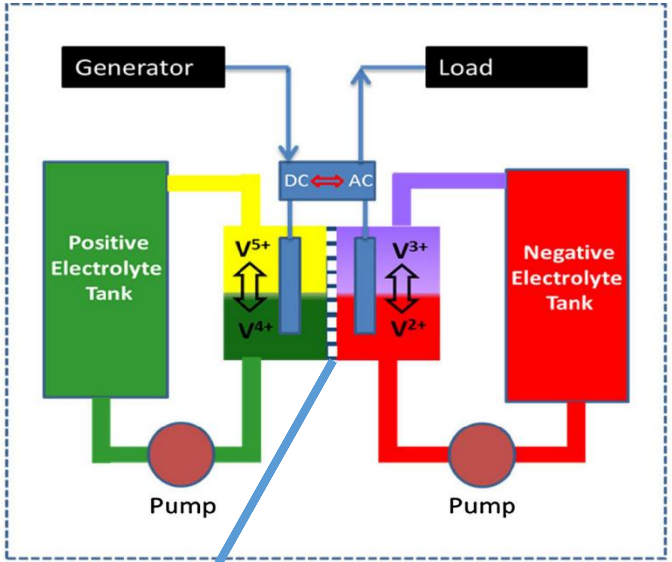
Urgent need for large scale stationary batteries in manufacturing industries

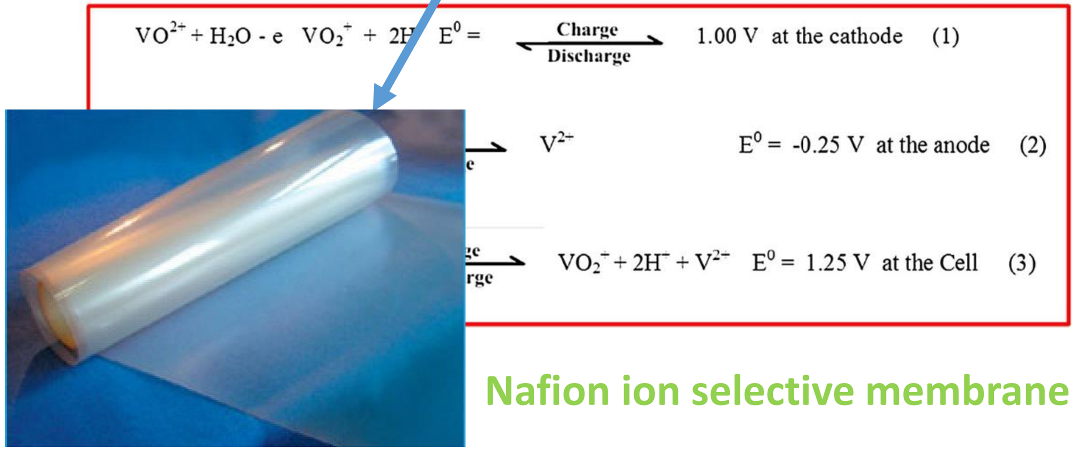
RFBs as prominent candidates due to their higher storage capacity, energy efficiency and life cycle.

Vanadium-sulphate redox flow batteries (VRFB) is getting attention because of its excellent electrochemical activity and reversibility.

VRFB systems suffer capacity loss due to vanadium diffusion across the membrane.

HYPOTHESIS: Employ highly stable oxide particles (SiO_2, TiO_2) in water-filled channels of Nafion to block cross contamination!!





Nafion ion selective membrane

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XPS in battery material characterization

Redox flow batteries (RFB):

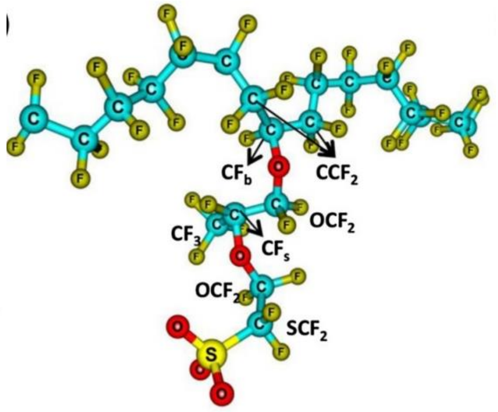
Absense of –CH peaks in C 1s and reduced intensity of –OS/-OH peaks in O 1s

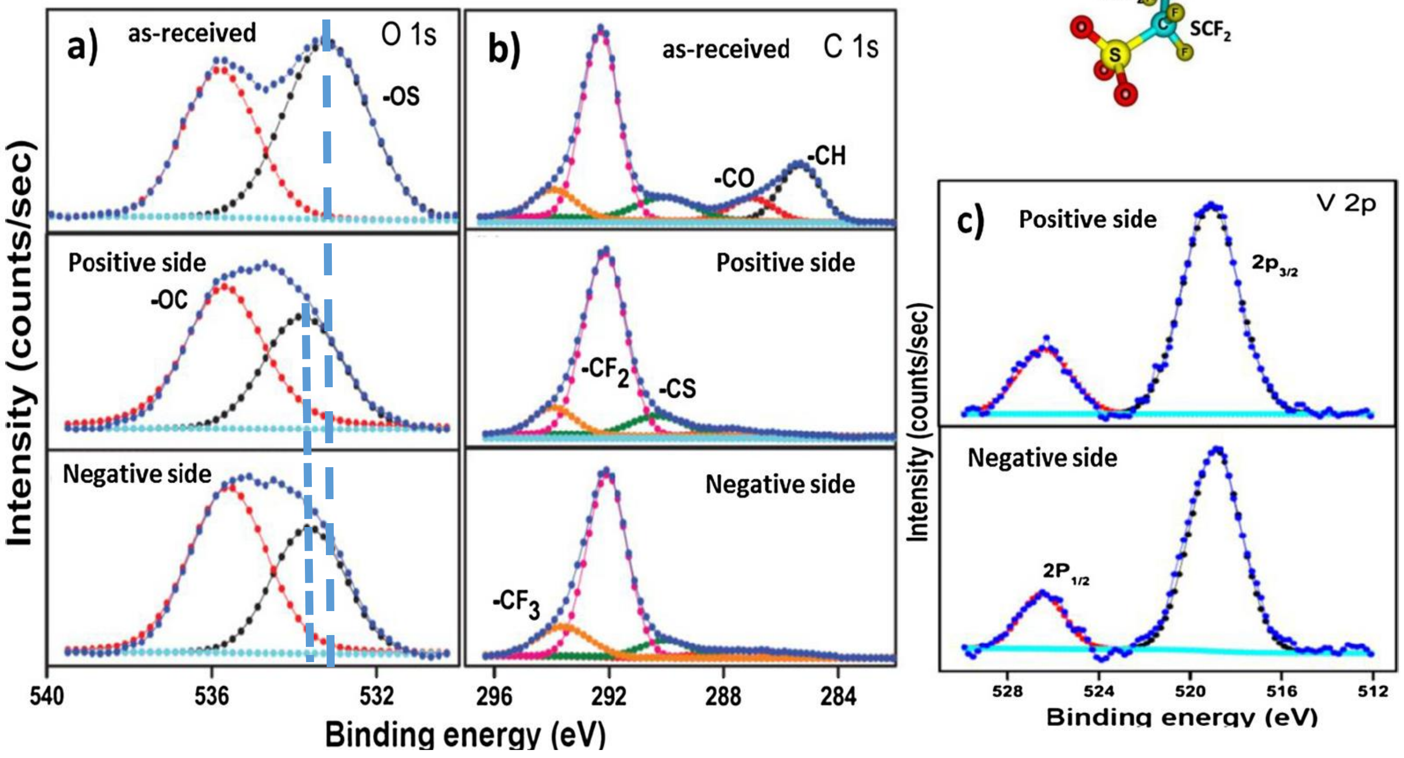
Replacement of expected water molecules by vanadium ions

Higher affinity of V ions to sulphonyl anionic groups

-OS/-OH peak shift in O 1s to higher BE values

Reduced electron density at sulphonyl anionic groups due to the higher electron affinity of vanadium cations





V. Shutthanandan, et. al., *Application of XPS in the characterization of battery materials*, J. Electron. Spectrosc. Relat. Phenom. 231 (2019) 2-10.

XPS in battery material characterization

Redox flow batteries (RFB):

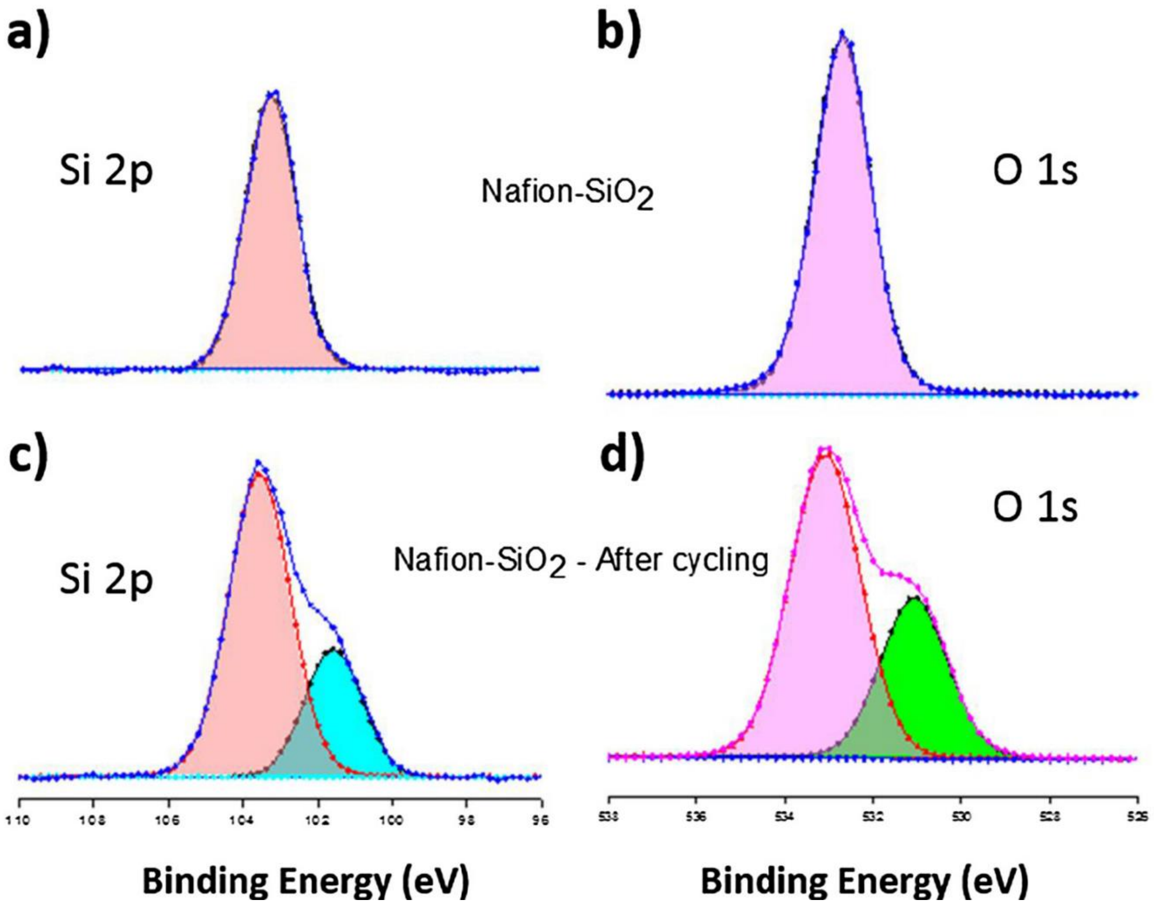
Nafion-SiO_2 composite membrane:

Additional small peaks at lower binding energies of Si 2p and O 1s

An atom with lower electronegativity (compared to Si) is bonded to SiO_2 network

Si-O-V binding network in the membrane

Less hydrophilic channels will be blocked by vanadium cations



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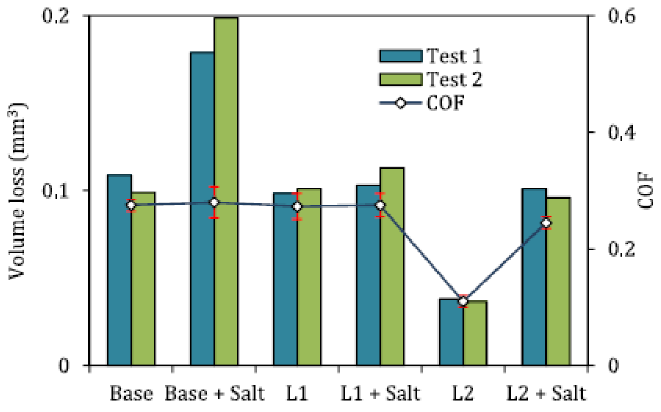
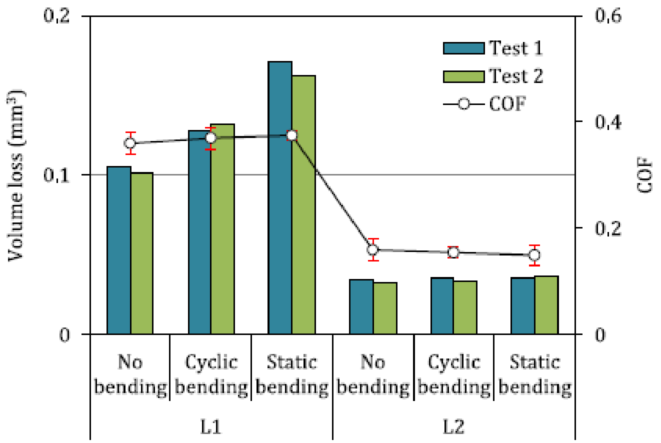
XPS in tribology and lubrication

Effect of friction modifiers on tribolayer formation

Multi-degradation test matrix.

Material	Normal Load (N)	Mechanical conditions	Number of reciprocating cycles	Electrochemical conditions	Lubricant
ASS	50	– No bending – Static bending at 90% of $Rp_{0.2}$ – Cyclic bending at 1.25 Hz and 90% of $Rp_{0.2}$	6000	Open circuit potential (OCP)	L1 (base + amine) L2 (base + amine + friction modifier)





Base lubricant: water-ethylenglycol friction modifier: palmitic acid ($C_{16}H_{32}O_2$) salt: NaCl

A.H. Zavieh, N. Espallargas, *The effect of friction modifiers on tribocorrosion and tribocorrosion-fatigue of austenitic stainless steel*, Tribol. Int. 111 (2017) 138-147.

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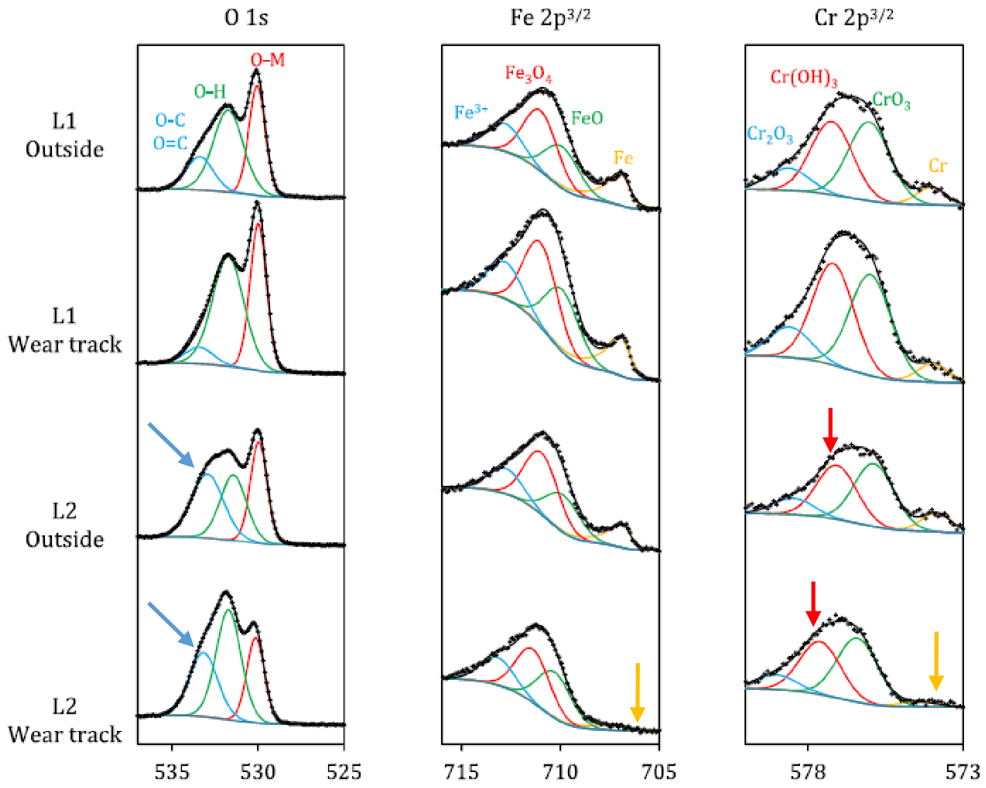

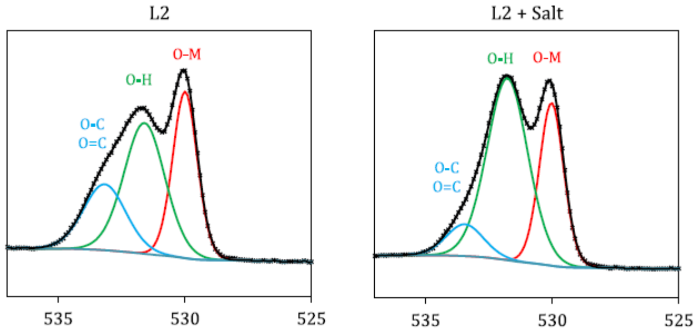

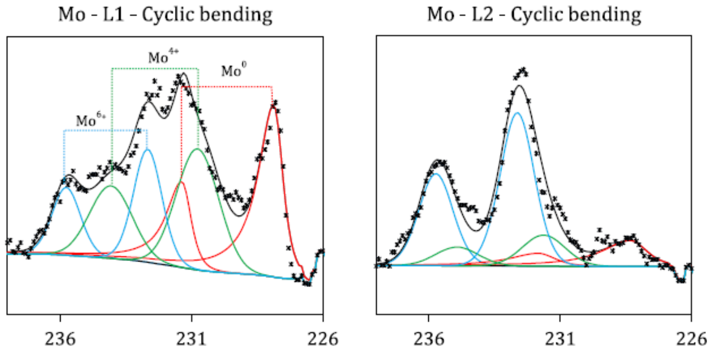

A.H. Zavieh, N. Espallargas, *The effect of friction modifiers on tribocorrosion and tribocorrosion-fatigue of austenitic stainless steel*, Tribol. Int. 111 (2017) 138-147.

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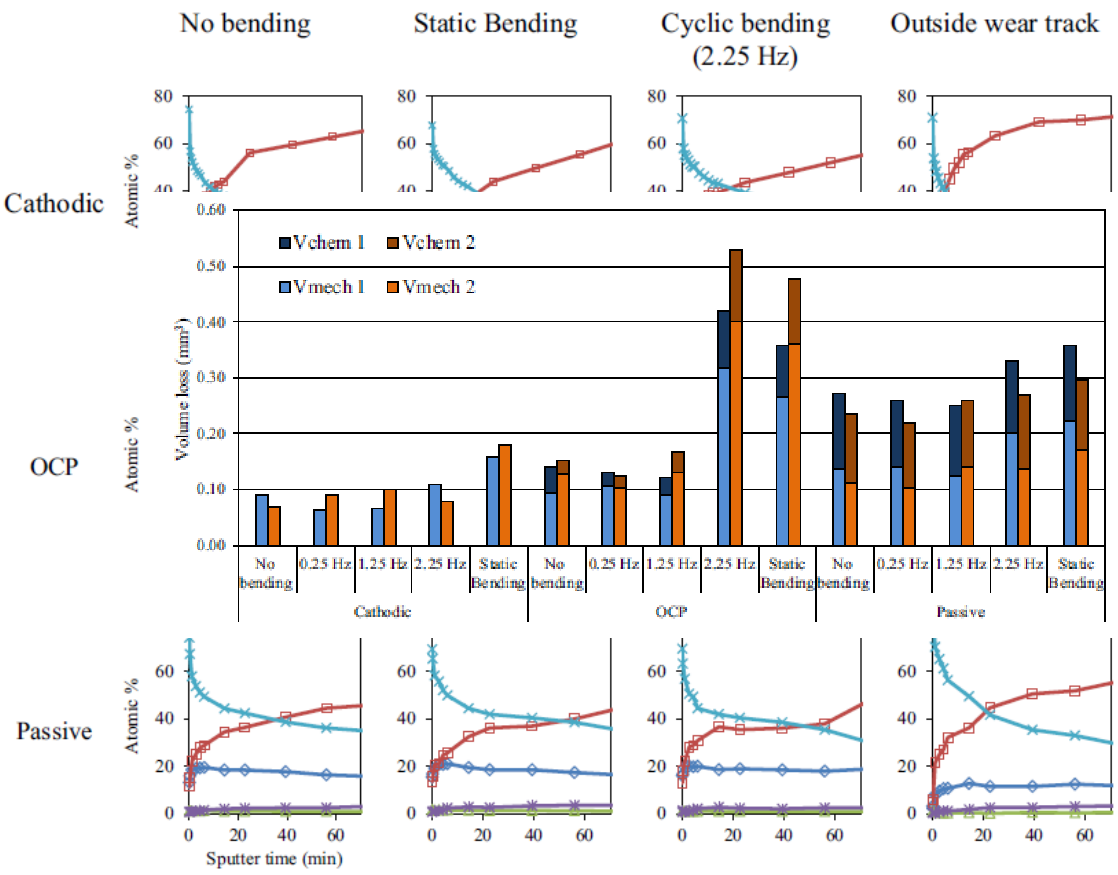
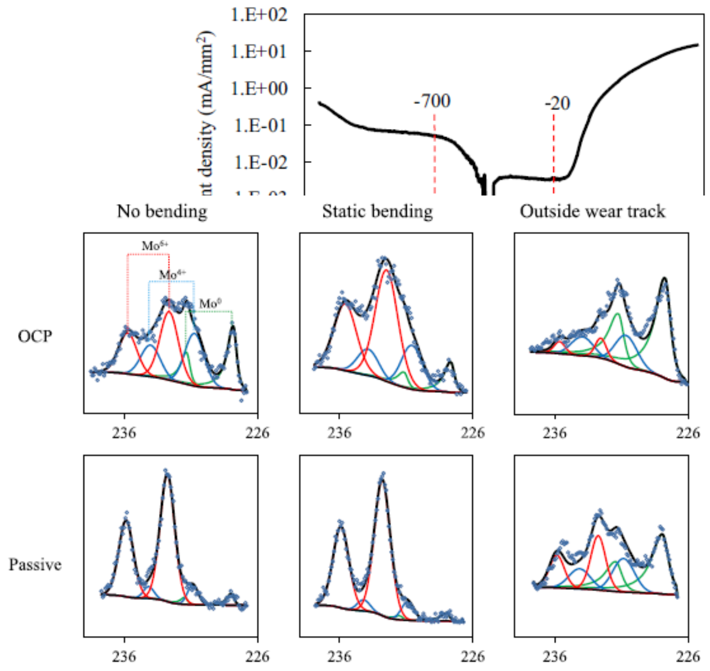
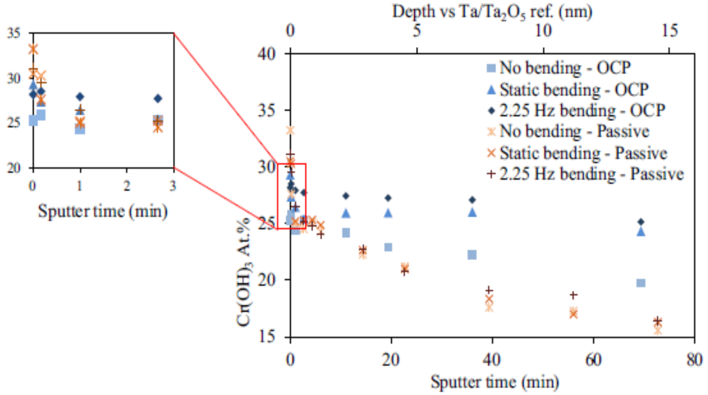
XPS in tribology and lubrication

Depth profiling of tribolayer



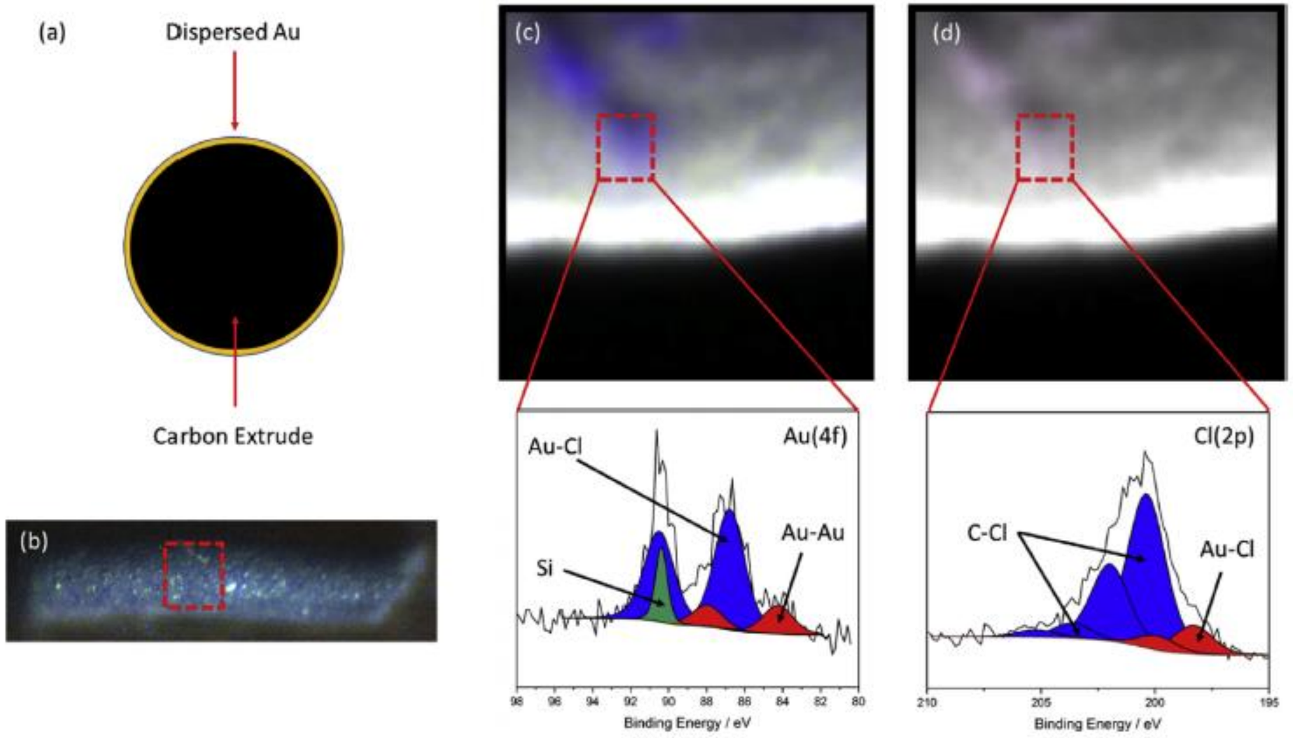




A.H. Zavieh, N. Espallargas, *The role of surface chemistry and fatigue on tribocorrosion of austenitic stainless steel,* Tribol. Int. 103 (2016) 368-378.

XPS in catalysis research

Egg-shell Au-C catalysts used for acetylene hydrochlorination



- The dispersion of gold is critical to the activity of the catalyst
- The poor dispersion is clearly the reason for the minimal activity of the catalyst

D.J. Morgan, *Imaging XPS for industrial applications*, J. Electron. Spectrosc. Relat. Phenom. 231 (2019) 109-117.

Cluster ion beam sputtering

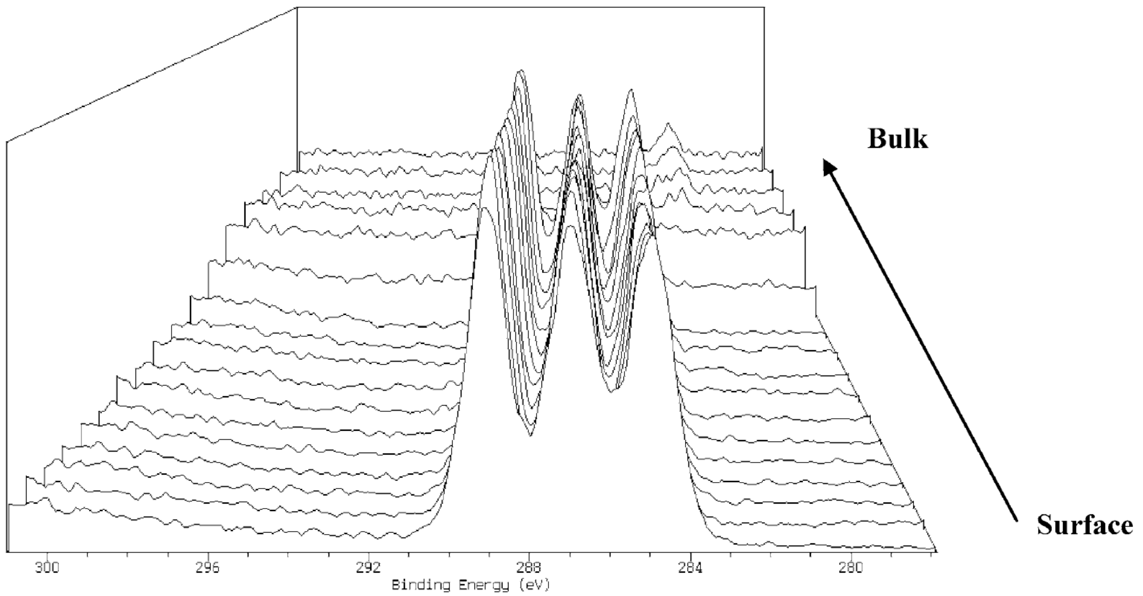
Conventionally: using monoatomic ions (such as Ar^+) to etch a few nm of the sample surface

Monoatimic ion sputtering is very useful for inorganic systems

Structural information in organic systems is very susceptible to damage from monoatomic ion beam

Minimally destructive XPS depth profiles with large cluster ion beams (such as C_{60} or coronene)

Coronene: $C_{24}H_{12}$



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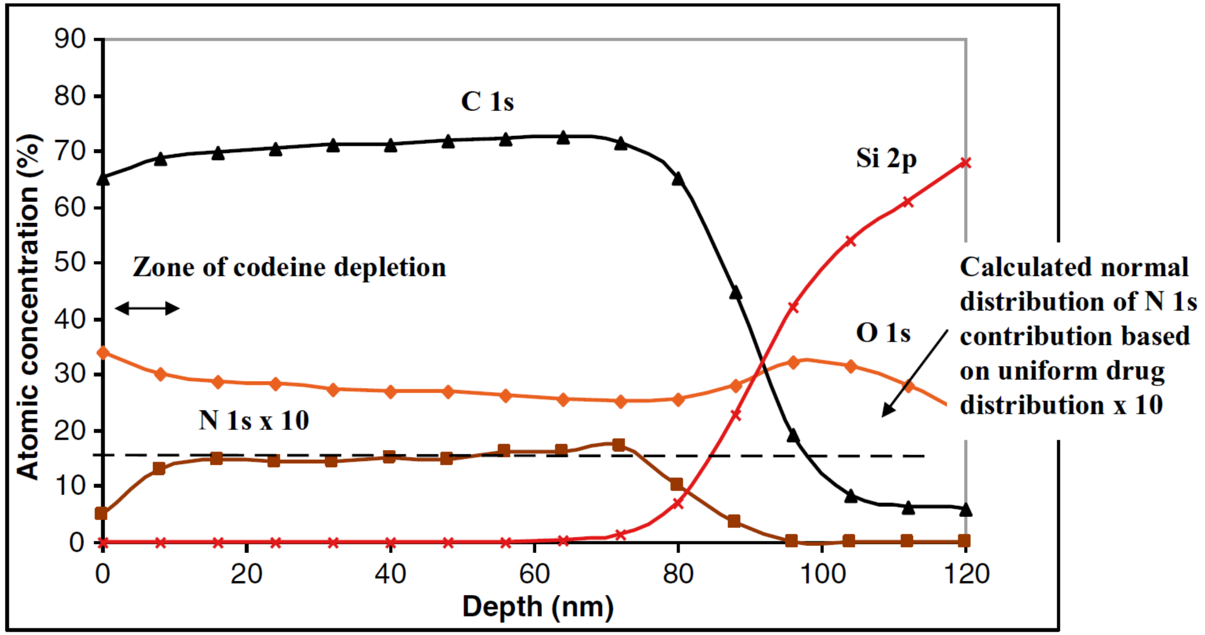
Introduction

XPS in material science

XPS in biotechnology

Cluster ion beam sputtering

Codeine ($C_{18}H_{21}NO_3$) in poly(L-lactic) acid matrix as a drug-loaded polymer coating



N 1s signals used to monitor the distribution of the drug as a function of depth

Codeine was depleted from the surface and segregated to the bulk of the polymer

Surface depletion of drug poses important implications for drug-loaded polymer delivery

S.L. McArthur, et al., *Application of XPS in biology and biointerface analysis*, Book Chapter. SURFACE ANALYSIS AND TECHNIQUES IN BIOLOGY, Ed. By V.S. Smentkowski, Springer, 2014.

Introduction

XPS in material science

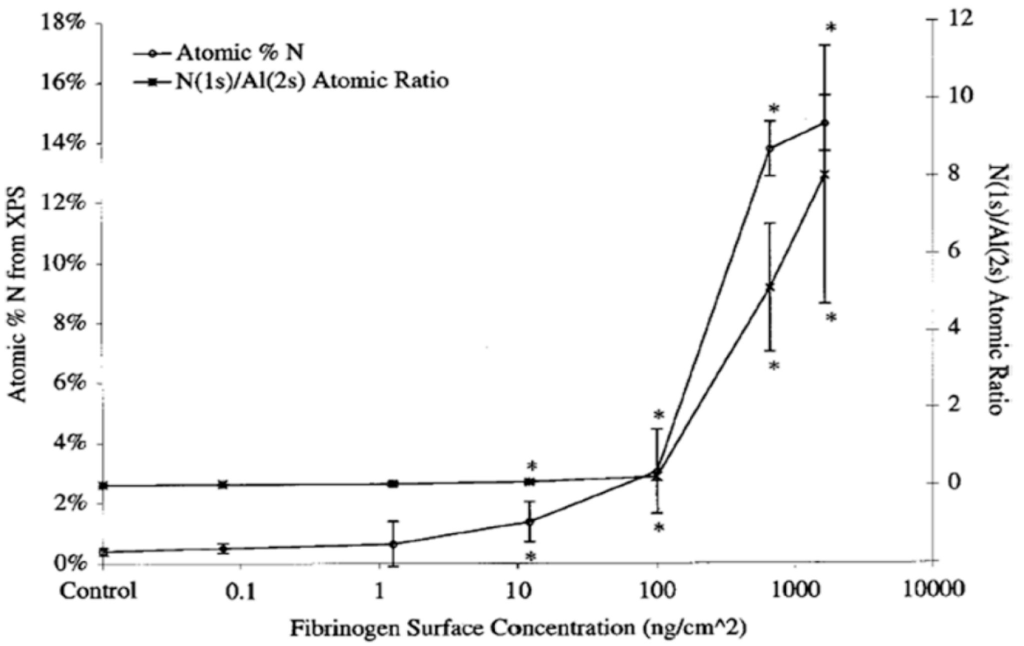
XPS in biotechnology

Characterization of proteins and petides

Similar chemical composition of most proteins → XPS cannot differentiate individual components

XPS: study adsorbed proteins, the orientation, surface coverage and layer thickness

Proteins mostly contain C, N and O. Typically monitoring changes in N signal, or an element of the substrate



S.L. McArthur, et al., *Application of XPS in biology and biointerface analysis*, Book Chapter. SURFACE ANALYSIS AND TECHNIQUES IN BIOLOGY, Ed. By V.S. Smentkowski, Springer, 2014.

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X-ray Photoelectron Spectroscopy

Introduction

XPS in material science

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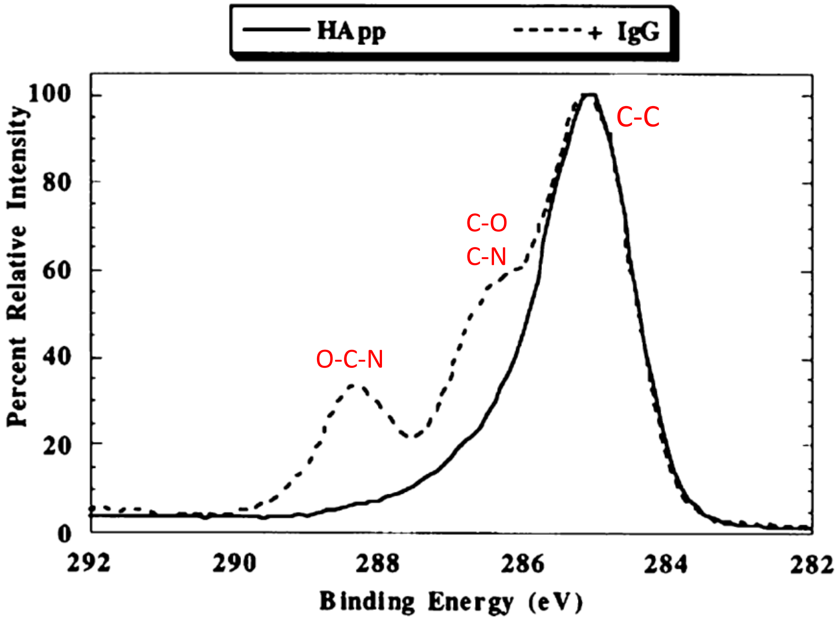
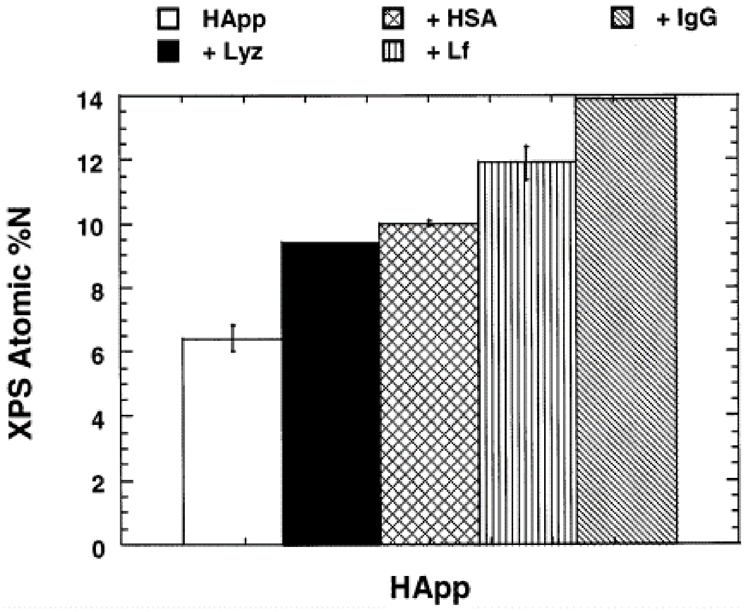
Characterization of proteins and petides

Plasma polymerized heptylamine thin film before and after the adsprtion of IgG:





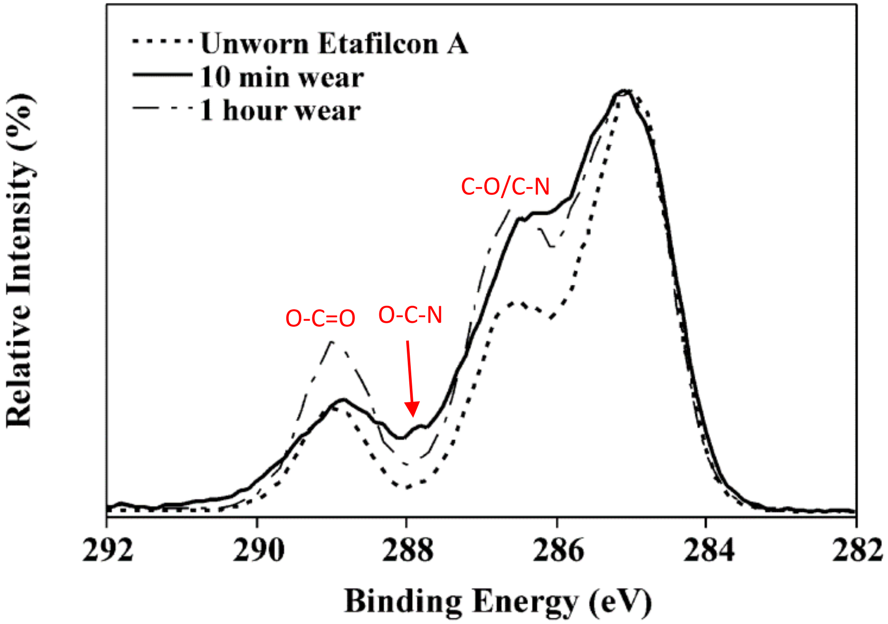
Atomic% of Nitrogen as a sign of adsorption of proteins to the surface

S.L. McArthur, et al., *Effect of polysaccharide structure on protein adsorption,* Colloids and Surfaces B: Biointerface 17 (2000) 37-48.

Characterization of proteins and petides

Characterization of biomaterials after in-vivo experimentation

XPS tests of contact lenses before and after 10 min and 1 h of patient wear:



	Atomic concentration (%)				Atomic ratios	
	C	O	N	Si	N:C	O:C
Unworn ($n=4$)	72.5 (1.2)	27.0 (1.6)	0.4 (0.2)	0.1 (0.1)	0.01 (0.00)	0.37 (0.03)
10 min ($n=10$)	72.6 (2.3)	24.5 (2.7)[a]	2.3 (0.8)[a]	0.1 (0.0)	0.03 (0.01)	0.34 (0.04)
1 h ($n=8$)	67.9 (1.0)[a]	28.2 (1.7)[a]	3.7 (1.6)[a]	0.2 (0.3)	0.05 (0.02)	0.42 (0.03)

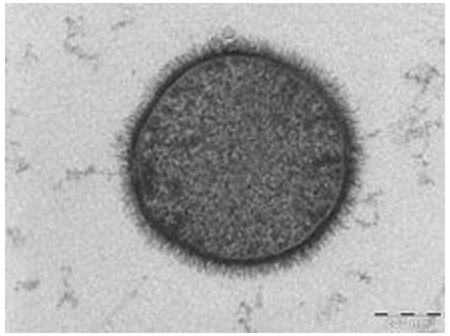
After 10 min: C-O/C-N species (286.5 eV), O-C-N (288 eV)
After 1 h: O-C=O (289 eV)

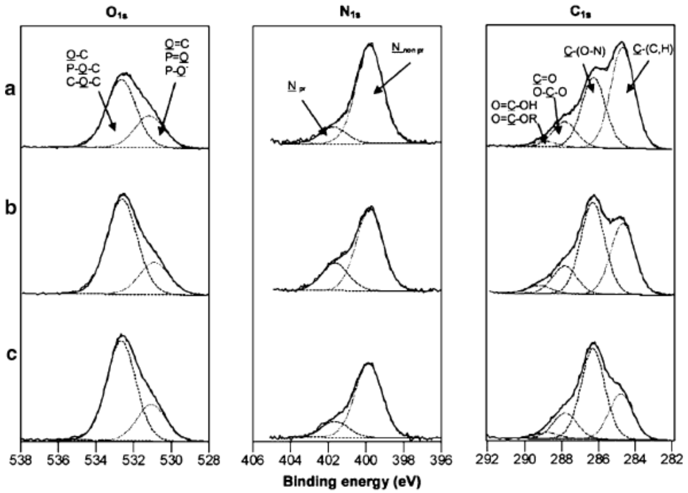
Adsorption processes were initially dominated by proteins and at longer wear times oxygen-rich species e.g., polysaccharides adsorbed alongside the proteins

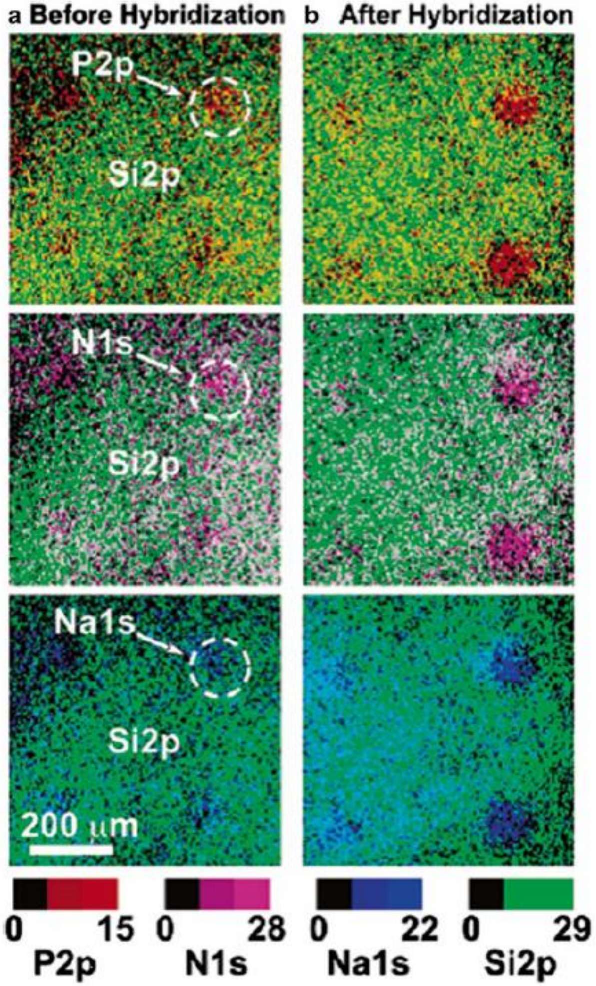
S.L. McArthur, et al., *XPS and surface-MALDI-MS characterization of worn HEMA-based contact lenses*, Biomaterials 22 (2001) 3295-3304.

Characterization of microbs

Bacillus subtilis:







S.L. McArthur, et al., *Application of XPS in biology and biointerface analysis,* Book Chapter. SURFACE ANALYSIS AND TECHNIQUES IN BIOLOGY, Ed. By V.S. Smentkowski, Springer, 2014.

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X-ray Photoelectron Spectroscopy

Summary

XPS checklist

- **X-ray photoelectron spectroscopy (XPS) is a surface analytical technique**
- **XPS is used to identify elemental and chemical information on the surface (~ 10nm) of the sample**
- **The most important advantage: Very Surface Sensitive**

  The most important disadvantage: Very Surface Sensitive
- **Vaccum compatible materials**
- **Possibility of elemental mapping**
- **Depth profiling using ion etching**
- **Semi-quantitative technique**
- **Applicable in diferent research areas and industries: Aerospace, automotive, biotechnology, electronics, photonics, solar photovoltaics and ….**

Thanks for your attention!!

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