

# Surface Analysis - XPS



ANTON MANAKHOV  
PHD IN PHYSICS



**CEITEC**

Central European Institute of Technology  
BRNO | CZECH REPUBLIC

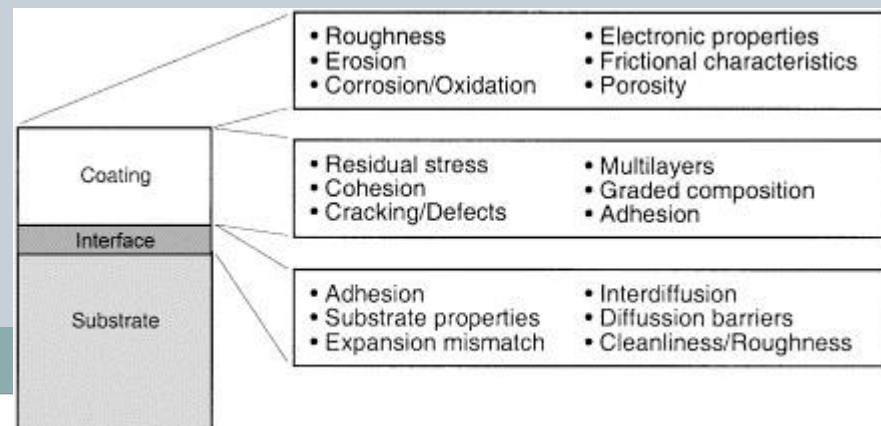


**MASARYK UNIVERSITY**  
*Czech Republic*

# Why we need to know surface chemistry?



- Surface properties affects interaction of material (metals, plastic, powder, etc.) with the environment (water, polymers, in vivo...) and specific chemical composition and morphology is required for particular application.
- Surface Chemistry influences cell adhesion, fouling of bioorganisms, adhesion between different phases of composite materials.
- Often the application of material with noble bulk properties (hardness, flexibility, chemical stability) is not possible due to low surface free energy, or too reactive surface instead.
- Deposition of thin film can tune surface properties without degradation of the bulk of the material



# Surface analysis methods :



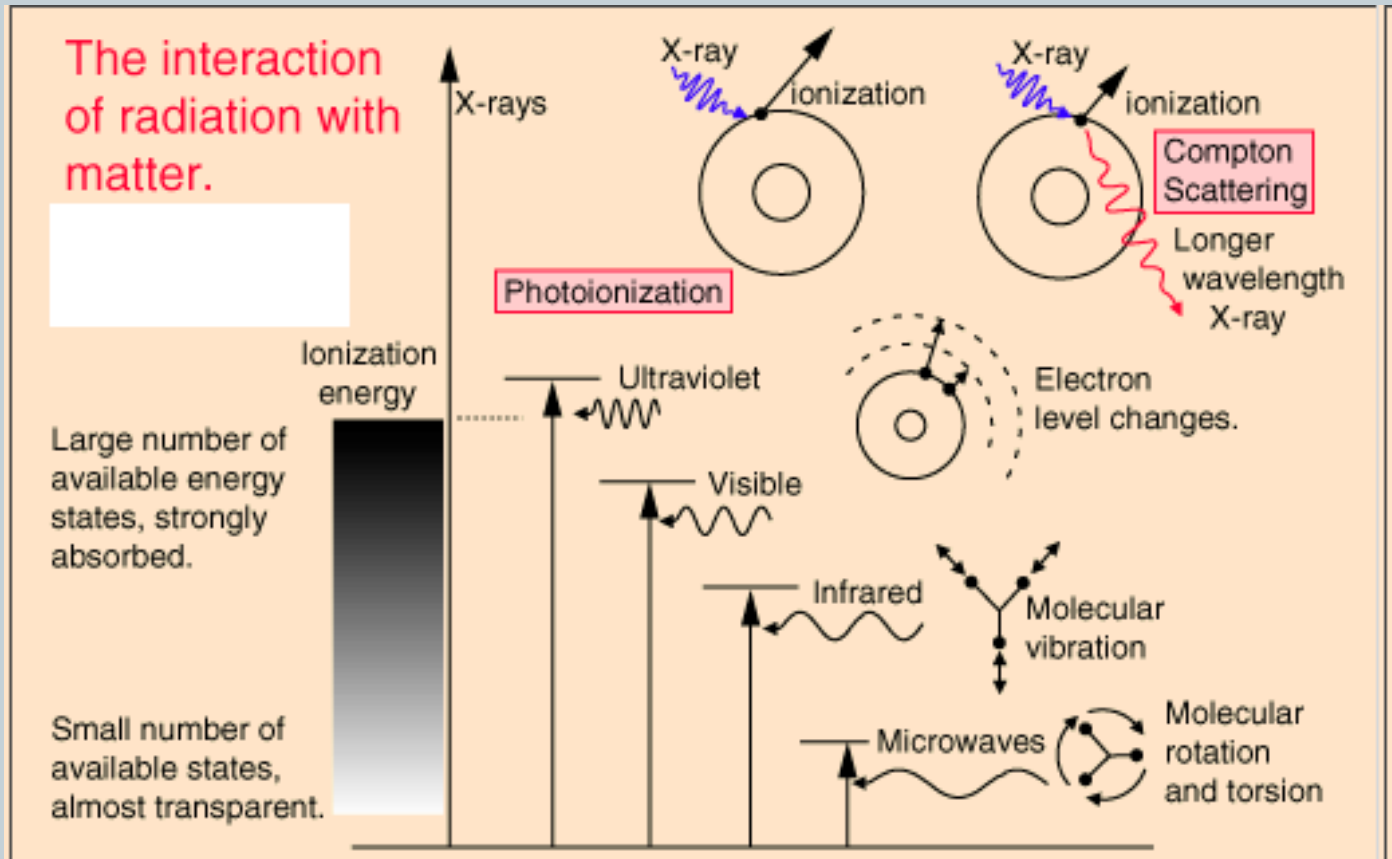
Technique	Probe In/Out	Depth resolution, nm	Lateral resolution, nm	Information	Advantage (+) and drawback (-)
Contact angle	Liquid water droplet	0.1	1000	Surface energy	+ Fast acquisition - No molecular information
X-Ray photoelectron spectroscopy XPS	X-Ray/ electrons	5	3000	Elemental composition (except H), binding state	+ Quantitative + Information about the neighbours of the atoms - Limited Molecular information - sensitivity >0.1 at%
Scanning electron microscopy , SEM	Electrons/ electrons	3	2	Surface image	- No direct information regarding the topography.

Technique	Probe In/Out	Depth resolution, nm	Lateral resolution, nm	Information	Advantage (+) and drawback (-)
Energy Dispersive analysis	Electrons/ X-Ray	2000	100	Elemental information	- Low precision of quantification
IR attenuated total reflection ATR-FTIR	IR/IR	~2000	2000	Surface composition binding state	+ Fast acquisition + Information regarding the molecular functions - Overlap of some chemical domains  - Quantification is not possible
Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)	Ions/Ions	1	100	Surface composition	+ Highly Sensitive (>1 ppm) + Molecular information is possible + 3D reconstruction of the layer - non quantitative



- **Methods based on the radiation of material by photons :**
  - XPS
  - XRD
  - UPS
- UV-Vis spectrophotometry
  - IR spectroscopy

# Interaction of photons with matter



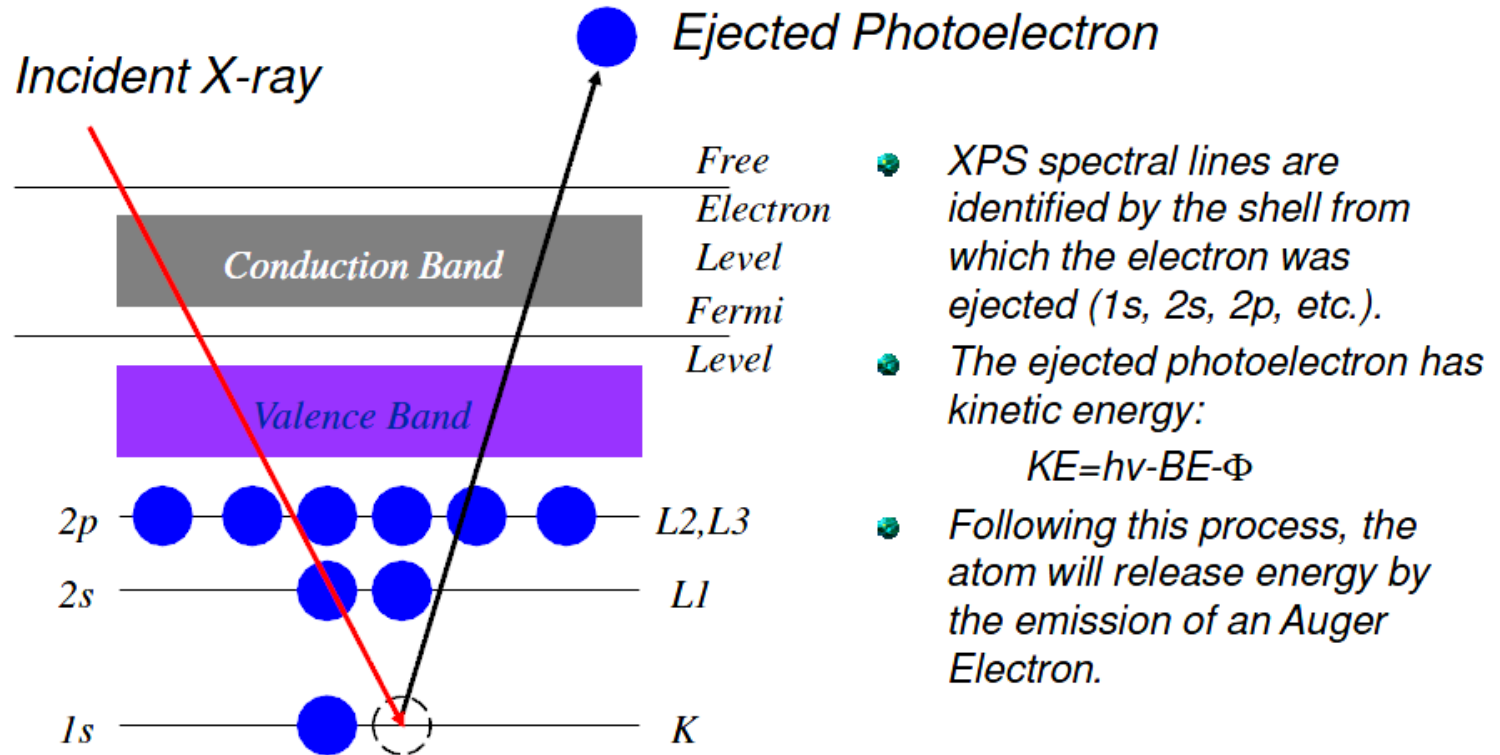
# *X-ray Photoelectron Spectroscopy XPS*



*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, was developed in the mid-1960's by Kai Siegbahn and his research group at the University of Uppsala*

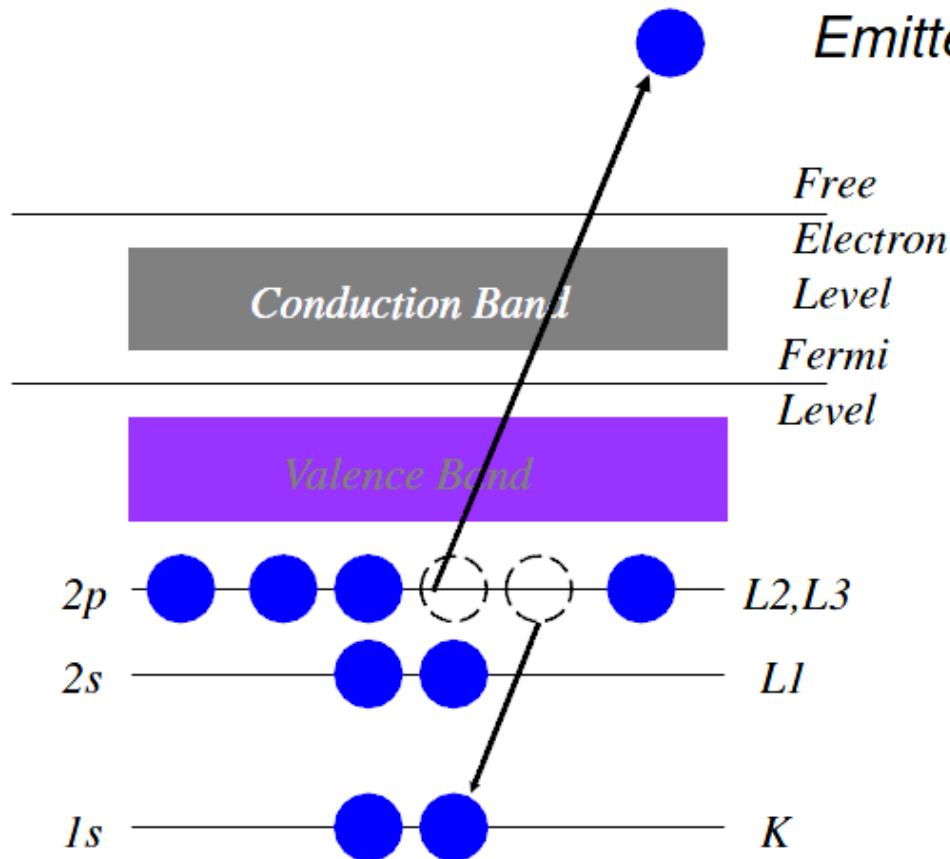


# The Photoelectric Process



XPS involves irradiating a sample with X-rays of a characteristic energy and measuring the flux of electrons leaving the surface. The energy spectrum for the ejected electrons is a combination of an overall trend due to transmission characteristics of the spectrometer, energy loss processes within the sample and resonance structures that derive from electronic states of the material under analysis. The instrumental contribution is an unwelcome fact of the measurement process, but the background and resonance peaks offer information about the sample surface

# Auger Relation of Core Hole

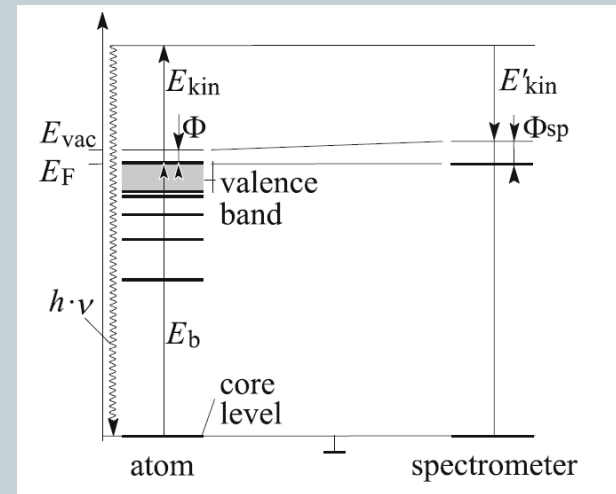
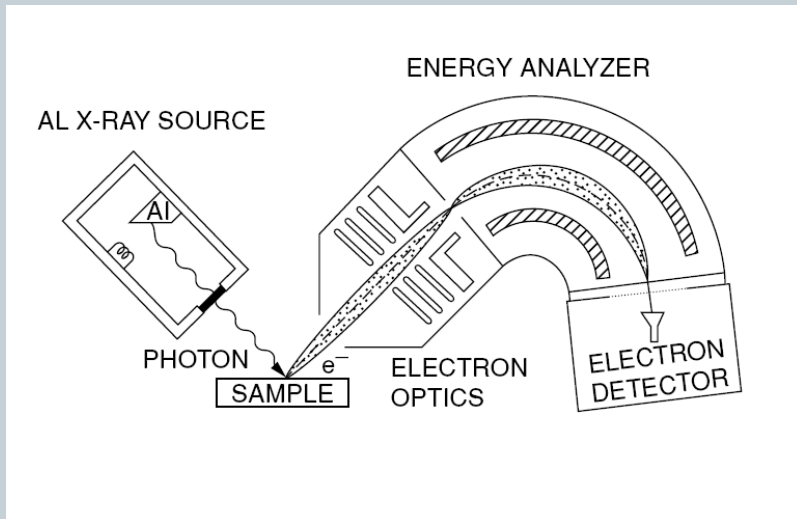


*Emitted Auger Electron*

- *L electron falls to fill core level vacancy (step 1).*
- *KLL Auger electron emitted to conserve energy released in step 1.*
- *The kinetic energy of the emitted Auger electron is:*  
$$KE = E(K) - E(L2) - E(L3).$$



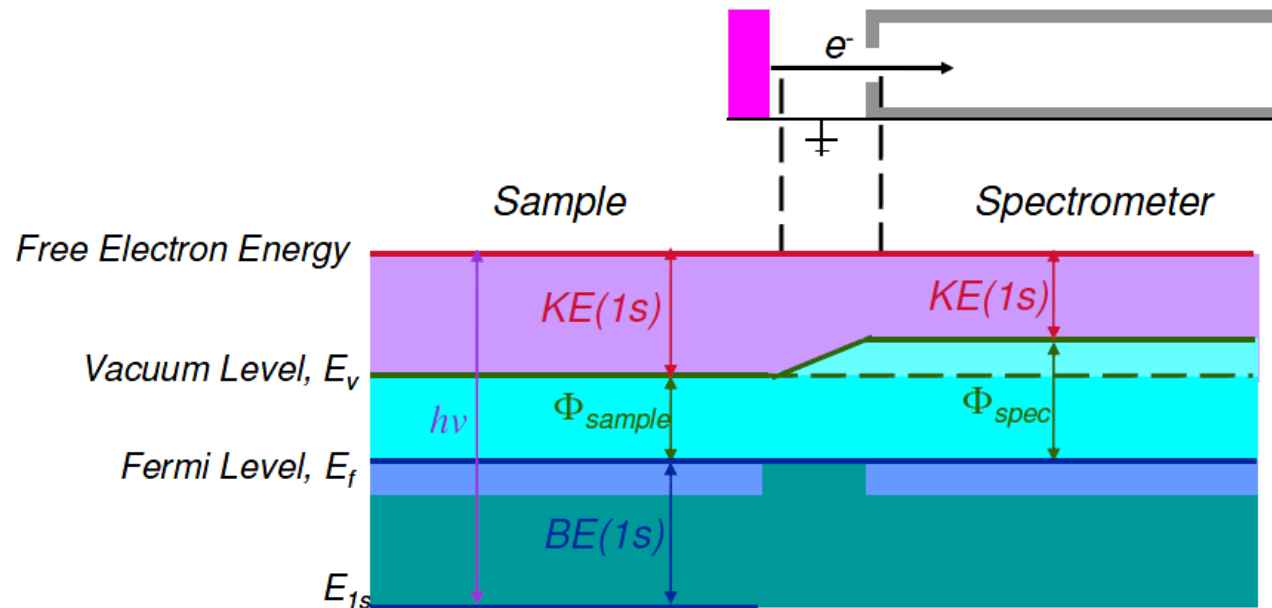
# XPS



$$h \cdot \nu = E_b + E_{kin} + \Phi$$



# Sample/Spectrometer Energy Level Diagram- Conducting Sample



Because the Fermi levels of the sample and spectrometer are aligned, we only need to know the spectrometer work function,  $\Phi_{\text{spec}}$ , to calculate  $BE(1s)$ .

# Chemical Shifts



## Chemical Shifts - Electronegativity Effects

### Carbon-Fluorine Bond

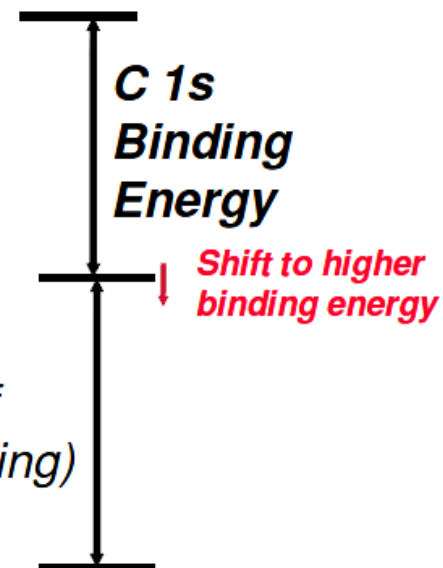
**Valence Level**  
C 2p

**Core Level**  
C 1s



*Fluorine Electro-  
negativity*

*Electron-nucleus  
attraction (Loss of  
Electronic Screening)*



# Chemical Shifts



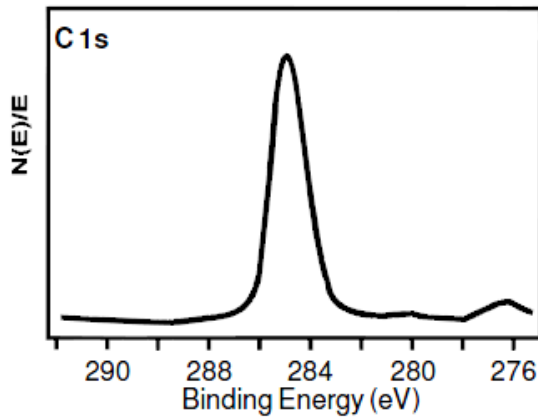
## Chemical Shifts- Electronegativity Effects

<b><i>Functional Group</i></b>		<b><i>Binding Energy (eV)</i></b>
<i>hydrocarbon</i>	<u>C</u> -H, <u>C</u> -C	285.0
<i>amine</i>	<u>C</u> -N	286.0
<i>alcohol, ether</i>	<u>C</u> -O-H, <u>C</u> -O-C	286.5
<i>Cl bound to C</i>	<u>C</u> -Cl	286.5
<i>F bound to C</i>	<u>C</u> -F	287.8
<i>carbonyl</i>	<u>C</u> =O	288.0

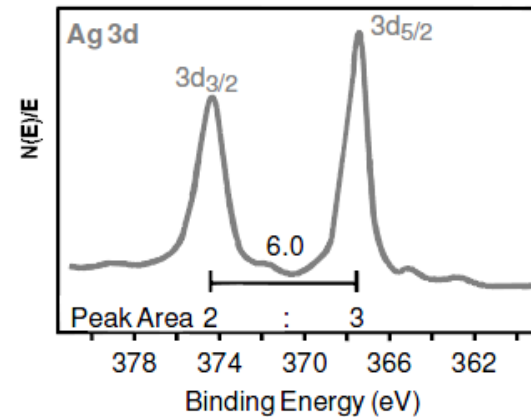
# Final Effects - Coupling



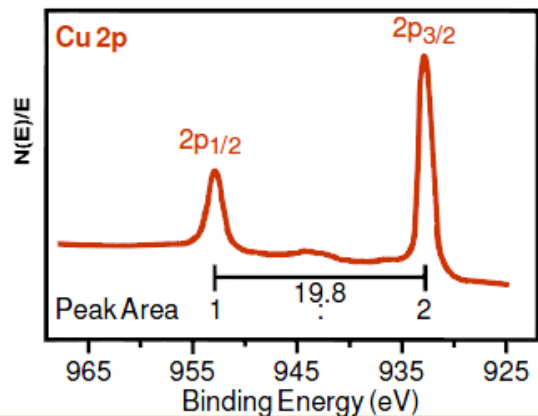
## Electronic Effects - Spin-Orbit Coupling



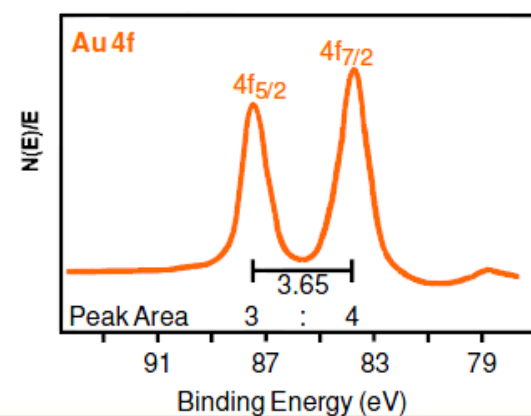
*Orbital=s*  
*l=0*  
*s=+/-1/2*  
*ls=1/2*



*Orbital=d*  
*l=2*  
*s=+/-1/2*  
*ls=3/2,5/2*

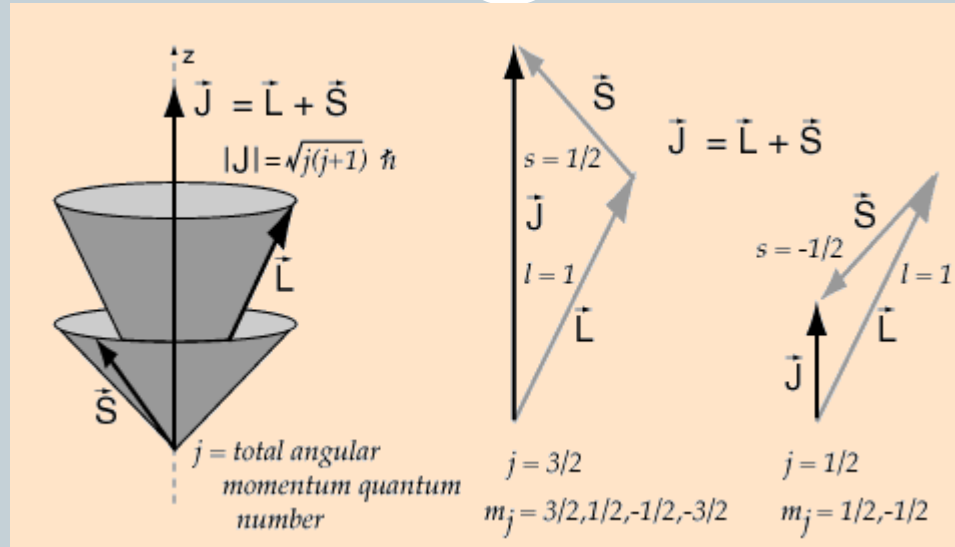


*Orbital=p*  
*l=1*  
*s=+/-1/2*  
*ls=1/2,3/2*



*Orbital=f*  
*l=3*  
*s=+/-1/2*  
*ls=5/2,7/2*

# Angular Momentum Coupling



L-S coupling

J-J coupling

$$\vec{L}_1 + \vec{L}_2 = \vec{L}$$

$$\vec{2} + \vec{2} = 0, 1, 2, 3, 4$$

$$\vec{S}_1 + \vec{S}_2 = \vec{S}$$

$$\vec{1/2} + \vec{1/2} = 0, 1$$

$$\vec{J} = \vec{L} + \vec{S} = 0, 1, 2, 3, 4$$

Light elements

$$\begin{aligned}
 \vec{J}_1 &= \vec{L}_1 + \vec{S}_1 \\
 \vec{J}_2 &= \vec{L}_2 + \vec{S}_2 \\
 &\dots
 \end{aligned}
 \quad
 \vec{J} = \sum_i \vec{J}_i$$

Heavy elements

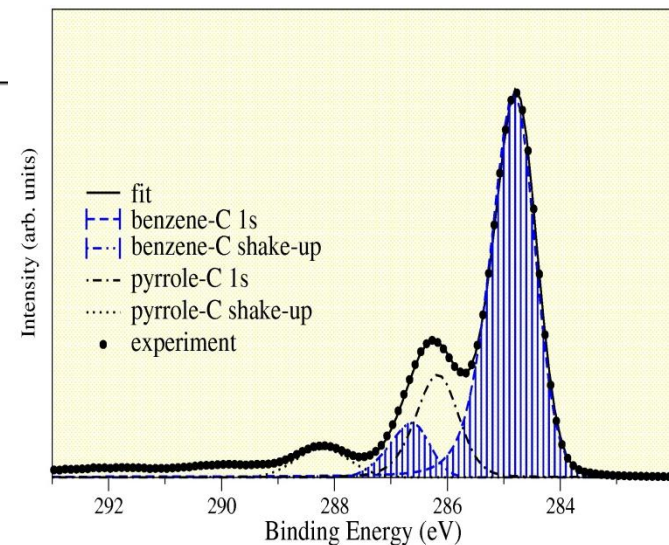
# Final Effects – shake-up

## Final State Effects - Shake-up/ Shake-off

*Results from energy made available in the relaxation of the final state configuration (due to a loss of the screening effect of the core level electron which underwent photoemission).*

**Shake-up:** Relaxation energy used to excite electrons in valence levels to bound states (monopole excitation).

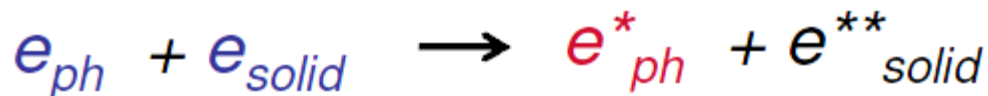
**Shake-off:** Relaxation energy used to excite electrons in valence levels to unbound states (monopole ionization).



970  
925  
Binding Energy (eV)

Figure 8. Examples of shake-up lines (s) of the copper 2p observed in copper compounds.

# Electron Scattering Effects Energy Loss Peaks



## Electron Scattering Effects Plasmon Loss Peak

*Metu*

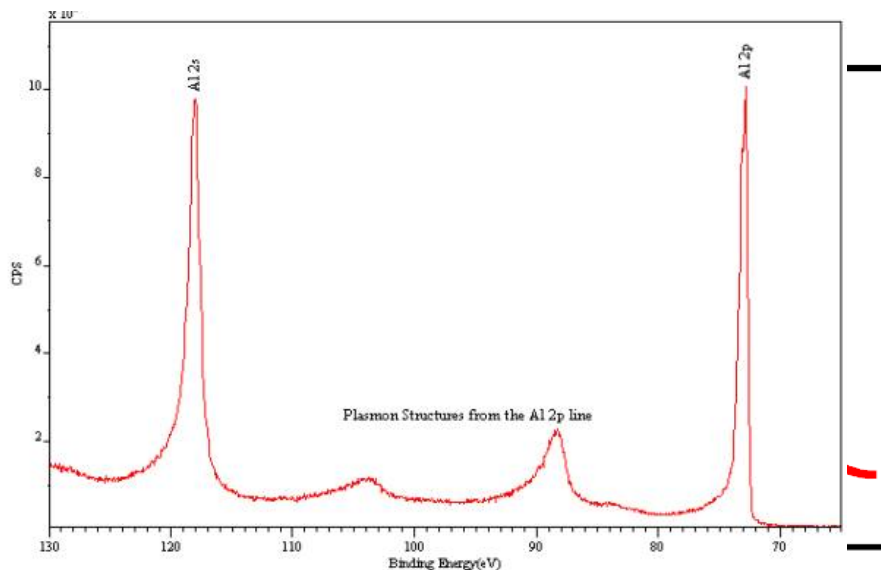
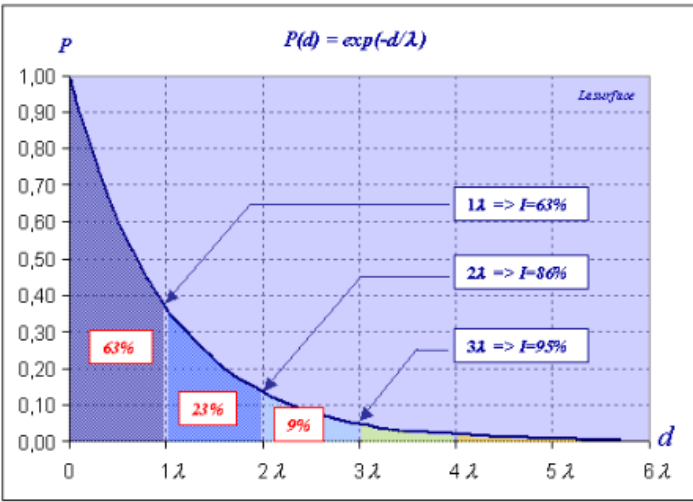


Figure 5: Clean Aluminium Spectrum showing plasmon resonance structures

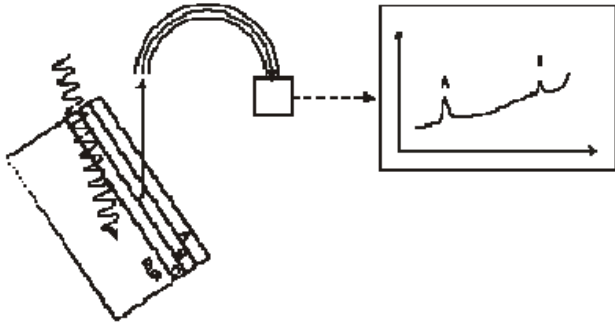
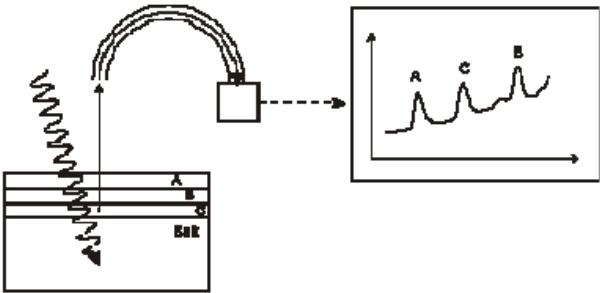
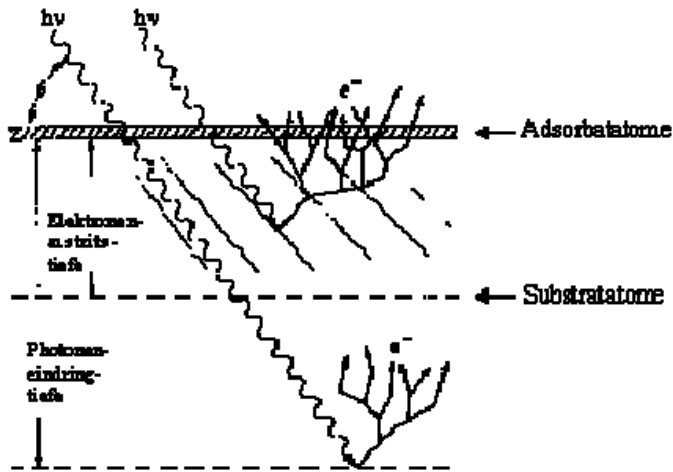
In metals the free electrons are constrained to move within energy bands that are characteristic of the material and these material properties influence the shape of the energy loss distribution, namely, scattering of the photoelectric electrons by free electrons with discrete energy bands produces energy loss distributions with relatively narrow structures.



# Depth of analysis and Mean Free Path



from www.lasurface.com



# Quantification



$$I_A^i \sim Q \mathcal{A} c_A \sigma_A^i \lambda^i T^i L_A^i f(\phi, \theta), \quad (7.25)$$

where  $Q$  is the photon flux [ $\text{cm}^{-1}\text{s}^{-1}$ ],  $\mathcal{A}$  effective area of the sample,  $c_A$  concentration of A,  $\sigma_A^i$  is the partial ionization cross section,  $\lambda^i$  mean free path,  $T^i$  the transmission,  $L_A^i$  angular asymmetry coefficient and  $f(\phi, \theta)$  function, depending on the geometry of the experiment.



$$\frac{I_A^i}{I_B^j} = \frac{c_A \sigma_A^i \lambda^i T^i L_A^i}{c_B \sigma_B^j \lambda^j T^j L_B^j} = \frac{c_A \sigma_A^i L_A^i}{c_B \sigma_B^j L_B^j} R.$$

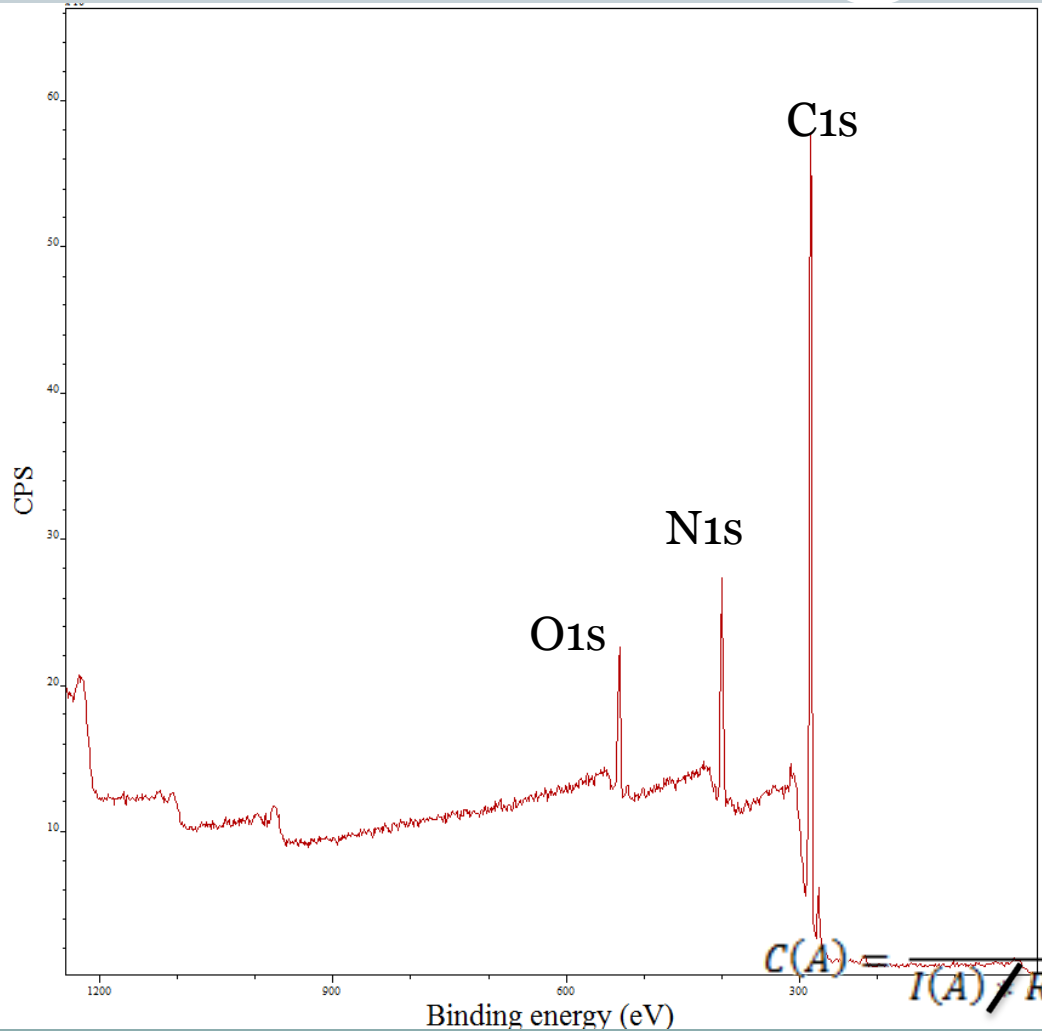
C- concentration  
RSF -relative sensitivity  
factor



$$\frac{I_A^i}{I_B^j} = \frac{c_A S_A^i}{c_B S_B^j}.$$

$$c(A) = \frac{I(A) / \cancel{RSF(A)}}{I(A) / \cancel{RSF(A)} + I(B) / \cancel{RSF(B)} + I(C) / \cancel{RSF(C)}}$$

# Survey Spectra



I (C1s) = 181 080

RSF C1s = 1

I (N1s) = 53 240

RSF (N1s)= 1.8

I (O1s) = 37 700

RSF (O1s) = 2.95

Atomic  
Concentrations :

C= ? at.%

O= ? at.%

N= ? at.%

$$C(A) = \frac{I(A) / RSF(A)}{I(A) / RSF(A) + I(B) / RSF(B) + I(C) / RSF(C)}$$

# Narrow Scan

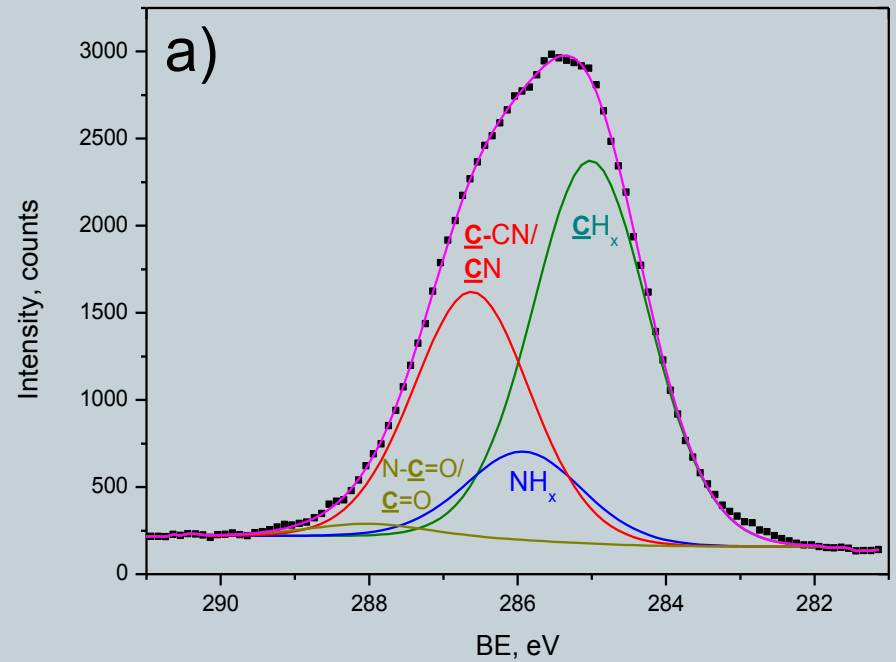
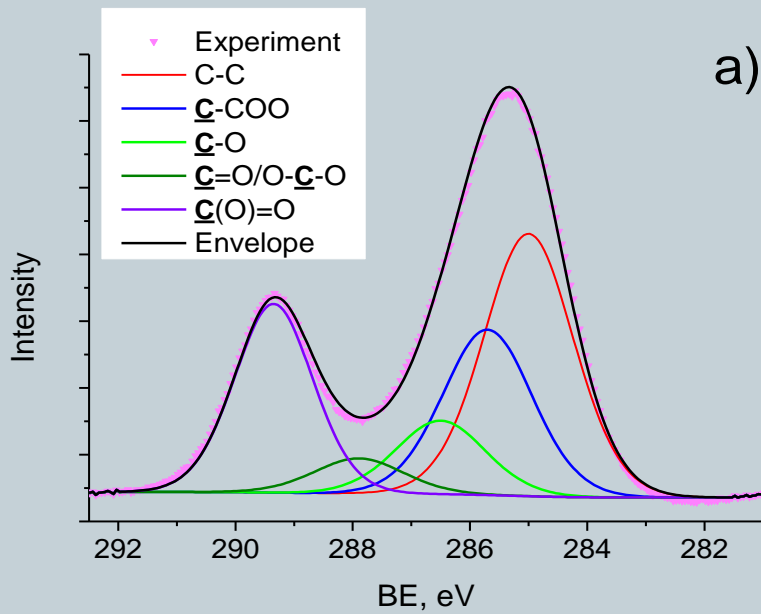


## C1s

## C1s

### Carboxyl Layer

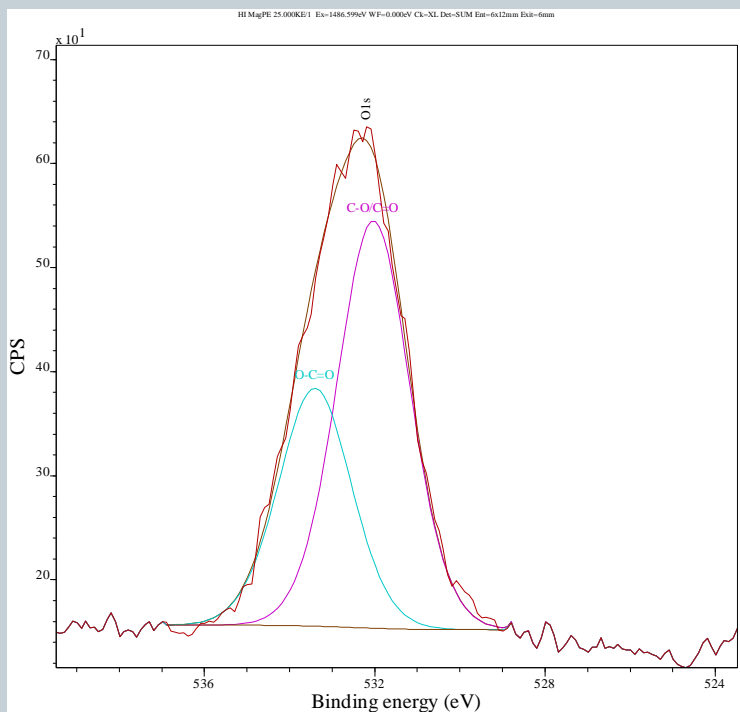
### Amine Layer



# Narrow Scan -> Environments

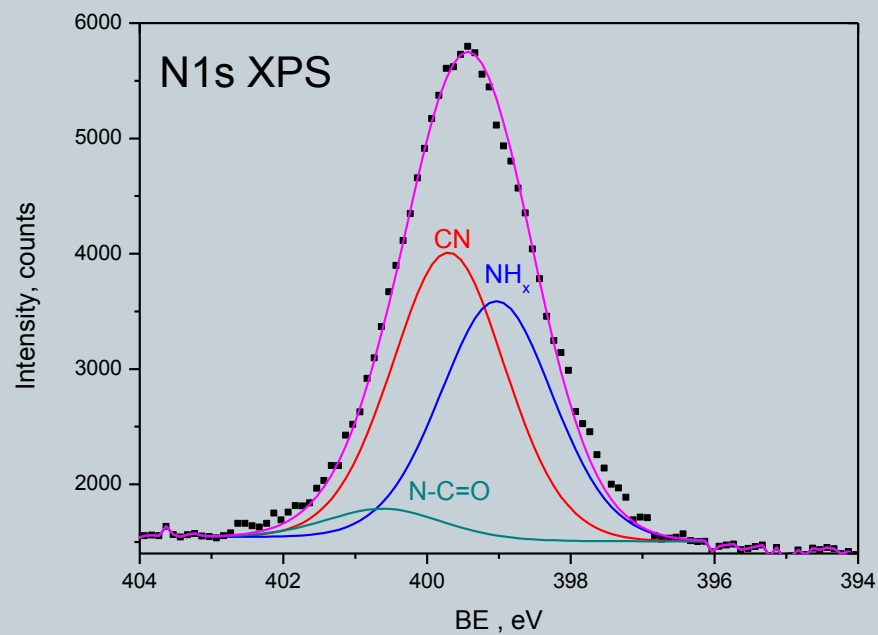


**O1s** Carboxyl Layer



Amine Layer

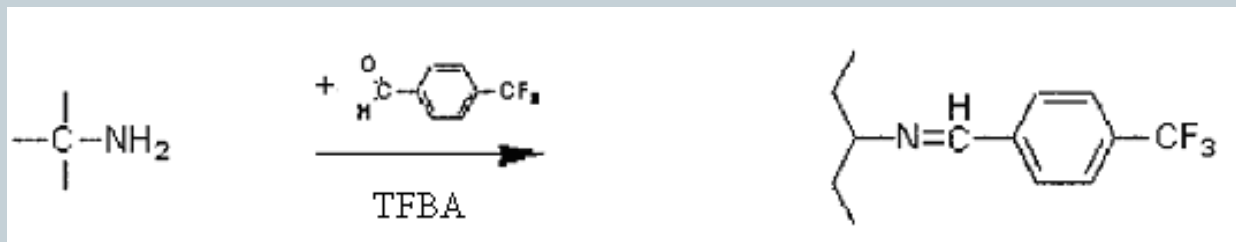
**N1s**



# Chemical derivatization CD-XPS



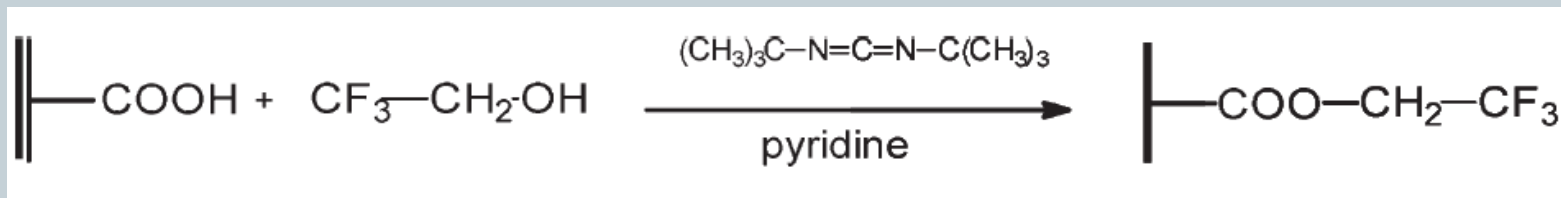
## Derivatization of Primary Groups



$$\frac{[NH_2]}{[C]} = \frac{[F]/3}{[C] - 8[F]/3} \times 100\%$$

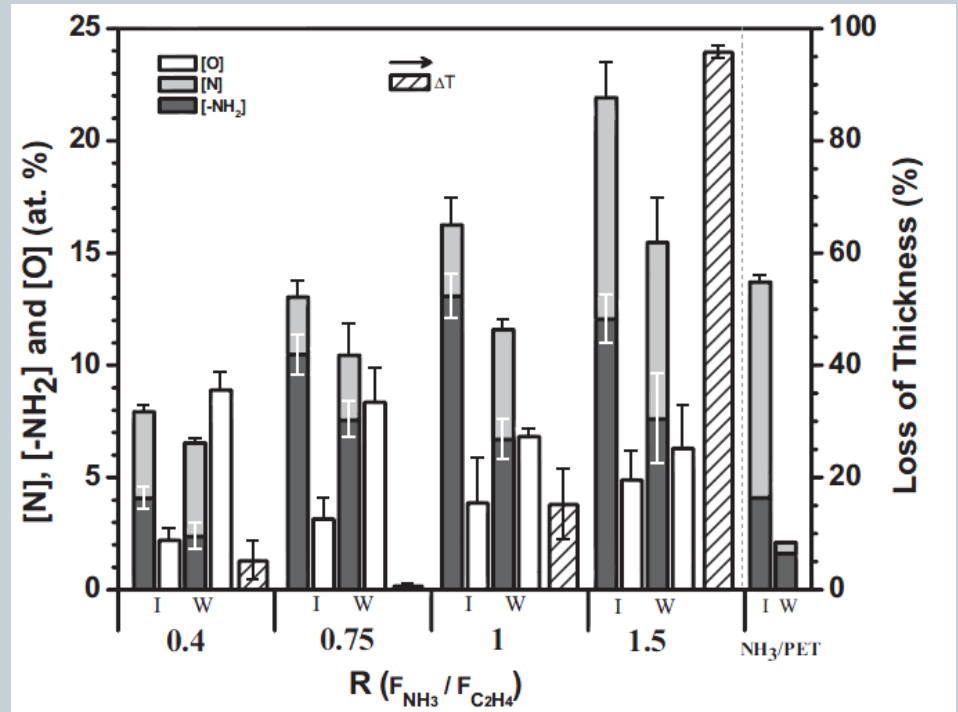
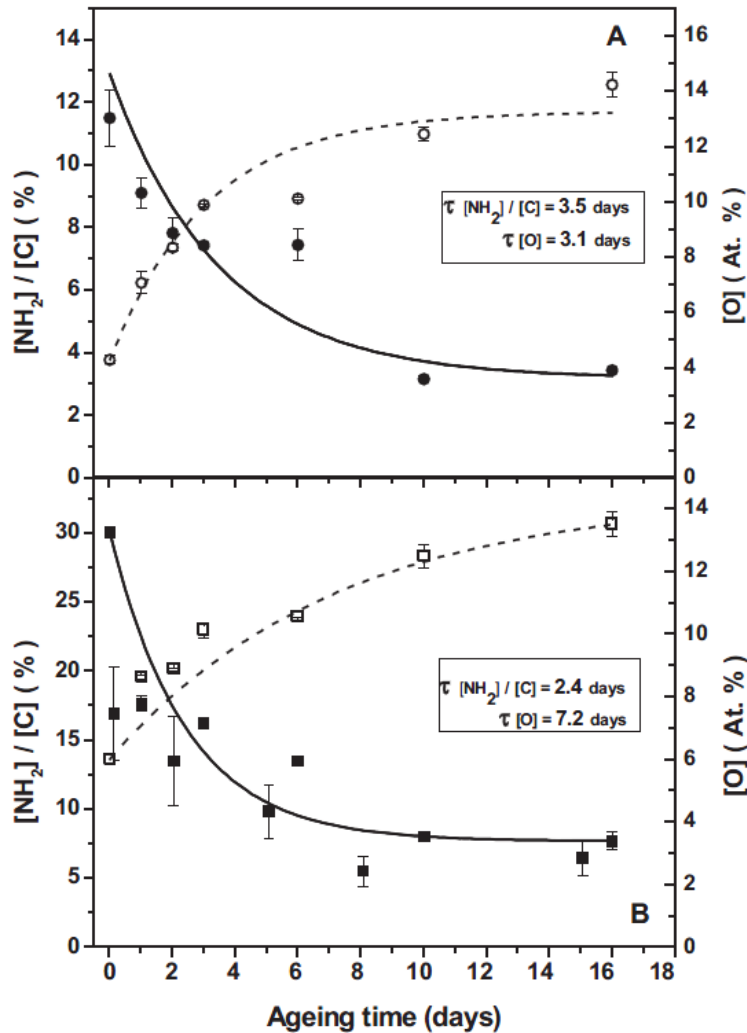
$$\frac{[NH_2]}{[N]} = \frac{[F]/3}{[N]} \times 100\%$$

## Derivatization of Carboxyl Groups



$$[COOH] = \frac{[F]}{3[C] - 2[F]} \times 100\%$$

# PECVD of C<sub>2</sub>H<sub>4</sub>+NH<sub>3</sub>



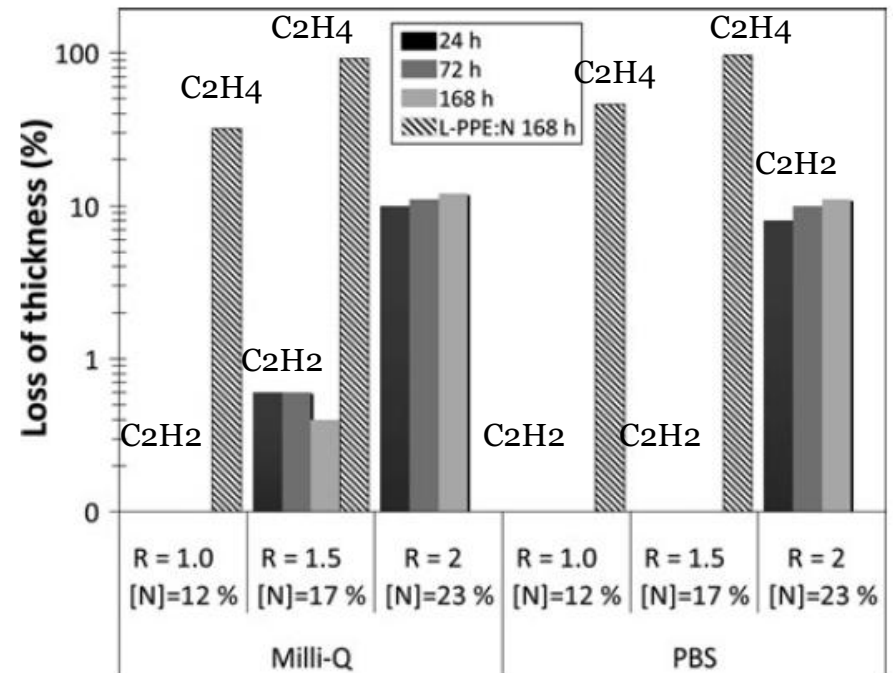
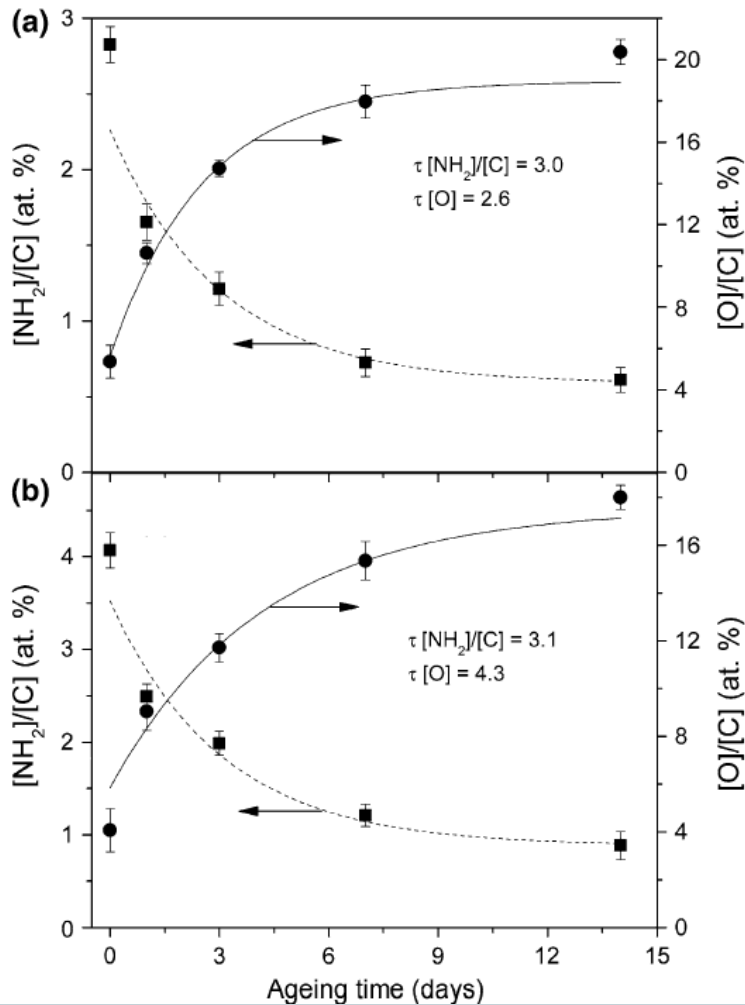
More nitrogen – more amines but higher thickness loss.

J.-C. Ruiz, A. St-Georges-Robillard, C. Thérèse, S. Lerouge, M. R. Wertheimer

*Plasma Process. Polym.* 2010, 7, 737–753

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# Stability of amine films prepared from $\text{NH}_3$ / $\text{C}_2\text{H}_2$ mixture

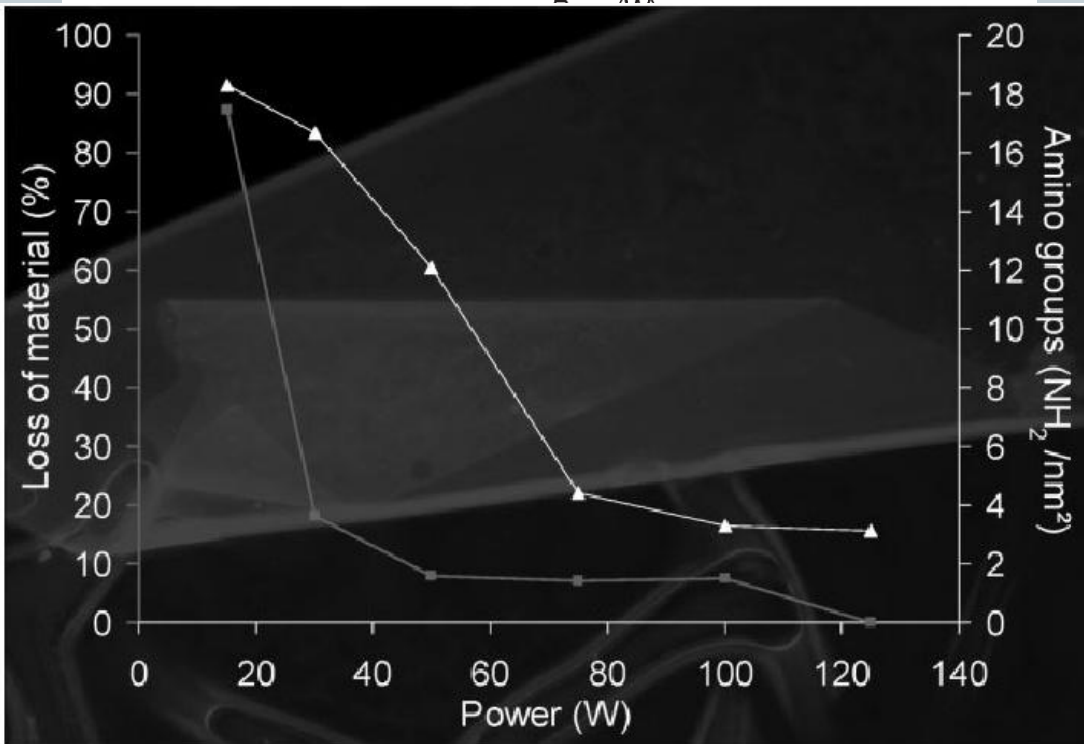
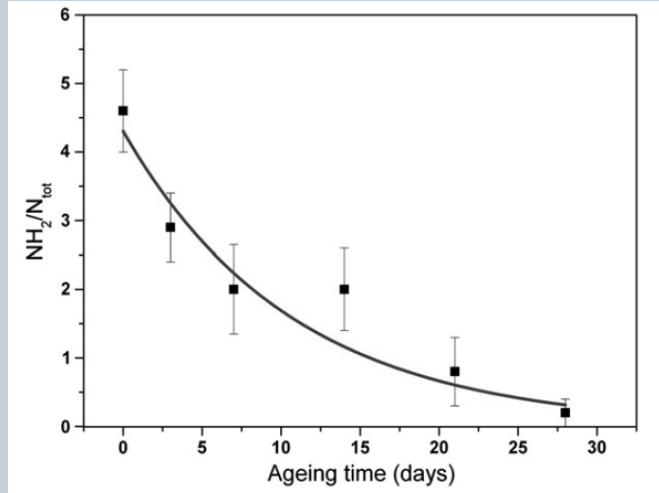
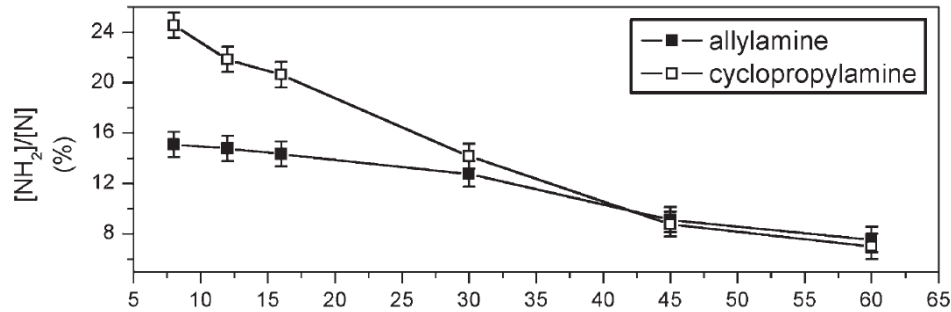


More nitrogen – more amines but higher thickness loss.

Angel Contreras-Garcia • Michael R. Wertheimer Plasma Chem Plasma Process (2013) 33:147–163



# AllylAmine Plasma Polymers



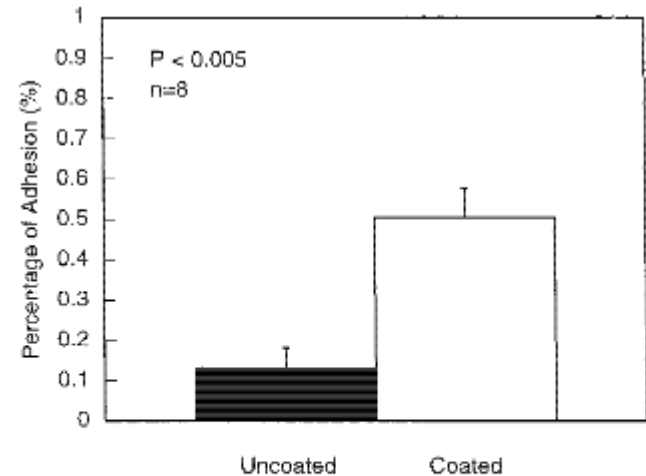
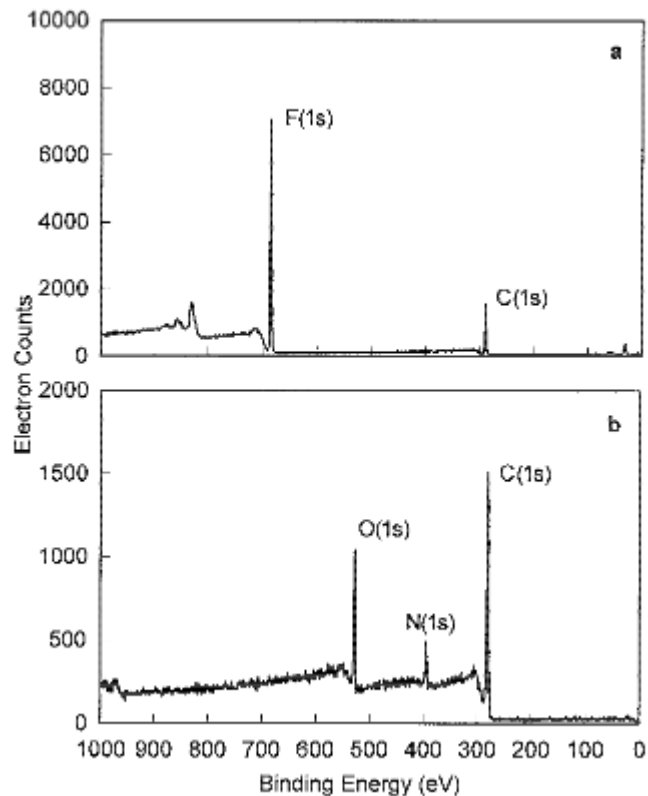
High concentration of amines in AA pp can be obtained only at low plasma power but it leads to huge loss of material.

# Effects of amide and amine plasma-treated ePTFE vascular grafts on endothelial cell lining in an artificial circulatory system

David Y. Tseng,<sup>1</sup> Elazer R. Edelman<sup>1,2</sup>

<sup>1</sup>Harvard-MIT Division of Health Sciences and Technology, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

<sup>2</sup>Department of Medicine, Cardiovascular Division, Brigham and Women's Hospital, Harvard Medical School, Boston, Massachusetts 02115



**Figure 6.** Bar graph showing the percentages of endothelial cell adhesion on plasma coated (open bar) and uncoated (solid bar) PTFE disks, respectively. Statistical analysis showed a significant difference of endothelial cell adhesion between uncoated and coated PTFE disks ( $p < 0.005$ ,  $n = 8$ ). The data are presented as mean  $\pm$  SE.

# Cell Proliferation



## Surface properties of and cell adhesion onto allylamine-plasma-coated polyethyleneterephthalat membranes

P. Hamerli, Th. Weigel\*, Th. Groth, D. Paul

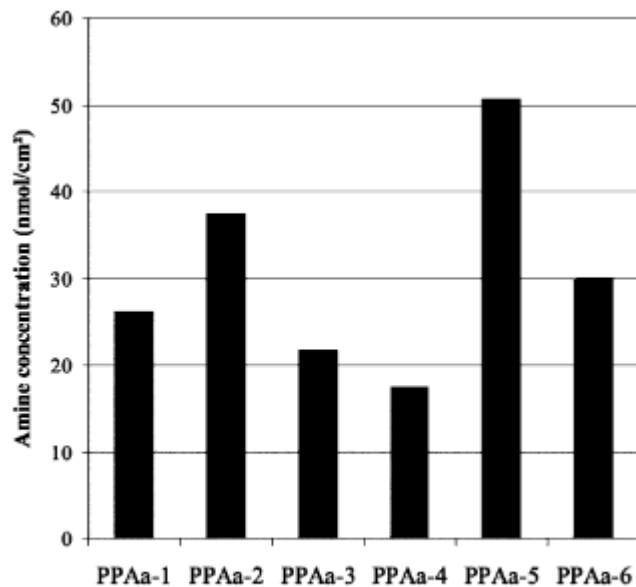


Fig. 4. Amine concentration of deposited allylamine films.

