Modeling of surfaces: the third dimension in XPS analysis of multilayer structures

Antonella Rossi

Universita' degli Studi di Cagliari (Italy)
and Laboratory for Surface Science and Technology
Department of Materials
Swiss Federal Institute of Technology (ETH)
Zürich, Switzerland

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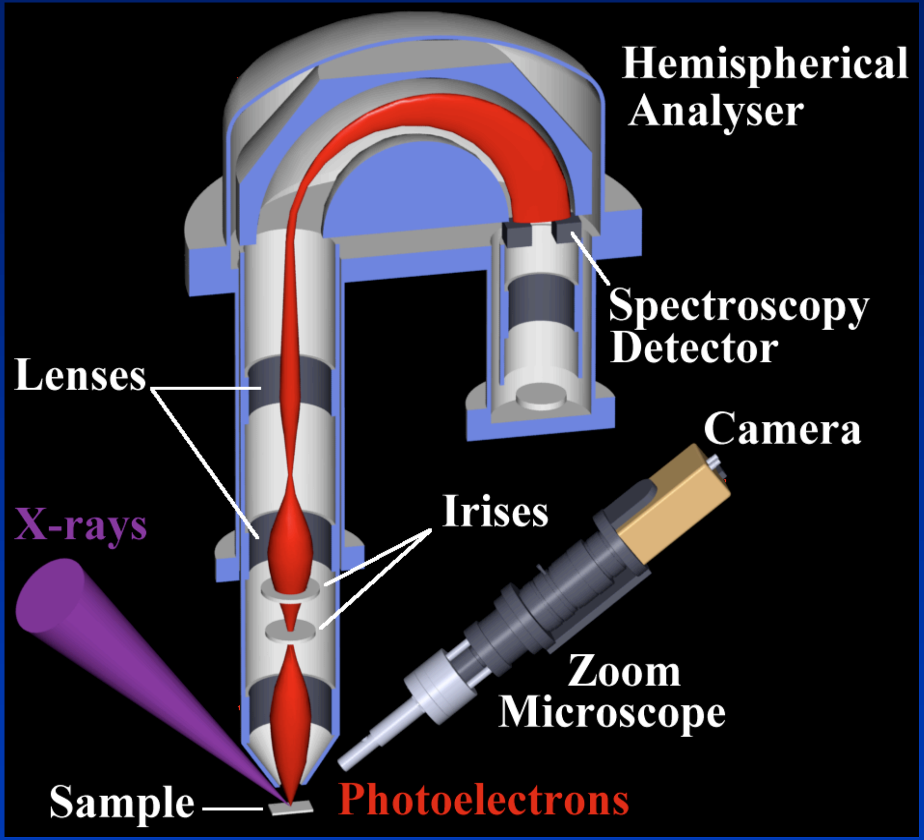
XPS Analysis

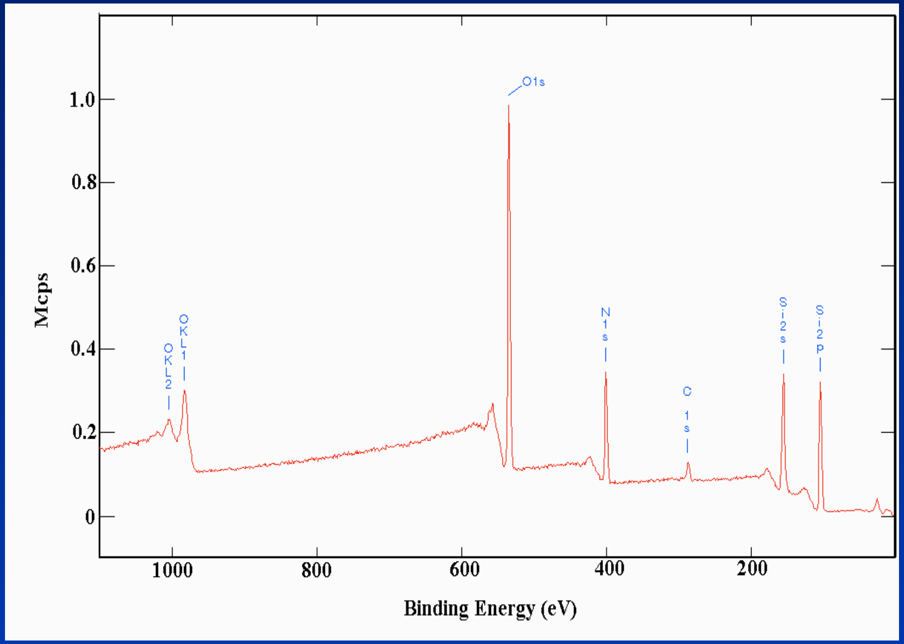
- The material to be analyzed is in UHV
- The surface is irradiated with photons in X-ray range (Alkα 1486.6 eV)
- The emitted e- are separated according to their energy by the analyzer and counted

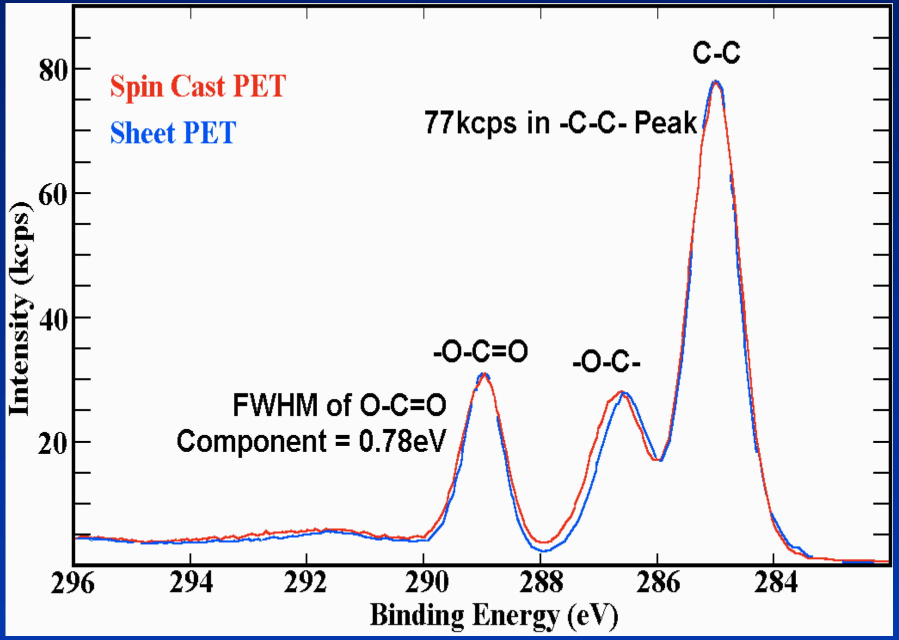


Courtesy of Thermo VG Scientific

X-ray Photoelectron Spectroscopy (XPS)

Type of information

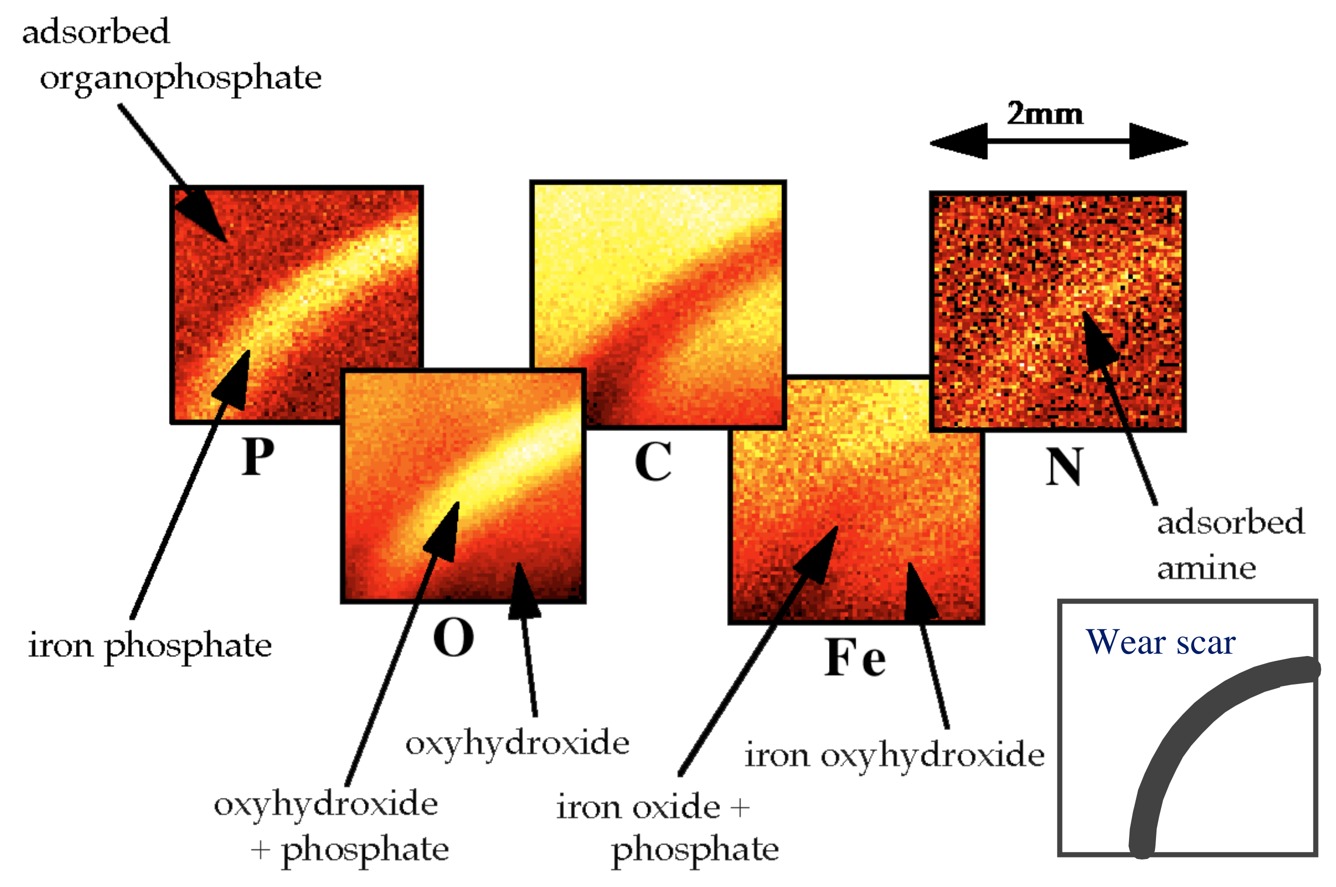




elemental identification

chemical state identification

Imaging XPS Study of Additive-Surface Interactions

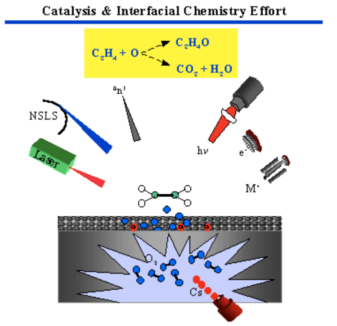


Irgalube® 349/PAO/100Cr6 following tribotesting

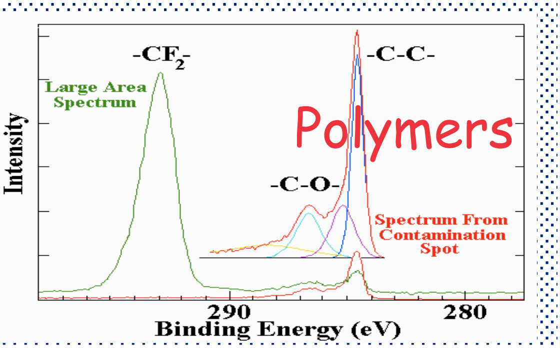
A. Rossi, K. Matsumoto, N.D. Spencer 1998 PPM Materials - ETH-LSST

Quantitative analysis is mainly performed under the assumption of the homogeneity of a material.

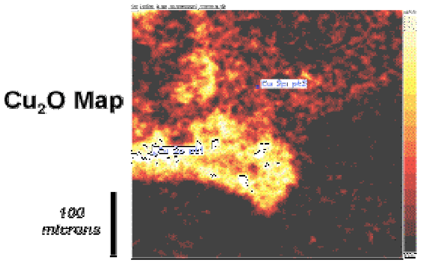
Catalysis



Polymers

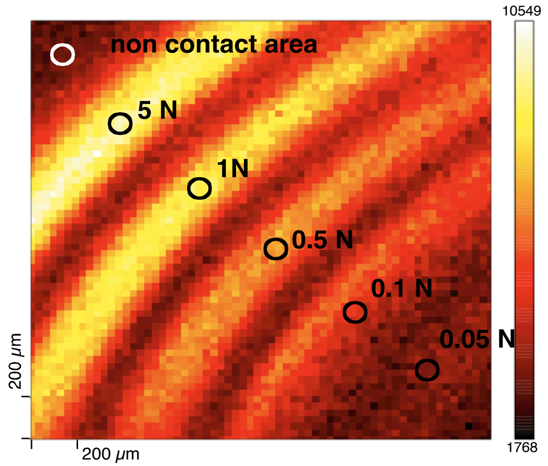


Corrosion



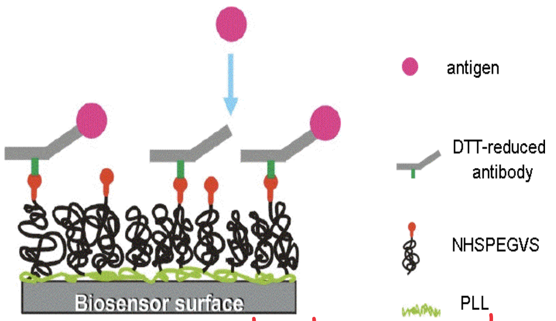
www.uwo.ca/ssw/

Tribology



M.Eglin, A. Rossi, N.D.Spencer, Trib. Letters,

Biomaterials



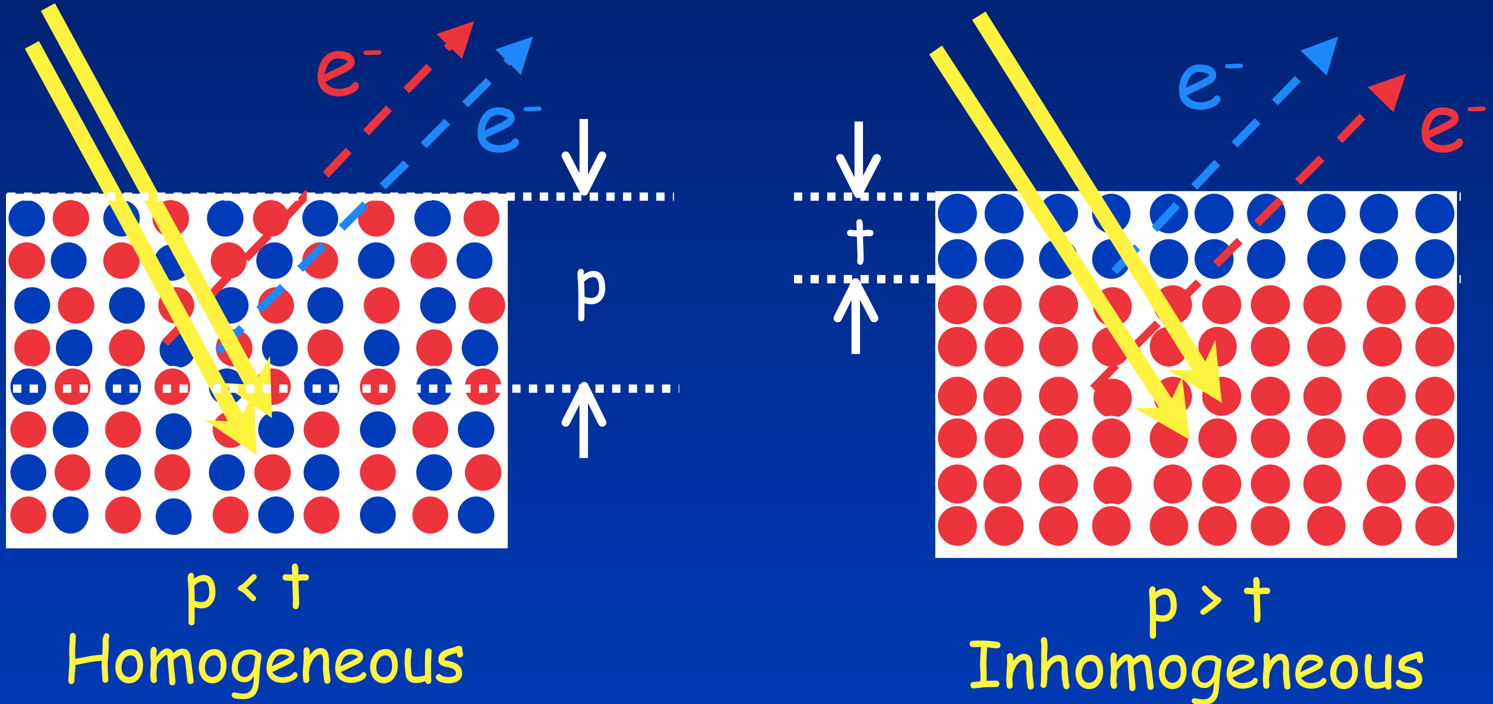
www.textorgroup.ch

The need of the study of very thin films with a depth resolution on the nanometers range stimulates the proposal of **new models** for XPS quantification.

Outline

- The need for quantitative XPS information
- Real surfaces
- Modeling of real surfaces: the three layer model
- Examples
- Outlook

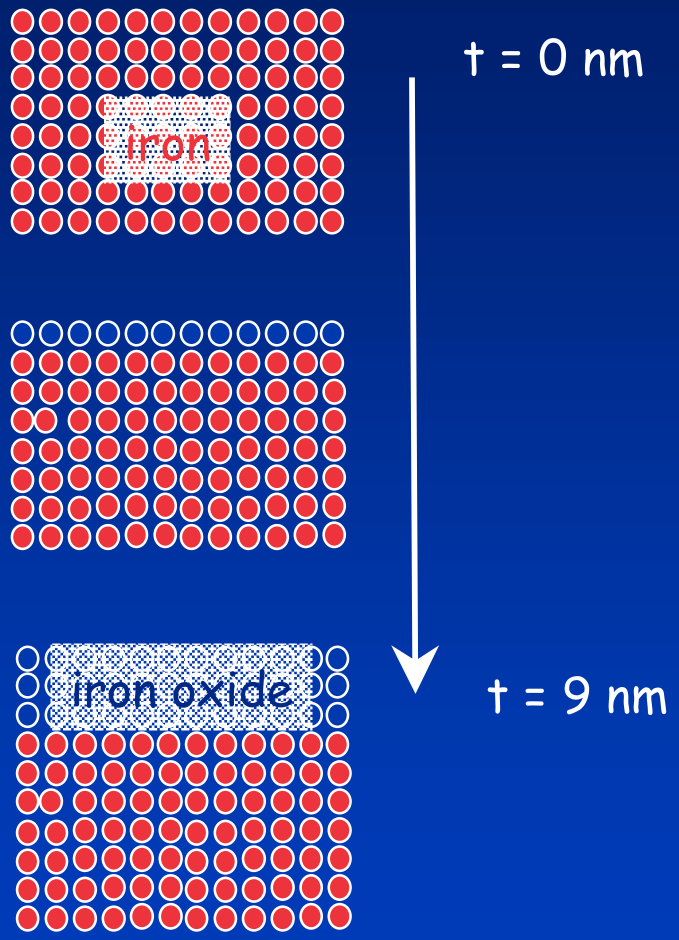
XPS depth resolution in the nanometer range

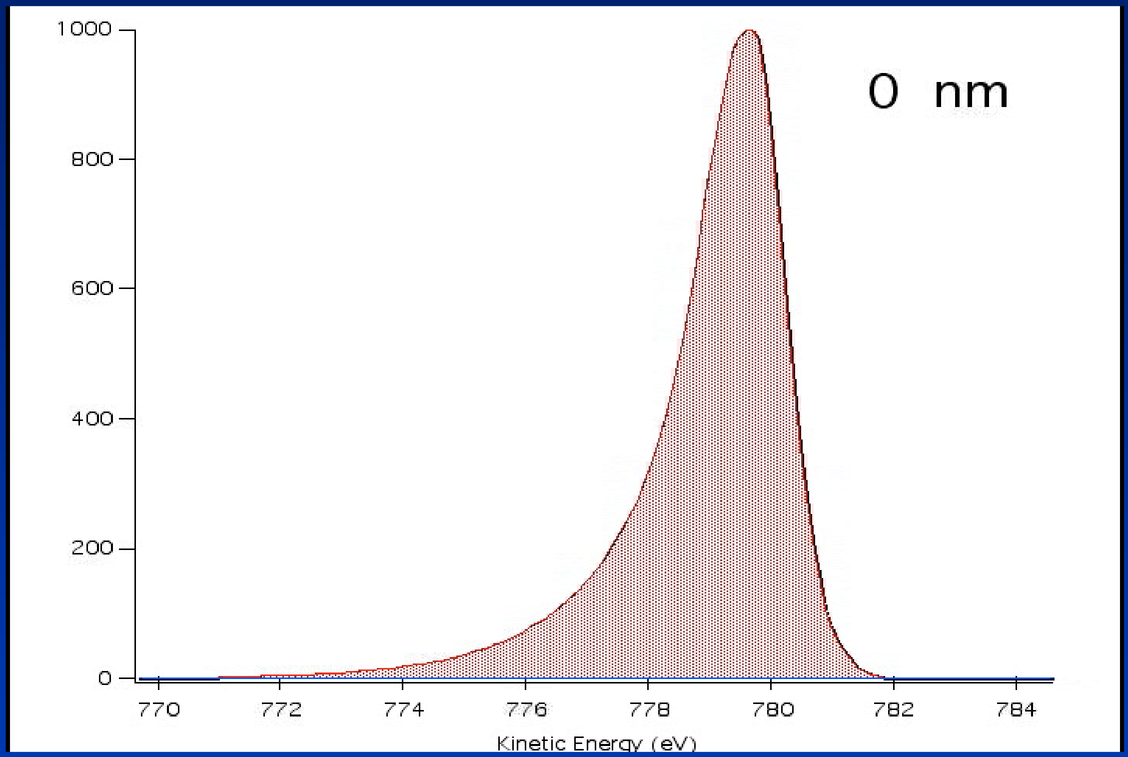


p sampling depth, t thickness of layer

Attenuation of XPS photoelectrons

Example of an iron oxide layer on iron

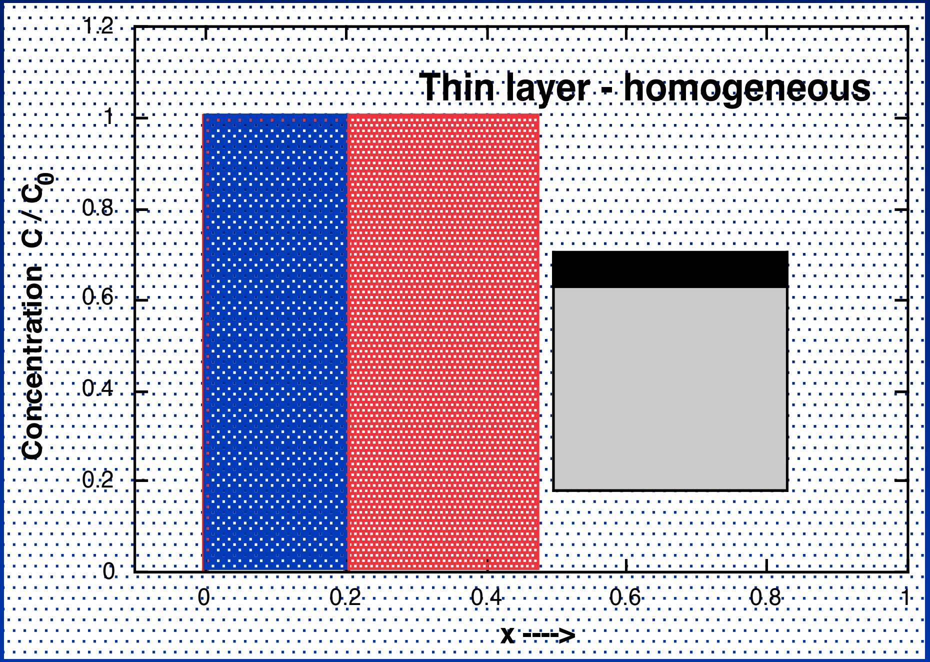


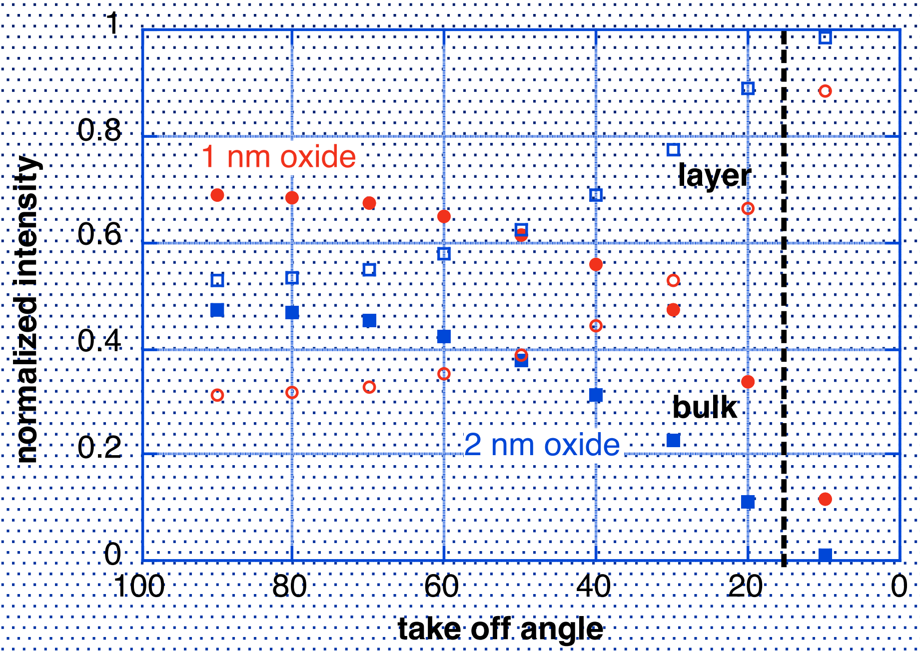


Electrons from the bulk are attenuated by any layer on the surface

Modeling oxide layer - ARXPS

Example of an iron oxide layer on iron





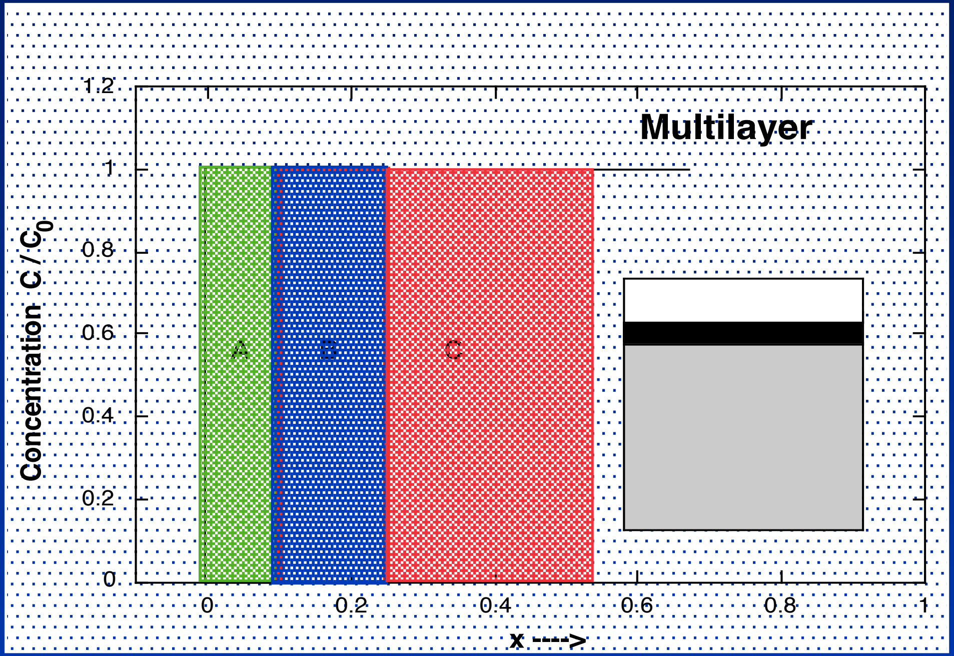
$I_{bulk} = I_{bulk}^{0}\ \mathrm{exp}\ (-x_L\ /\ (\square_L\ \sin(\square)\ )$ decreases with x_L and angle

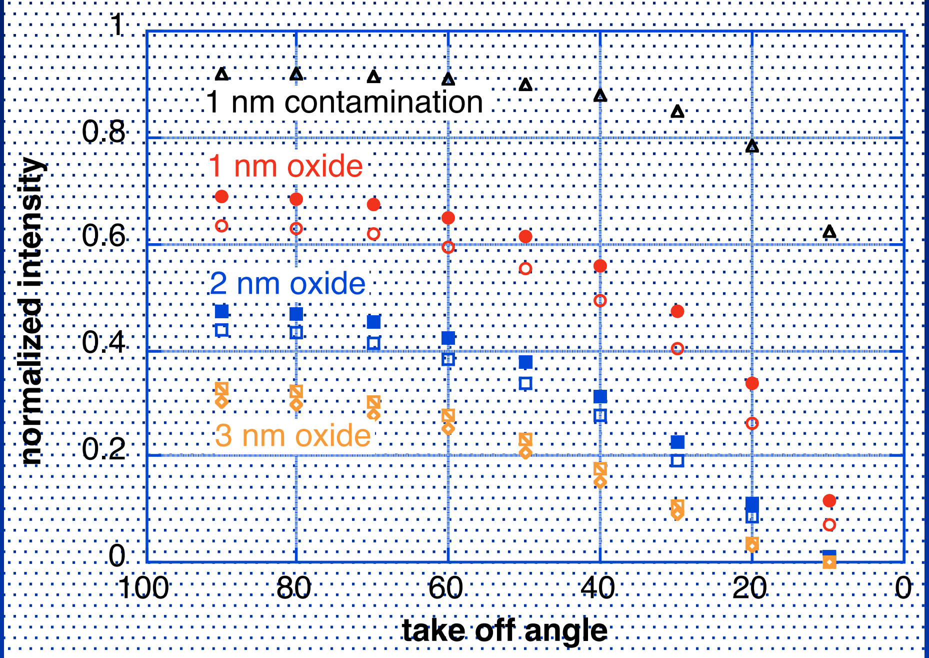
$I_{Layer} = I_L^{\infty}\ (1 - \mathrm{exp}\ (-x_L\ /\ (\square_L\ \sin(\square)\ )$ increases with x_L and angle

Electrons from the bulk are progressively attenuated at lower take off angles.

Modeling contamination overlayer - ARXPS

Example of an iron oxide layer on iron with contamination





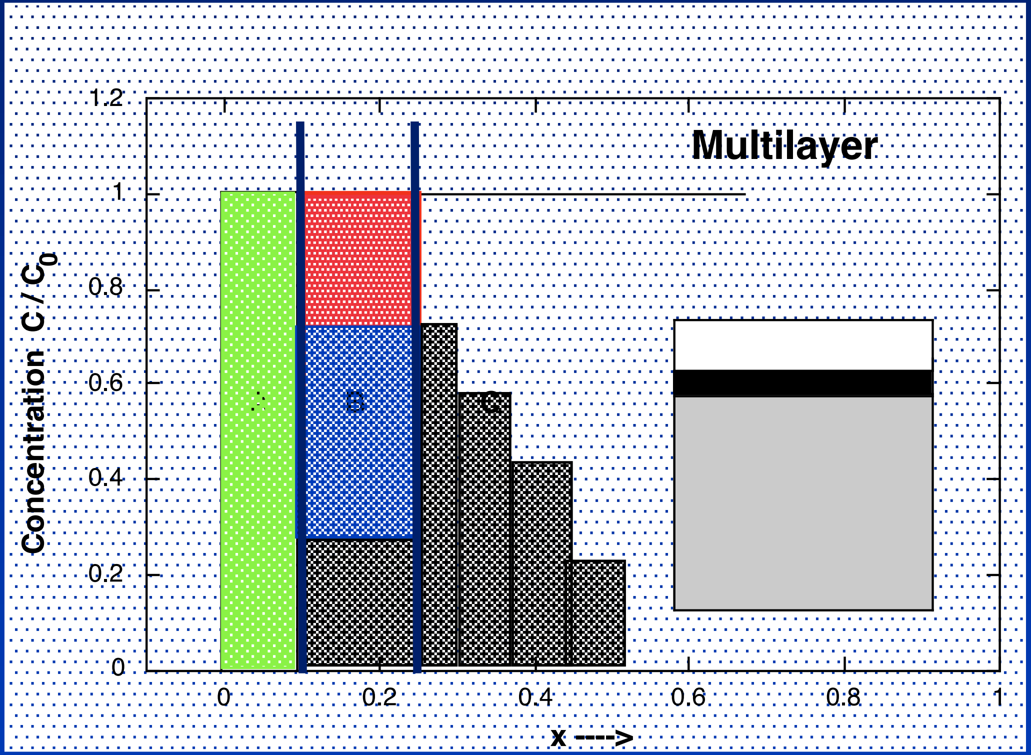
$$I_{bulk} = I_{bulk}^{0} \exp\left(-x_L / (\lambda_L \sin(\theta)\right) * \exp\left(-x_C / (\lambda_L \sin(\theta)\right)$$

$$I_{Layer} = I_L^{\infty} \left(1 - \exp\left(-x_L / (\lambda_L \sin(\theta)\right)\right) * \exp\left(-x_L / (\lambda_L \sin(\theta)\right)$$

Layer thickness x_L and x_c are corrected for density

Modeling of multicomponent real surfaces

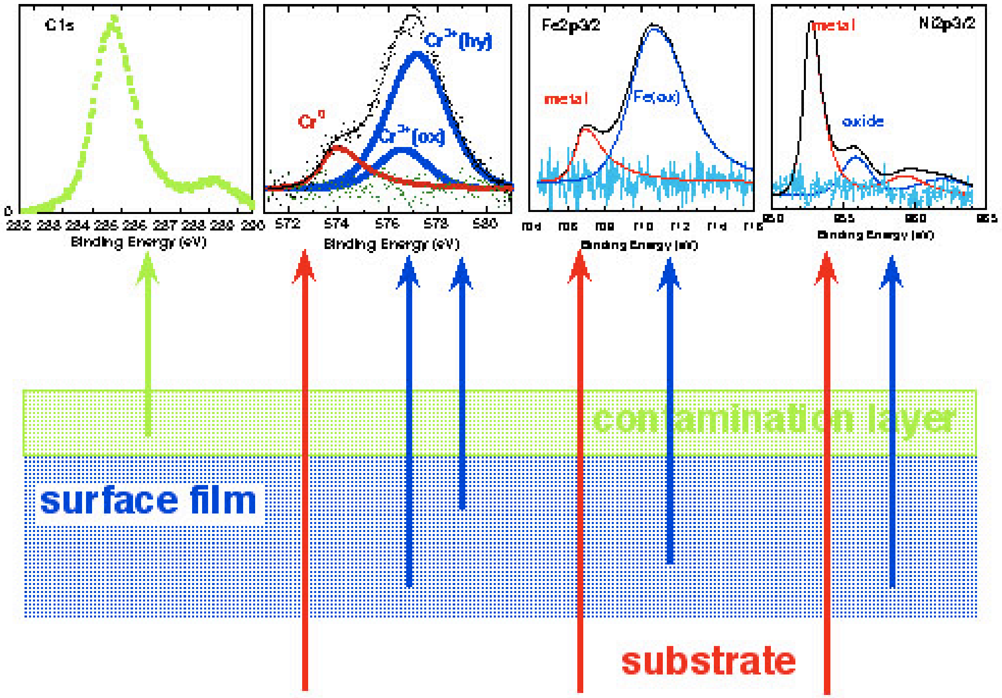
Real surfaces are multicomponent with unknown in-depth
Distribution and a contamination overlayer



- ➢ Electron attenuation
- ➢ Effect of layer density
- ➢ Gradients in composition
- ➢ Contamination overlayer

How to calculate composition and thickness from XPS data ?

Three layer model for real surfaces



Each layer is homogeneous in thickness, composition and density

Electron attenuation

K. Asami, K. Hashimoto, Corrosion Science, 24, 83, 1984

A.Rossi and B. Elsener, Surface and Interface Analysis, 18, 1992, 499-504.

B. Elsener and A. Rossi, Electrochimica Acta, 37, 1992, 2269-2276

Three-layer model: the equations

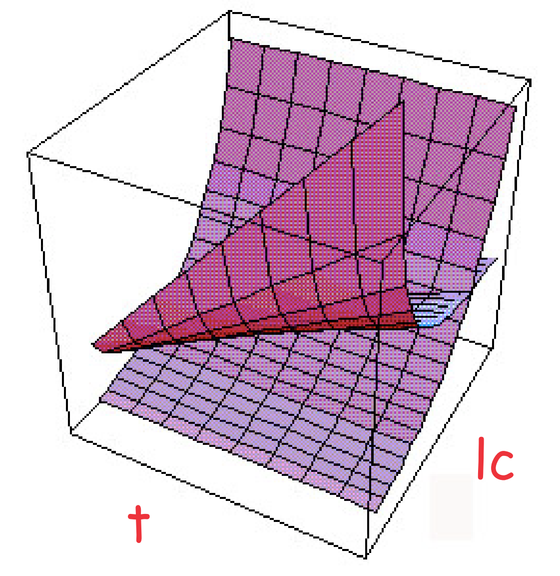
$$I_i^{ox} = \left[\frac{[g_i \square_i^{ox} C_i^{ox} \square^{ox} \square_i^{ox}]}{A_i} \right] * \left[1 \square \exp\left(\square t \big/ \square_i^{ox} \right) \right] * \exp\left(\square l_c \big/ \square_i^{c} \right)$$

$$I_i^{sub} = \left[\frac{[g_i \square_i^{sub} C_i^{sub} \square^{sub} \square_i^{sub}]}{A_i} \right] * \left[\exp\left(\square t \big/ \square_i^{ox} \right) \right] * \exp\left(\square l_c \big/ \square_i^{c} \right)$$

Three-layer model: parametric equations

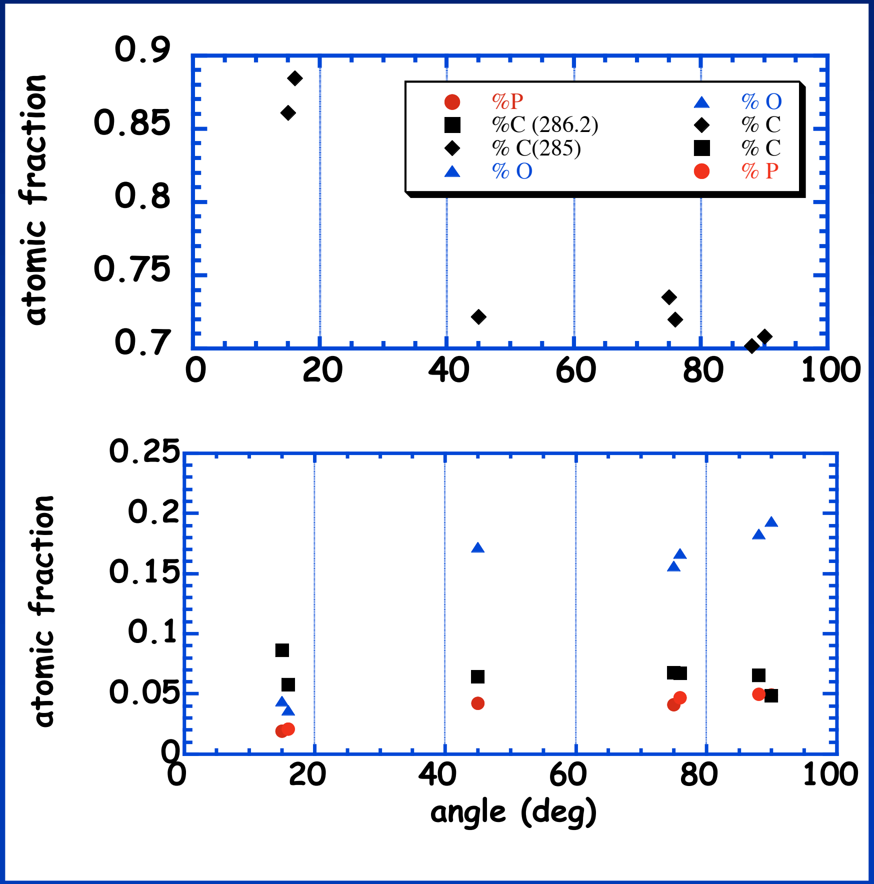
$$f_1(t,lc) = \left(\frac{\square^{ox}}{\square^{sub}}\right)\square_i I_i^{sub}k_i^{sub}\exp\left(\square t/\square_i^{ox}\right) * \exp\left(\square l_c/\square_i^{c}\right)\square\square^{ox}$$

$$f_2(t,l_c) = \left(\frac{l_c K_c \square_{ox}}{1\square\exp\left(\square l_c/\square_i^{c}\right)}\right)\square\square^{ox}$$

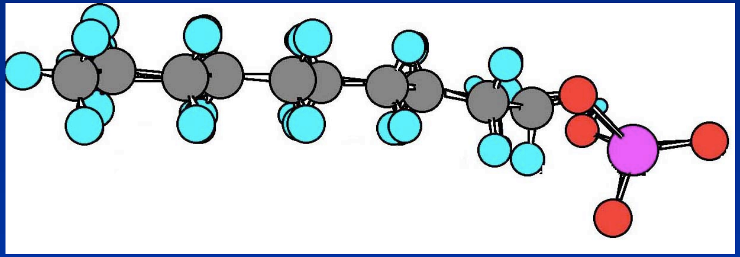


Numerical methods based on versions of Newton's method are used to find numerical approximations to the solutions of the equations. The composition of each layer are calculated simultaneously.

Self-Assembled Monolayers
ODP on Ta_2O_5 ARXPS



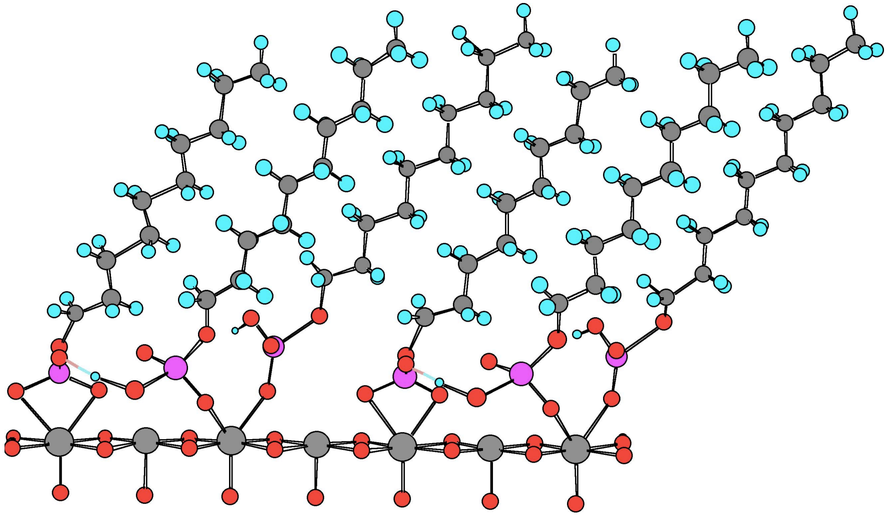
ODP = $C_{18}H_{37}OPO(O_2)$



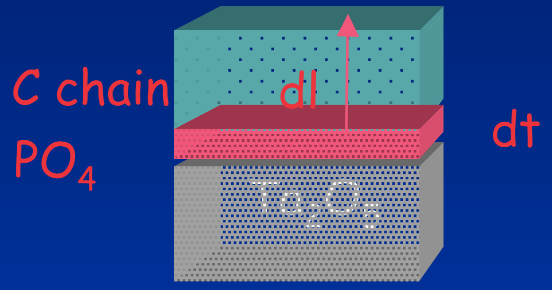
Phosphate head is at the interface

*M. Textor, L.Ruiz, R. Hofer, A. Rossi, K.Feldman, G. Hähner and N.D. Spencer, Langmuir, 2000, 16, 3257-3271

Self-Assembled Monolayers
ODP on Ta_2O_5



C is dark grey, H is light blue, **P is pink**,
O is red, Ta is grey



layer homogeneity
e- attenuation according
to Lambert-Beer law
no gradients

*M. Textor, L.Ruiz, R. Hofer, A. Rossi, K.Feldman, G. Hähner and N.D. Spencer,
Langmuir, 2000, 16, 3257-3271

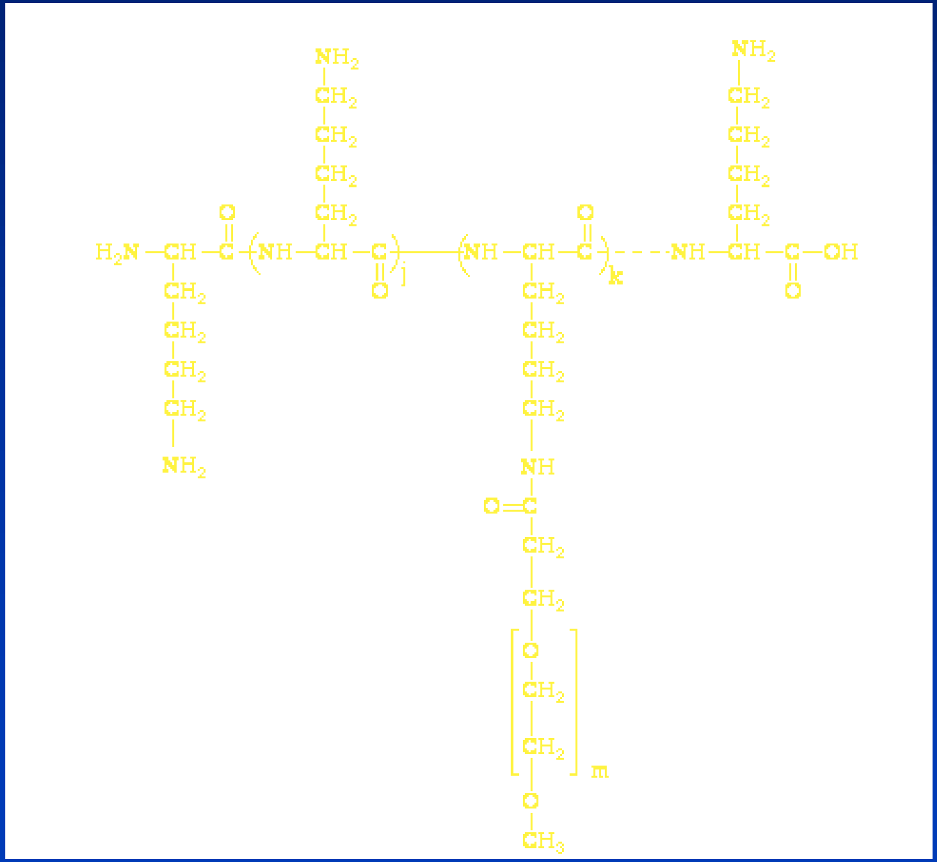
Self-Assembled Monolayers
ODP on Ta_2O_5

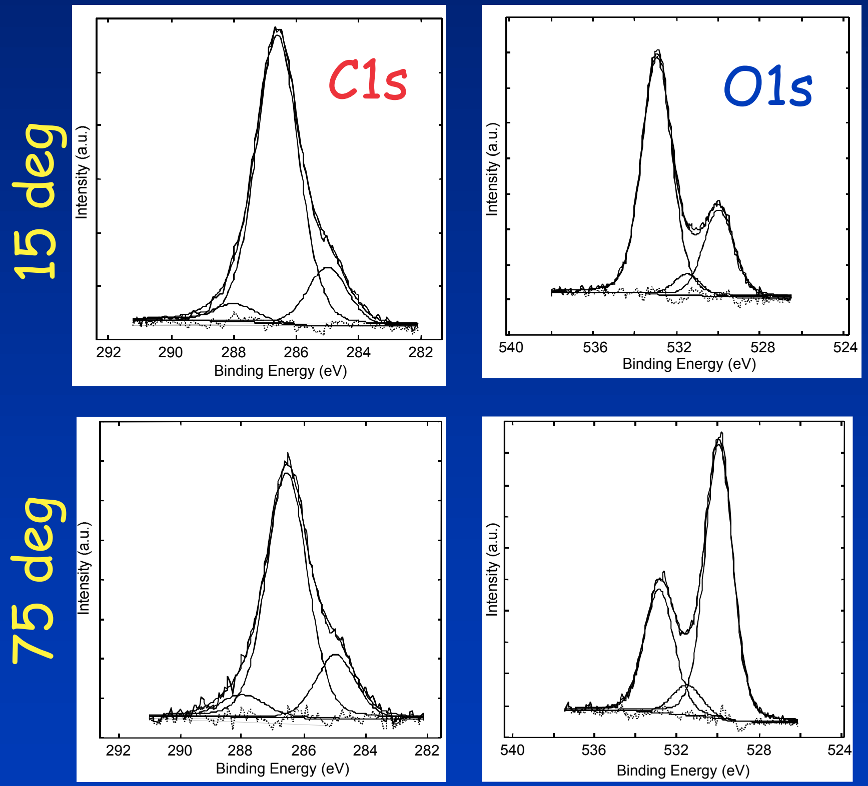
Thickness and composition of self-assembled ODP monolayer on Ta2O5 *.

	C	O	P	O	Ta
	ODP chain	polar head		substrate Ta2O5	
thickness (nm)	lc = 1.2±0.2	$t = 1.2 \pm 0.1_5$		semi infinite	
composition weight%					
theoretical	-	67.4	32.6	18.1	81.9
experimental	-	69±1	31±1	17.3±1	82.7±1

*M. Textor, L.Ruiz, R. Hofer, A. Rossi, K.Feldman, G. Hähner and N.D. Spencer, Langmuir, 2000, 16, 3257-3271

Protein resistant biomaterials
PLL-g-PEG on Nb_2O_5





N. Huang, R. Michel, J. Voros, M.Textor, R. Hofer, A. Rossi, D.L. Elbert, J. A. Hubbell, and N.D. Spencer, Langmuir, 2001, 17, 489-498.

Protein resistant biomaterials
PLL-g-PEG on Nb_2O_5

angle	thickness (nm)		composition interface (PLL)			composition bulk	
	PEG	PLL	C1s	N1s	O1s	metal	O1s
Exper.	1.1±0.3	0.6±0.2	59	21	20	72	28
Calc.	-	-	59	23	18	70	30

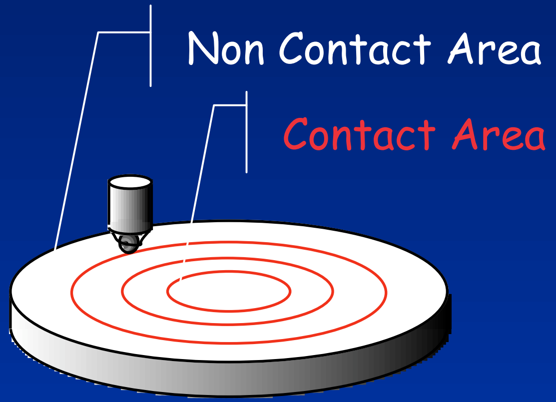
□ PEG = 2 g cm^{-3}
□ PLL = 1 g cm^{-3}
□ Nb_2O_5 = 4.47 g cm^{-3}

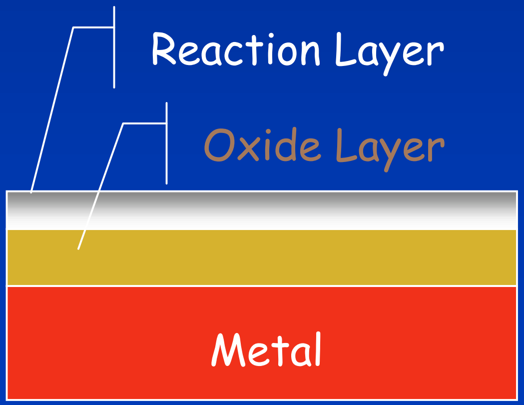
The thicknesses are fully consistent with monolayer coverage of PLL-g-PEG and with a surface coverage of 148 ng cm^{-3} measured by OWLS.

ETH Materials

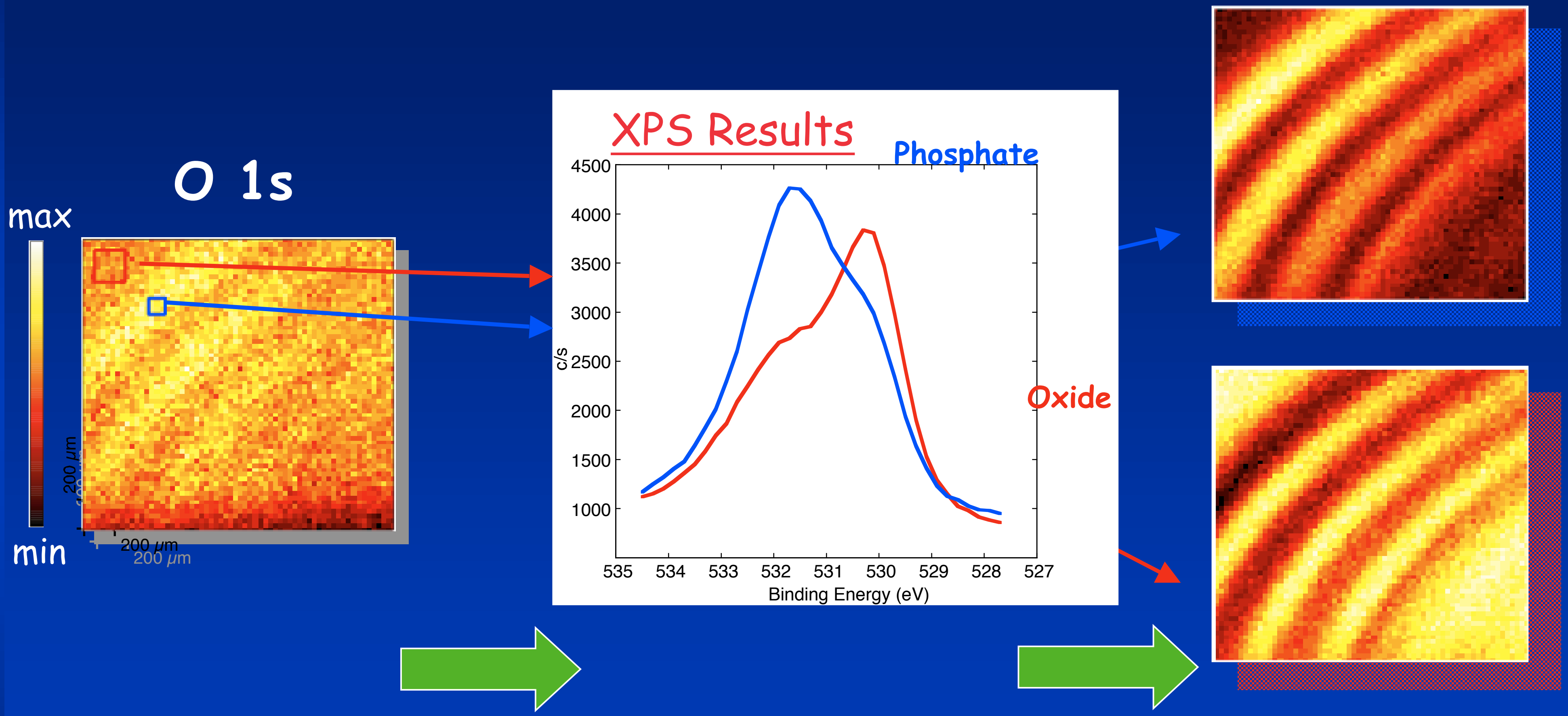
Real surfaces

- Sample
  - Lateral Distribution
    - Homogeneous Distribution
    - Inhomogeneous Distribution
  - Depth Distribution
    - Homogeneous Distribution
    - Inhomogeneous Distribution





Imaging XPS



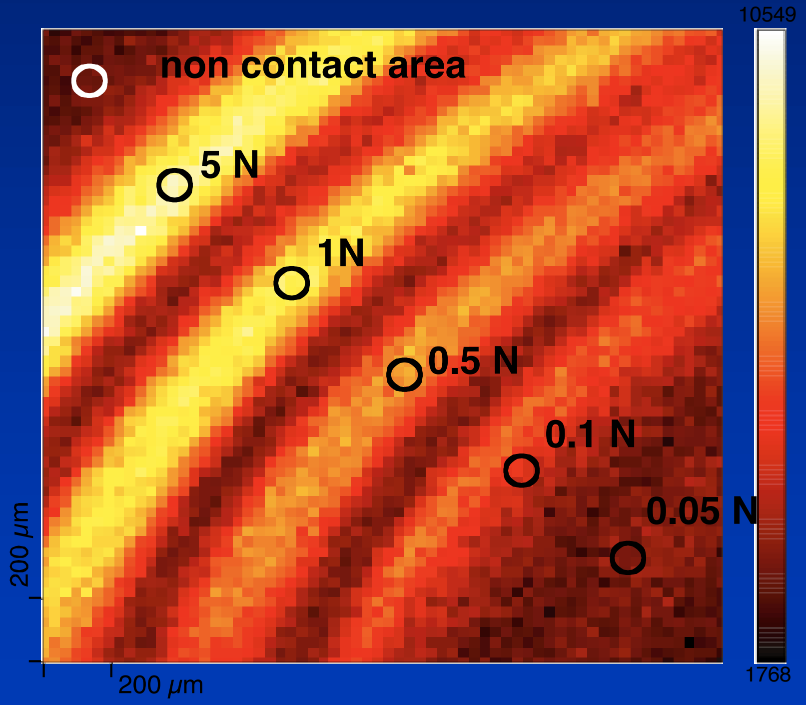
Extract Spectra

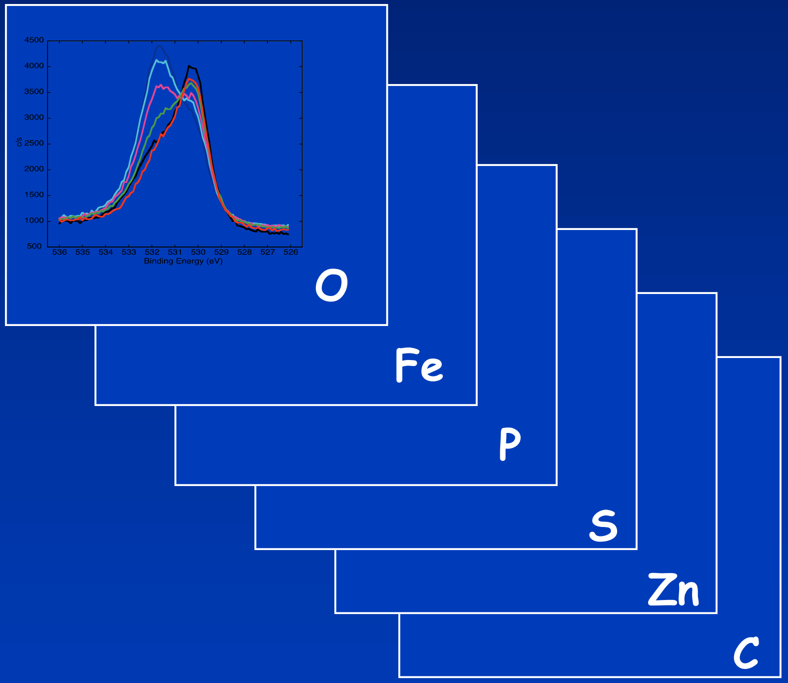
Reconstruct Map

M. Eglin, A. Rossi, N. D. Spencer, submitted to Tribology Letters

From Imaging to Spectroscopy

O 1s



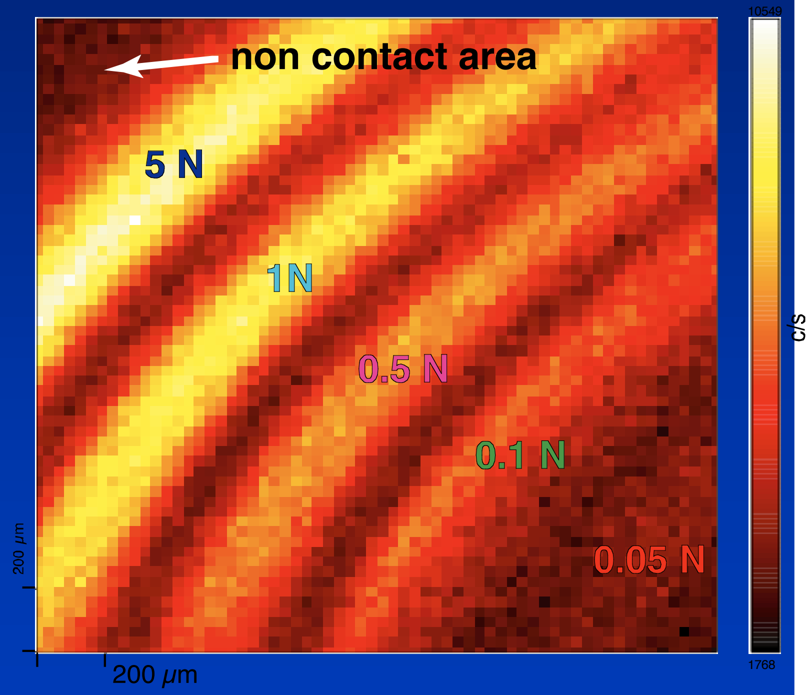


Select Areas for High Resolution-Small Area XPS

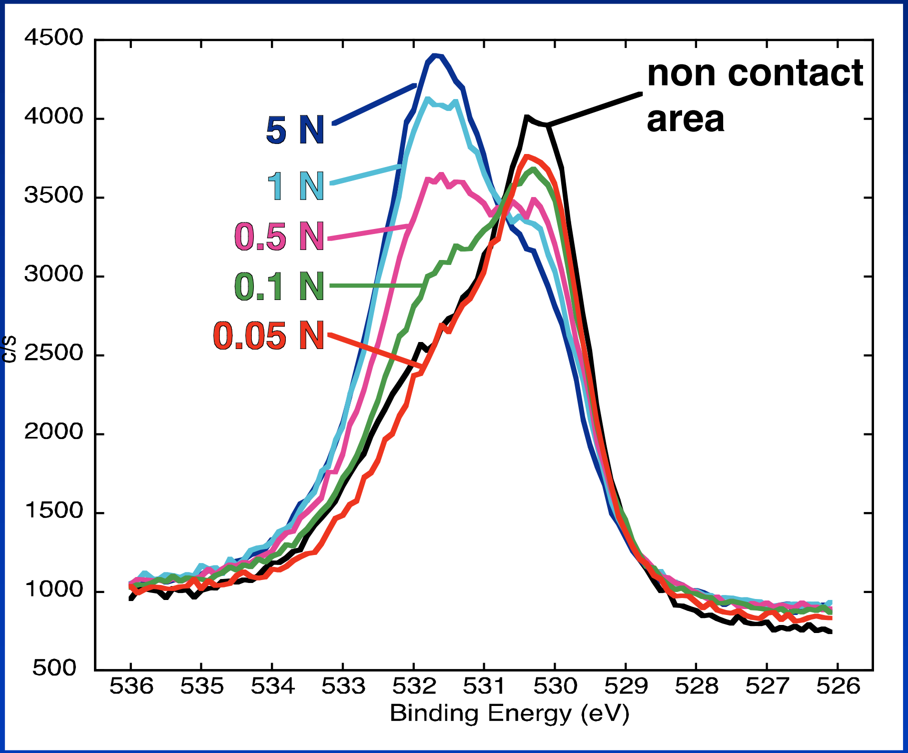
M. Eglin, A. Rossi, N. D. Spencer, submitted to Tribology Letters

XPS Results

O 1s

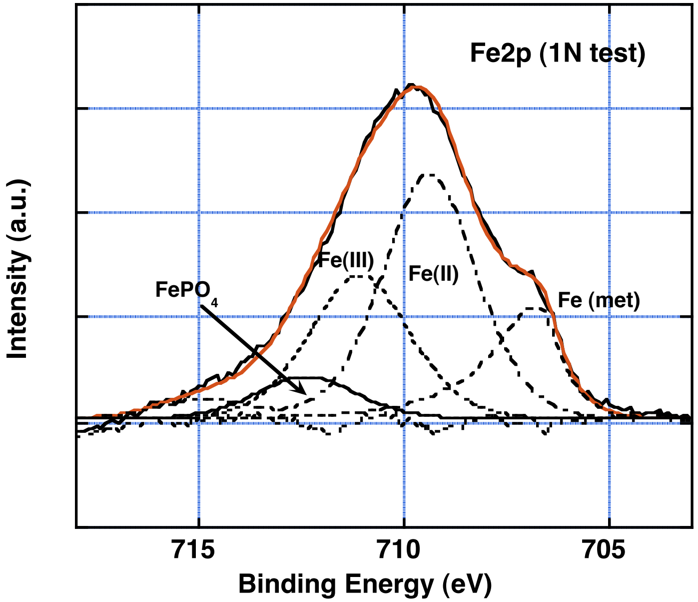


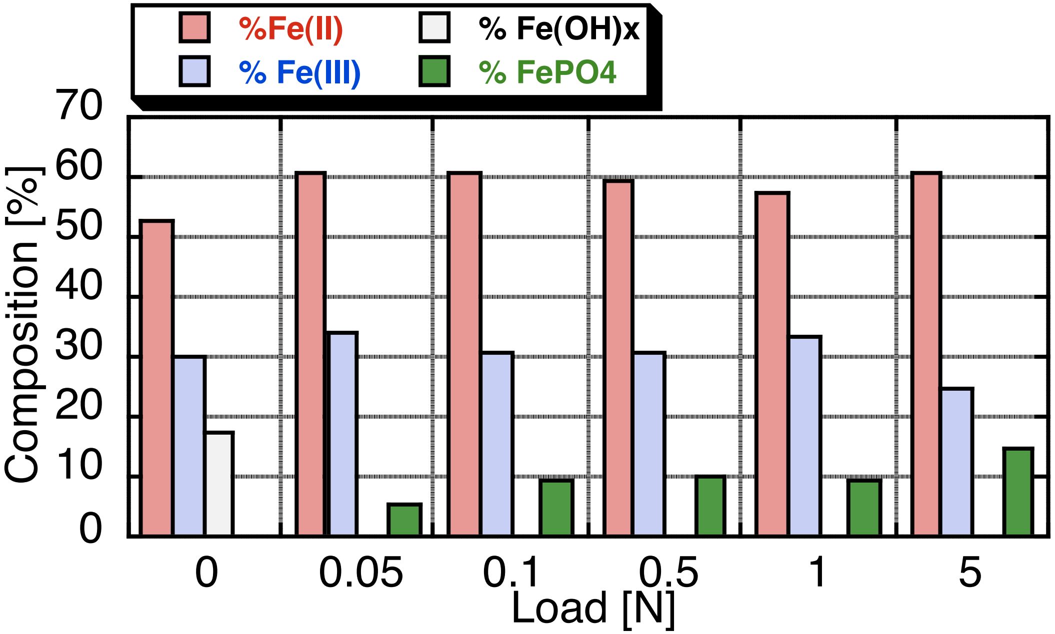
O 1s



M. Eglin, A. Rossi, N. D. Spencer, submitted to Tribology Letters

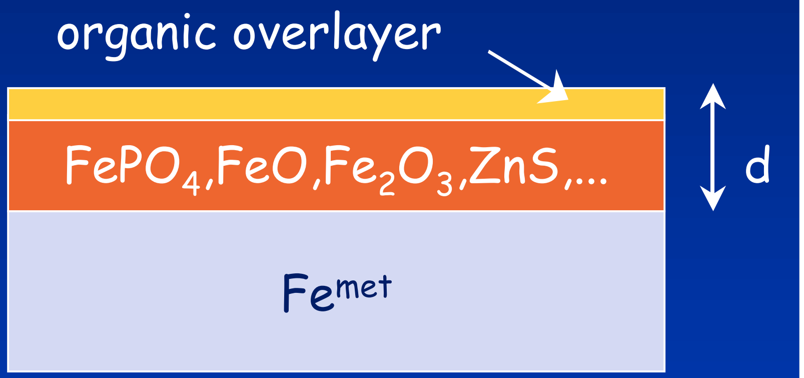
XPS Results (Iron)





M. Eglin, A. Rossi, N. D. Spencer, submitted to Tribology Letters

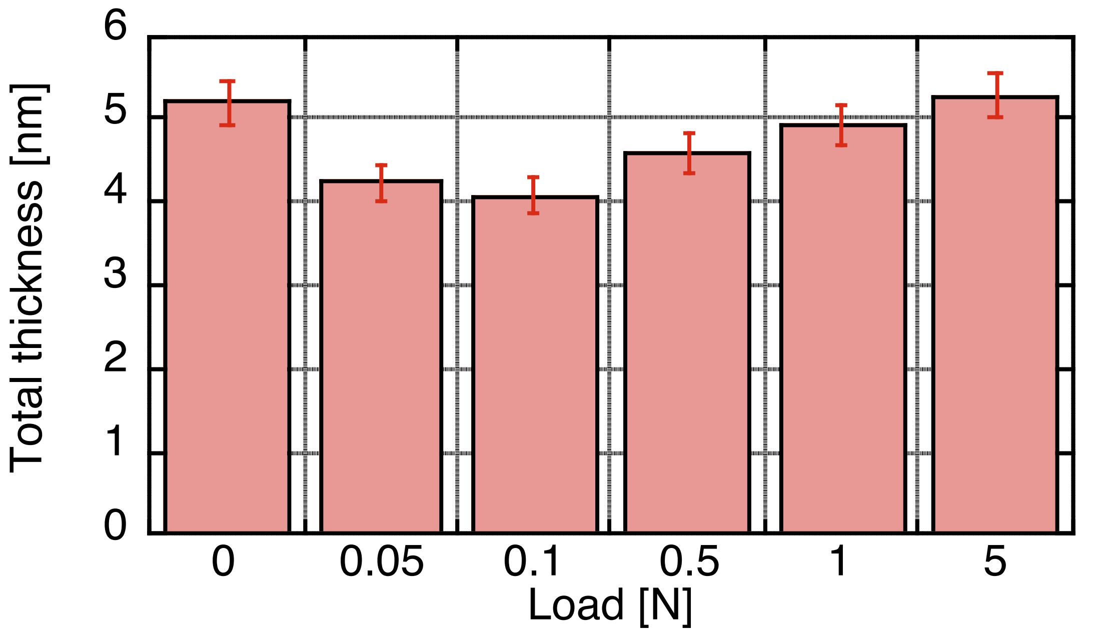
XPS Results - film thickness



organic overlayer

$FePO_4, FeO, Fe_2O_3, ZnS, \ldots$

Fe^{met}



M. Eglin, A. Rossi, N. D. Spencer, submitted to Tribology Letters

Outlook

The newest spectrometers allow imaging quantification with:

- higher lateral resolution (<3μm)
- collection of spectroscopic data with high sensitivity

The application of the **three-layer model** at any point of the image will provide information:

- local thicknesses variations
- local layer composition changes
- local interface composition variations

ETH Materials

Acknowledgments

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Michael Eglin, Ning-Ping Huang, Laurence Ruiz

ETH
Materials