High-Sensitivity LEIS
Principles & Applications

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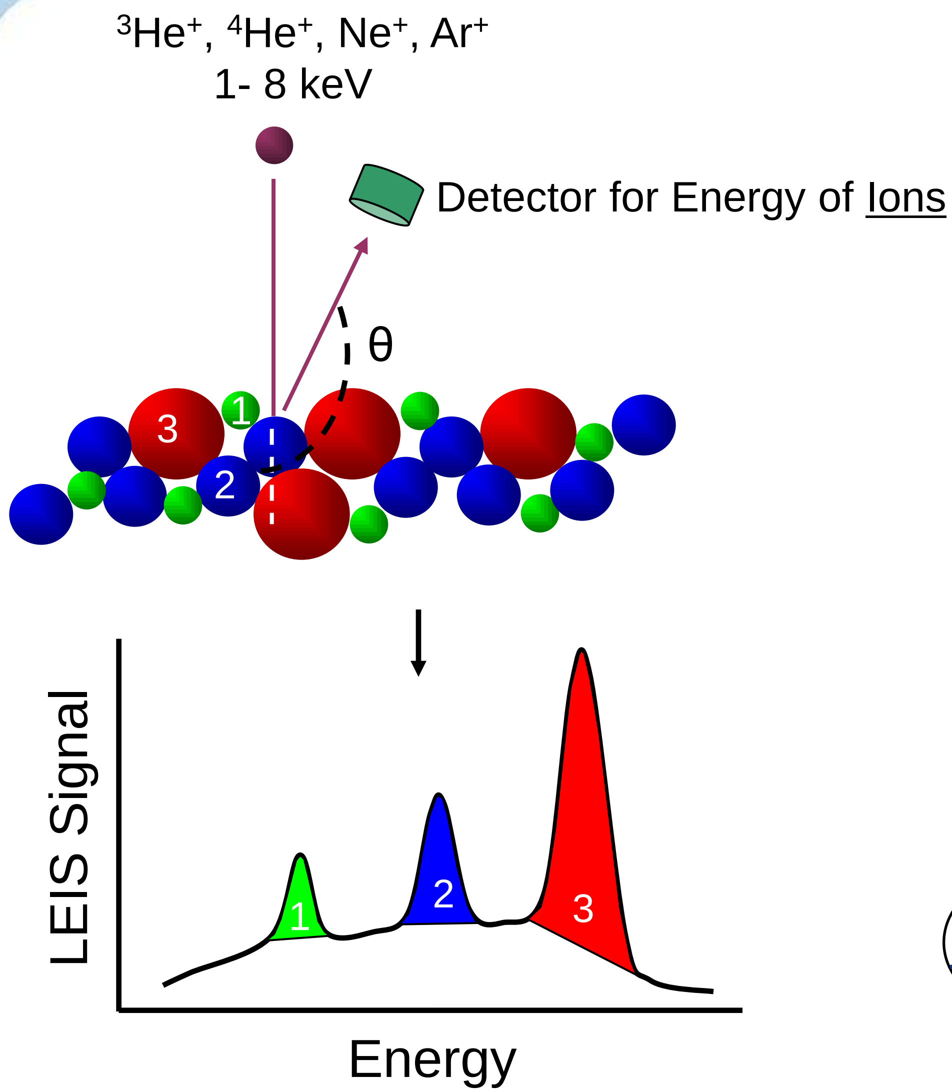
Outline

- **Introduction to LEIS**
- **Miscellaneous Applications**

  Imaging, NPs, segregation, surface modification, anti-wetting, NPs
- **Outer surface oxides**
- **SOFC, membranes**
- **Growth**
- **Summary**

Low Energy Ion Scattering

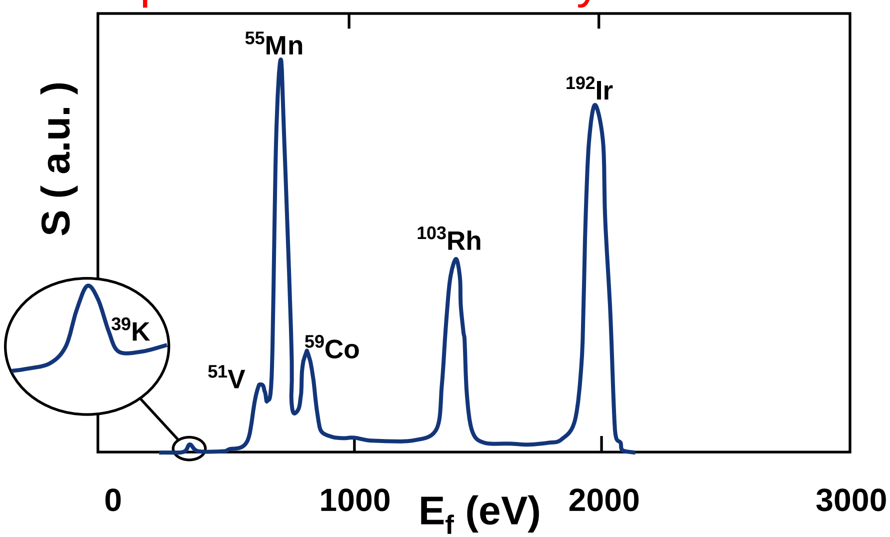
Studying the outermost surface of any material



Characteristics of the technique

- Atomic composition of outermost atomic layer
- Energy 1 – 8 keV
- Lateral resolution 0.01 – 1 mm
- In-depth (0 – 10 nm)
- No matrix effects

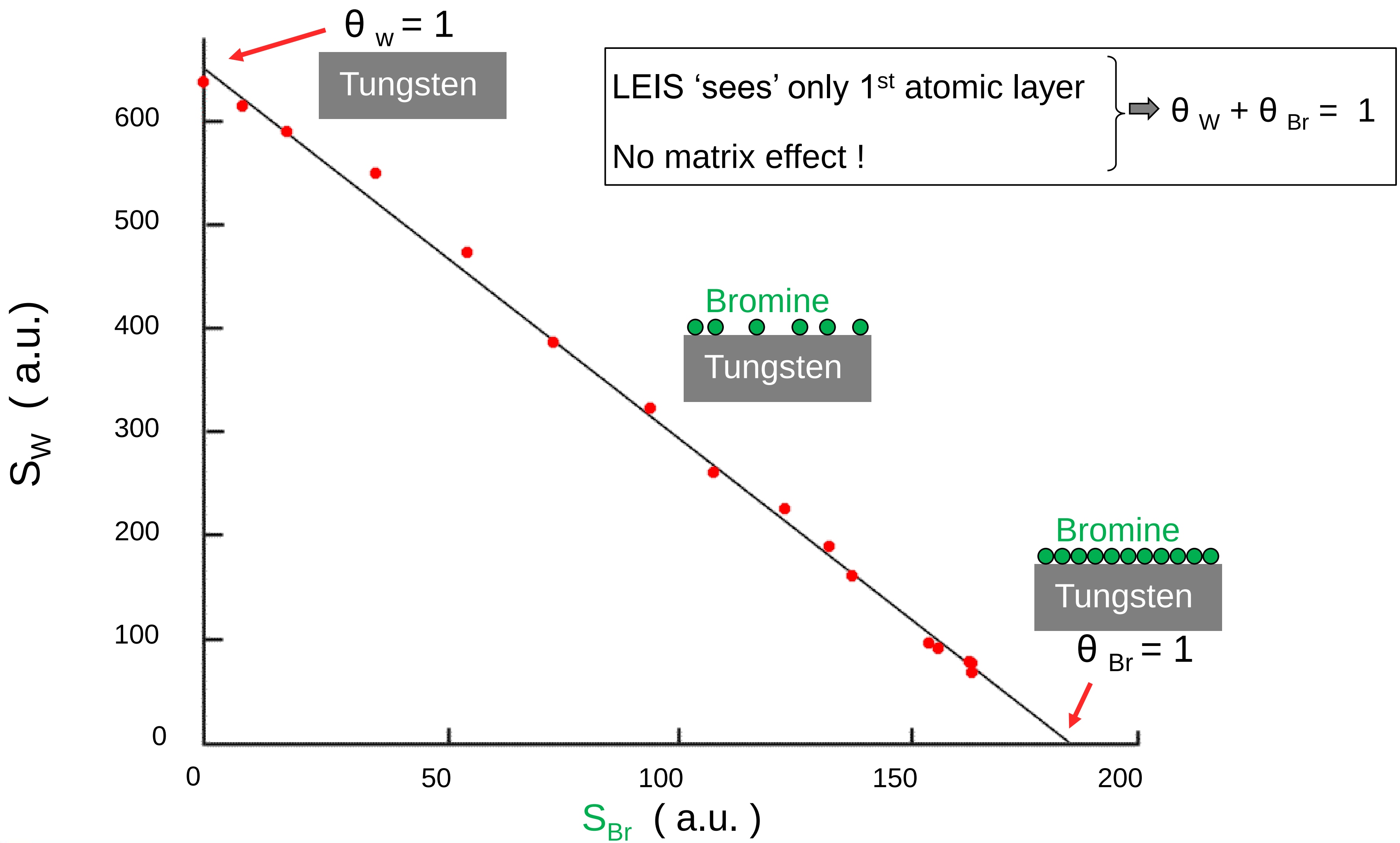
Example: 3 keV Ne → alloy



LEIS Enables Simple Quantification

Example: Coverage of Bromine adsorbed on Tungsten

LEIS can quantify the surface coverage θ in the 1st atomic layer



Qtac: Unique new Analyser

High – Sensitivity LEIS

- Large acceptance angle (360º)
- Parallel energy detection
  - only low ion fluence needed

↓

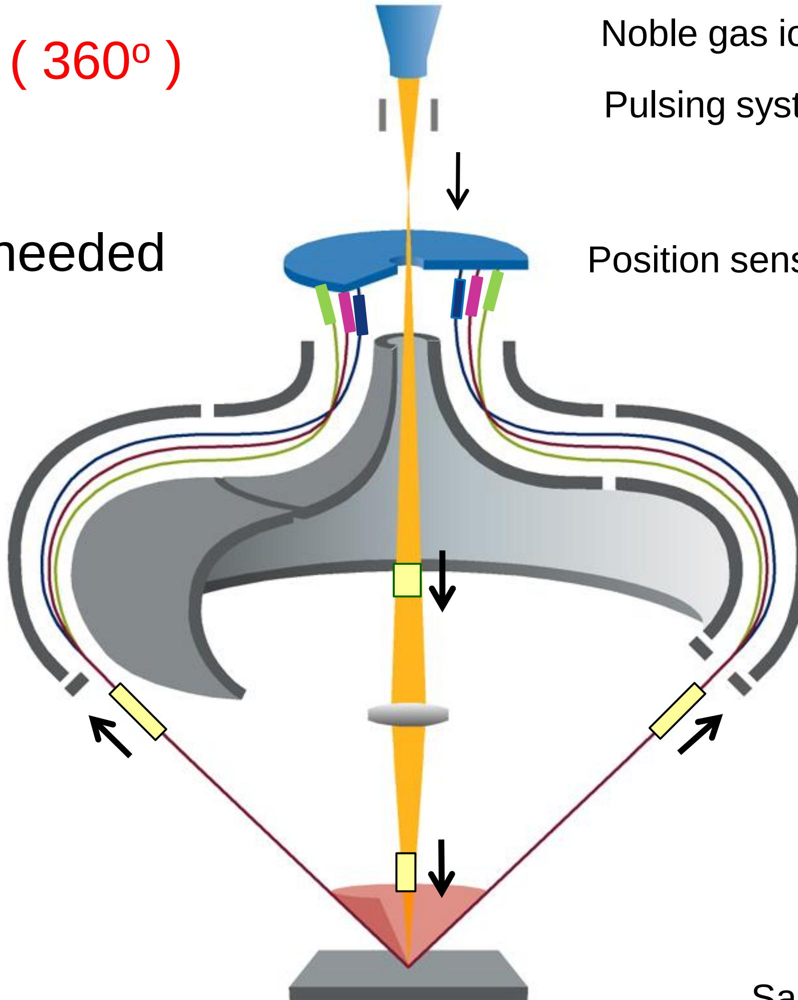
STATIC LEIS

“ Analysis *before* Damage ”

“ Hit same place only once “

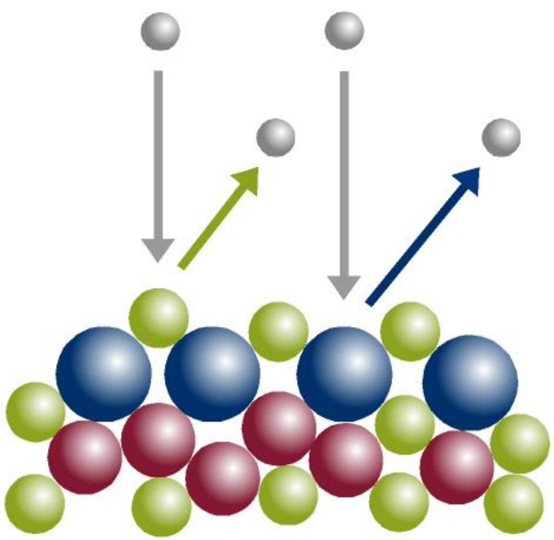
(Core/shell nanoclusters !)

ToF filtering eliminates SIMS ions



LEIS Technique

Features of Low Energy Ion Scattering (LEIS)



LEIS Features for elemental surface analysis:

- Ultra-high surface sensitivity, **top atomic layer**
- Reliable and straight-forward **quantification**
- **Non destructive** (static) analysis
- Detection limits:

Li - O	≥ 1 % **of 1 ML**	
F - Cl	1 % - 0.05 % **of 1 ML**	
K - U	500 ppm - 10 ppm **of 1 ML**	

- **Static depth profiling** (up to 10 nm)

Reviews

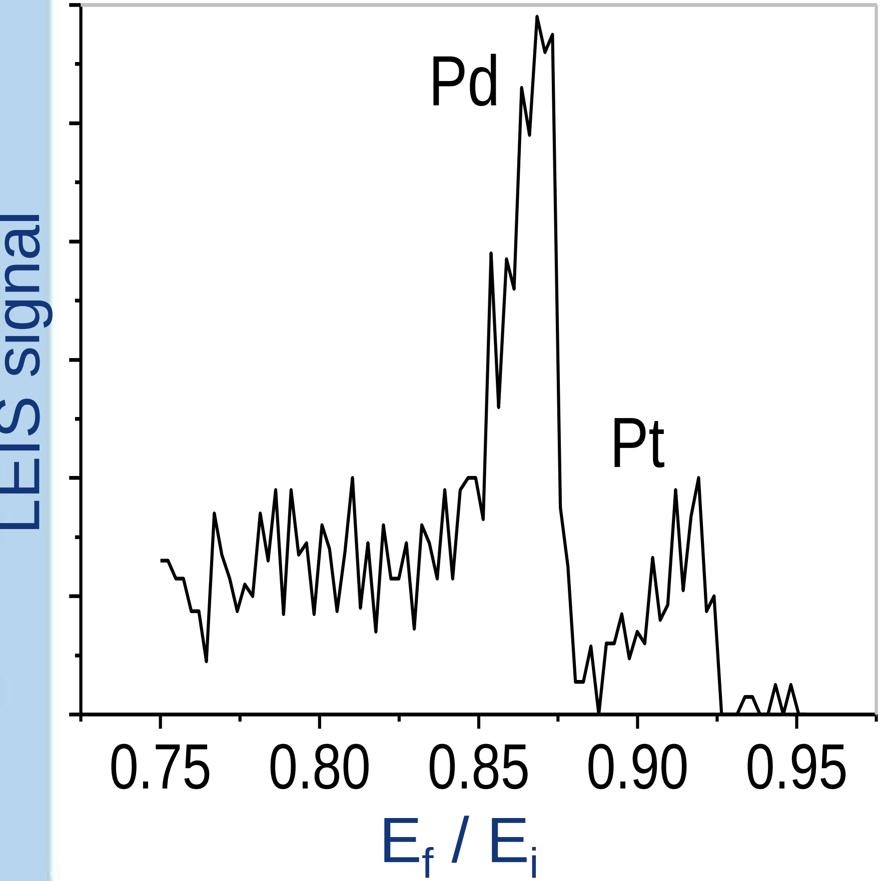
- Brongersma et al., Surf. Sci. Rep. 62 (2007) 63
- H.H. Brongersma, Low-Energy Ion Scattering in: Characterization of Materials, Ed. E.N. Kaufmann, pp. 2024-2044, Wiley (2012).

Conventional LEIS vs HS - LEIS

Pd / Pt-C (1000 m^2/g)

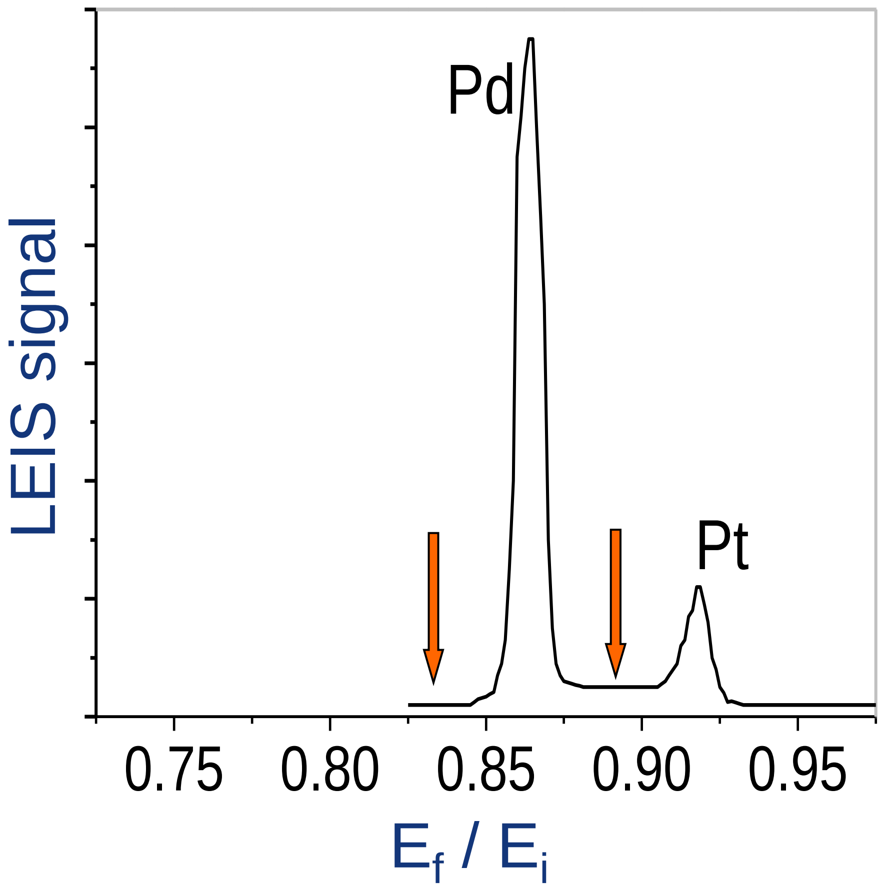
Conventional LEIS

^4He 10,000 nC



High-Sensitivity LEIS

^4He 5.4 nC



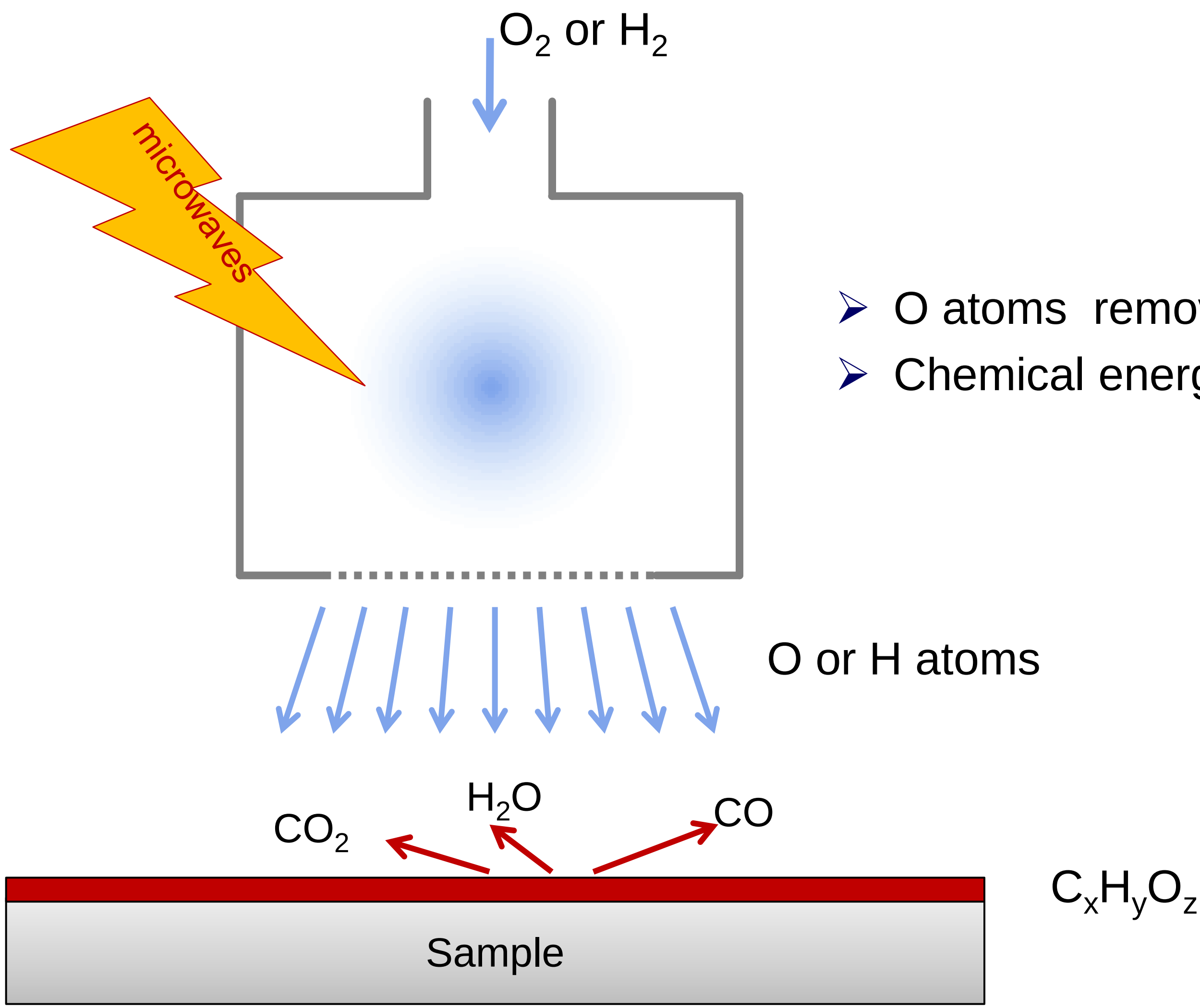
NIM B 68 (1992) 207

Promoters visible, but removed from spectrum

Sample Cleaning

Atom Source for O- and H-atoms

- O atoms remove organics, coke
- Chemical energy: *no sputtering*



In – Depth profiling

IONTOF

Two possibilities:

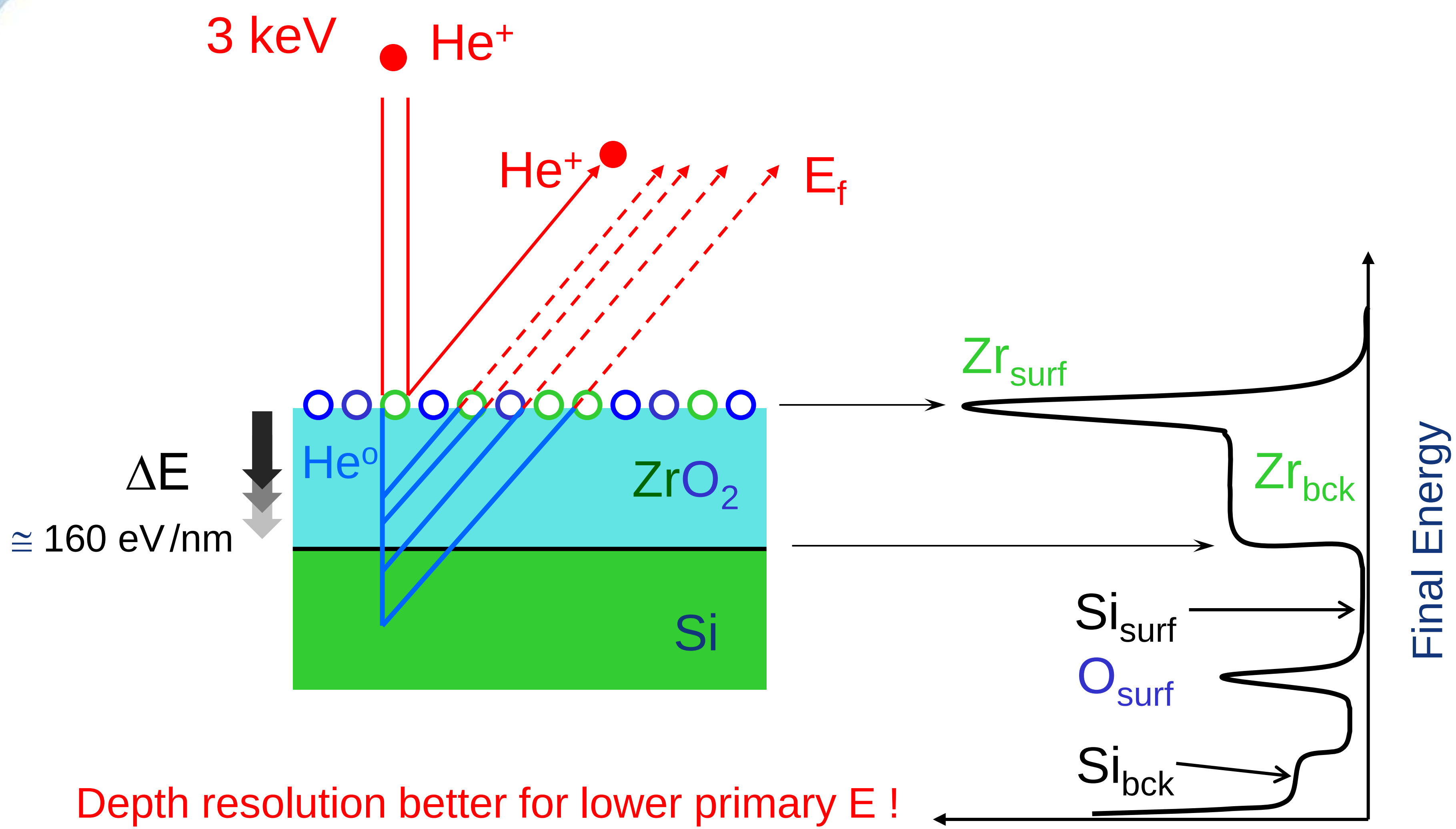
- 1. Static LEIS + Sputter depth profiling with dual ion beam

  (advantage of quantification, depth resolution LEIS)

- 2. Static LEIS (non destructive) for heavier elements

  (analogous to RBS and MEIS, but better depth resolution)

Depth info; non-destructive

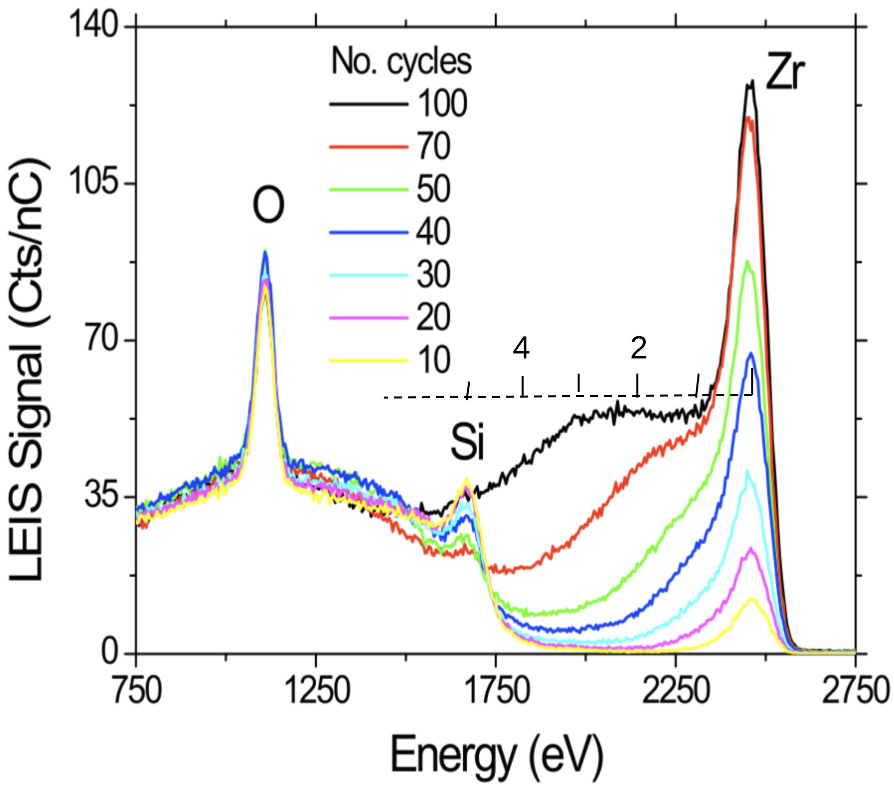


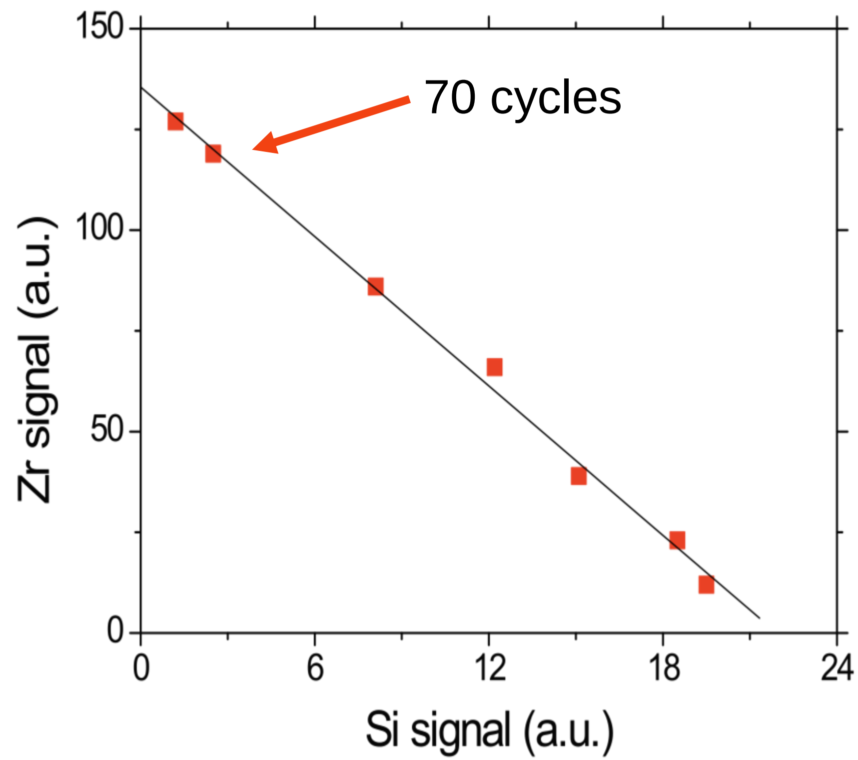
Depth resolution better for lower primary E !

1st atom and Static Depth Profile

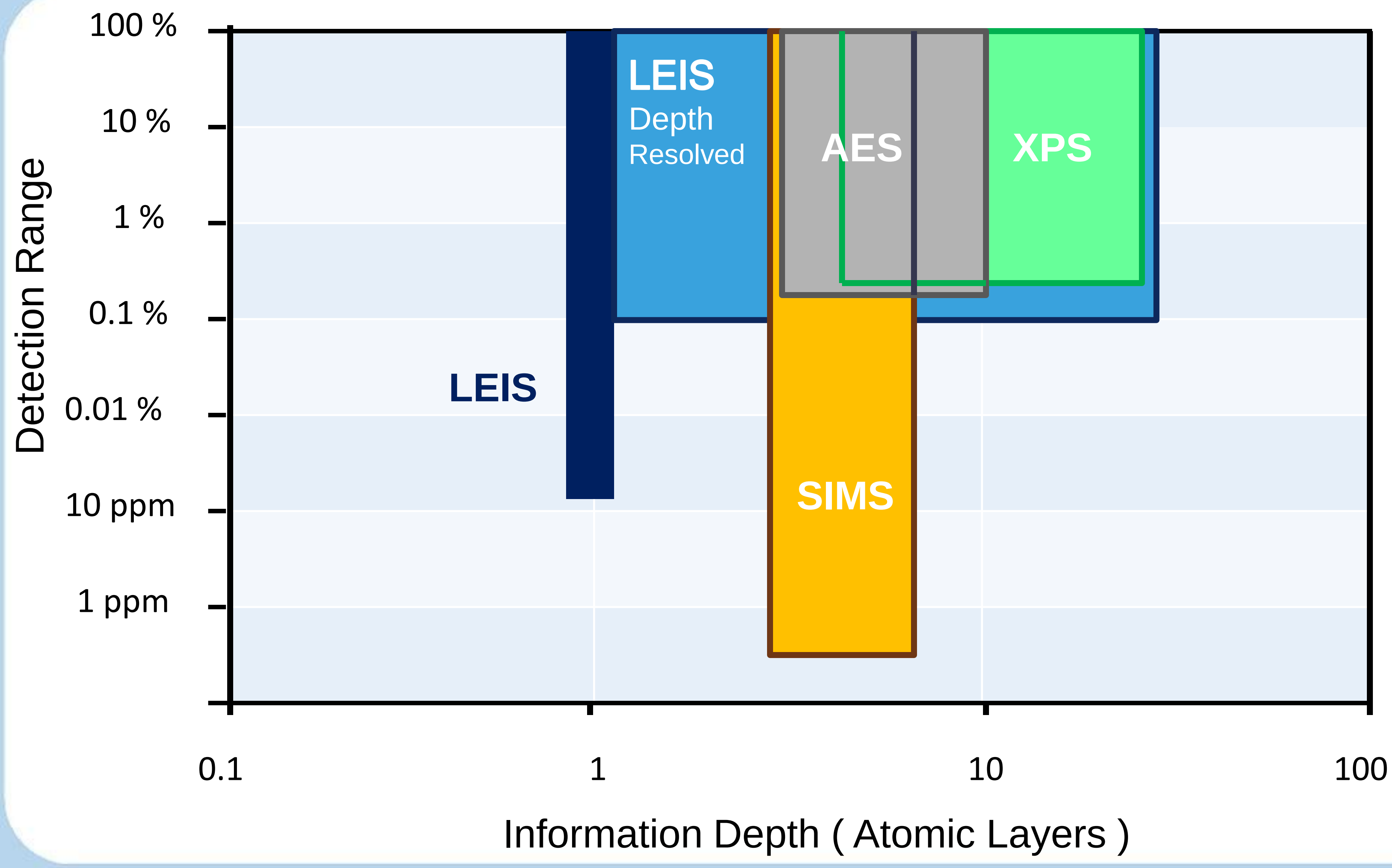
ZrO_2 Atomic Layer Deposition on Silicon

- Detection / quantification pinholes (still present after 70 cycles)
- Thickness distribution ZrO_2 layer (160 eV/nm)
- No matrix effect
- Example: calibration / quantification for a 2 component system





Detection range vs Information Depth for AES, LEIS, SIMS and XPS



Miscellaneous Applications

- Imaging
- Surface segregation, anti wetting
- Interdiffusion
- Surface modification
- Nano particles

Surface Imaging

iONTOF

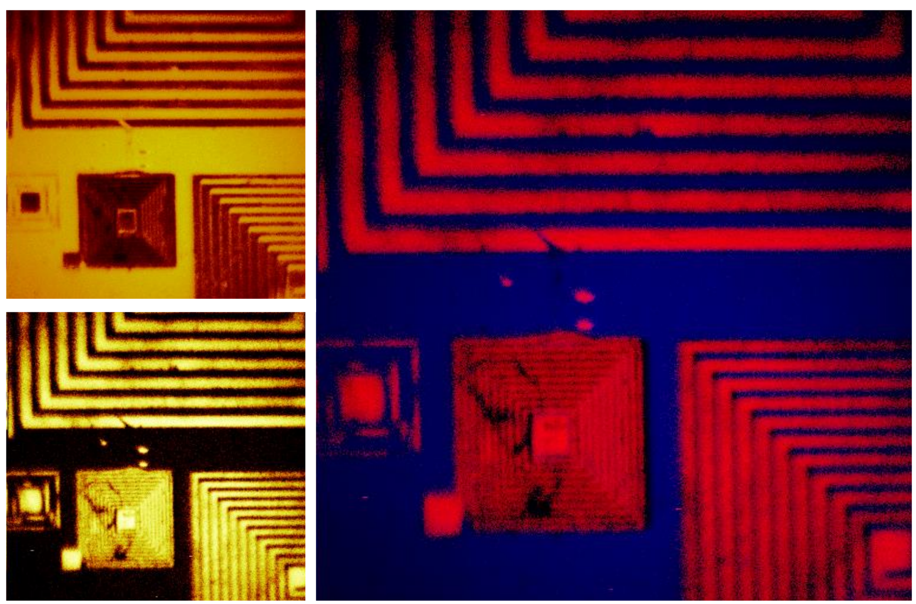
Lateral Resolution *and* Sensitivity required

Imaging in surface analysis:

- Probe or detector needs sufficient lateral resolution
- Data rate has to be high enough (acquisition time)
- Detection must be sensitive enough
  - sufficient information from each pixel before damage
  - detection sensitivity → "useful lateral resolution"

Ti

Cu

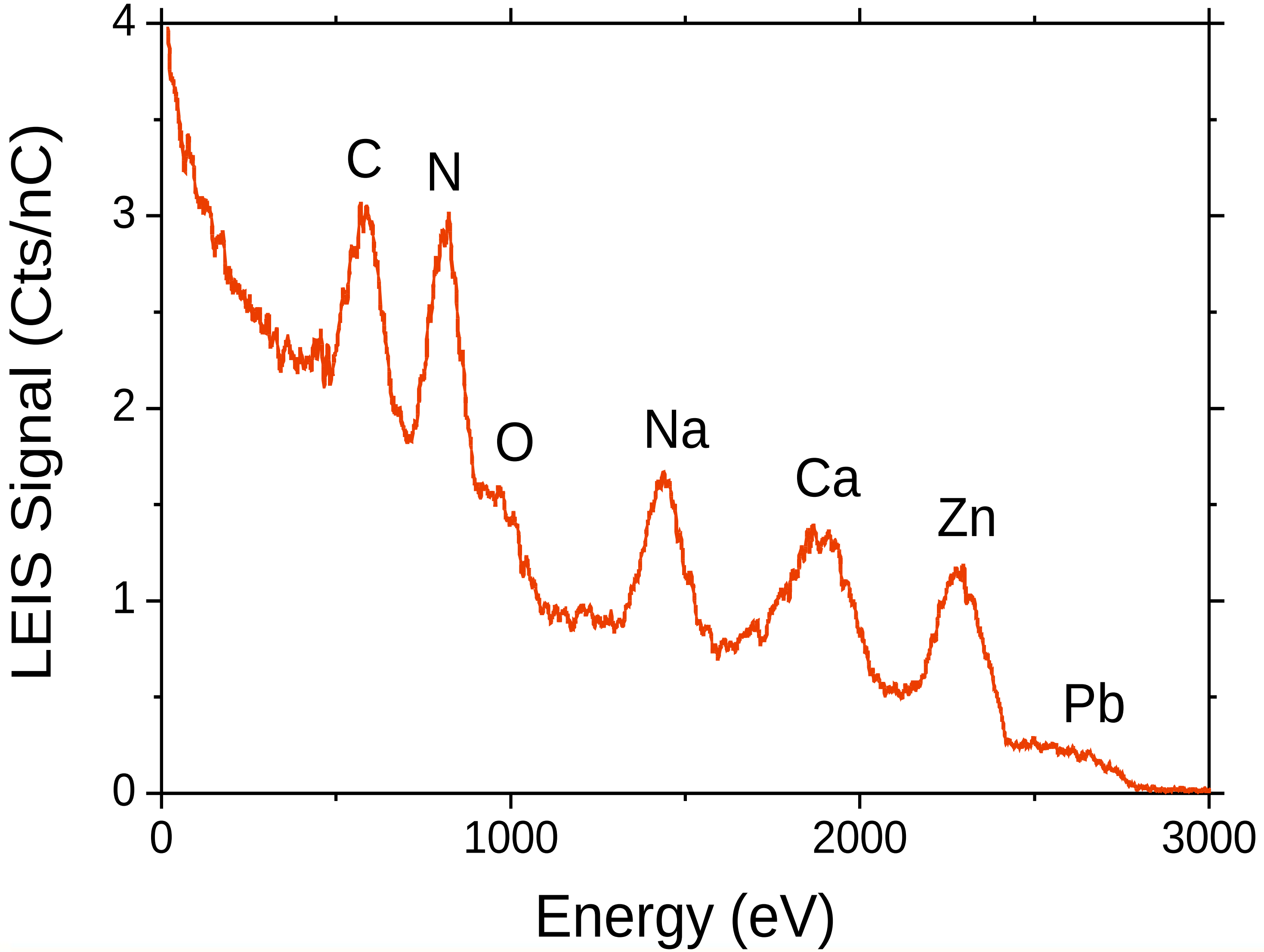


Field of view: 2 mm

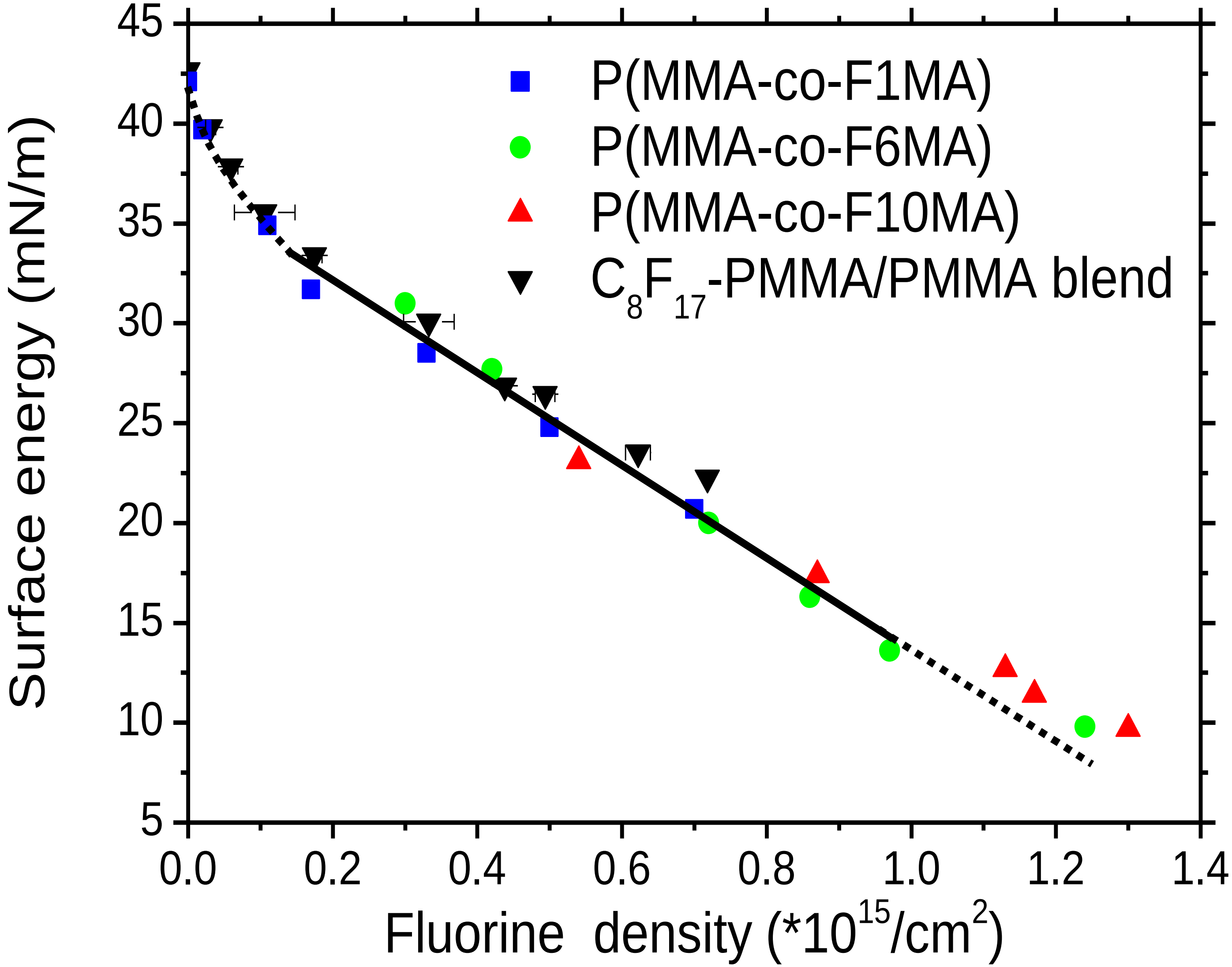
With new ion source lateral resolution ~ 10 um

Surface segregation: universal process

Example: Acrylonitrile-Butadiene-Styrene (ABS)

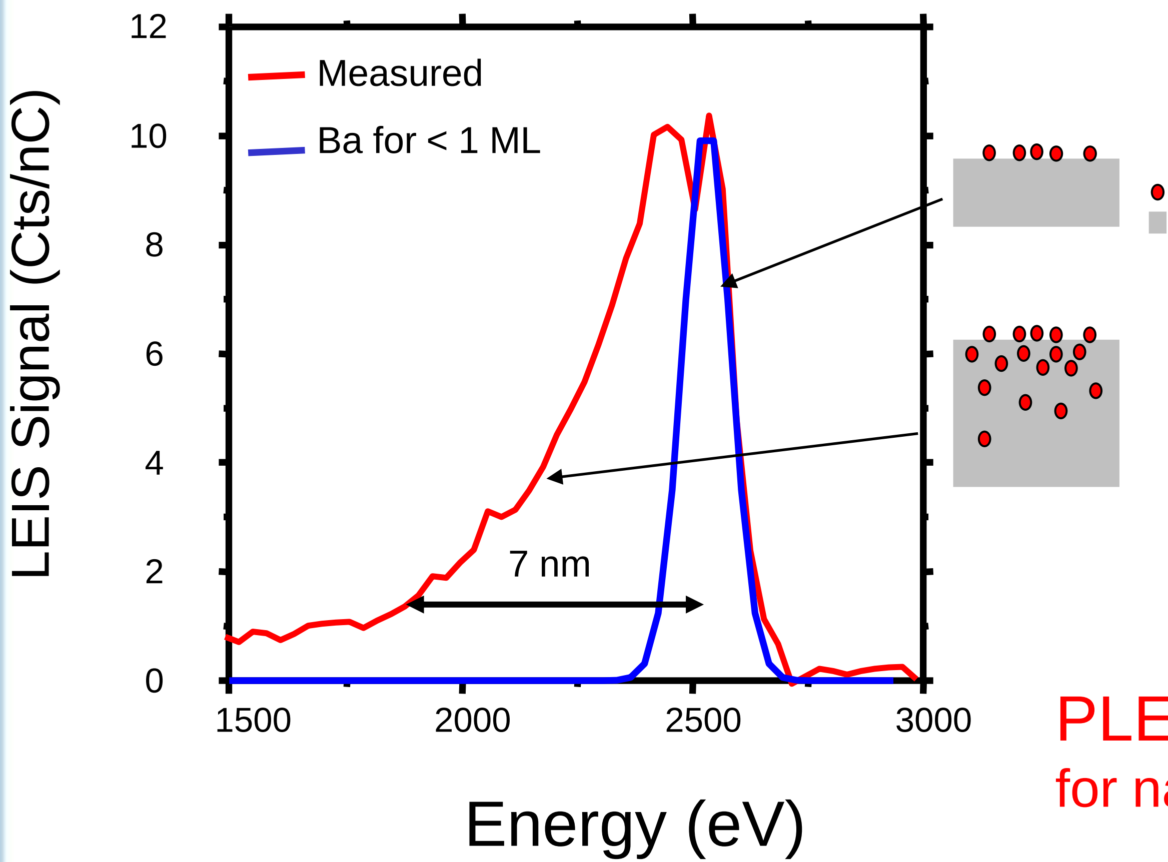


Anti wetting
Fluorine density vs surface energy



Metal - polymer interface in ultra - thin layers

PLED: Ba evaporation on PPV



During evaporation of barium on PPV, most of the Ba diffuses into the PPV.

Compare the peakshape of a sub-monolayer of Ba (blue) with the actual peak (red)

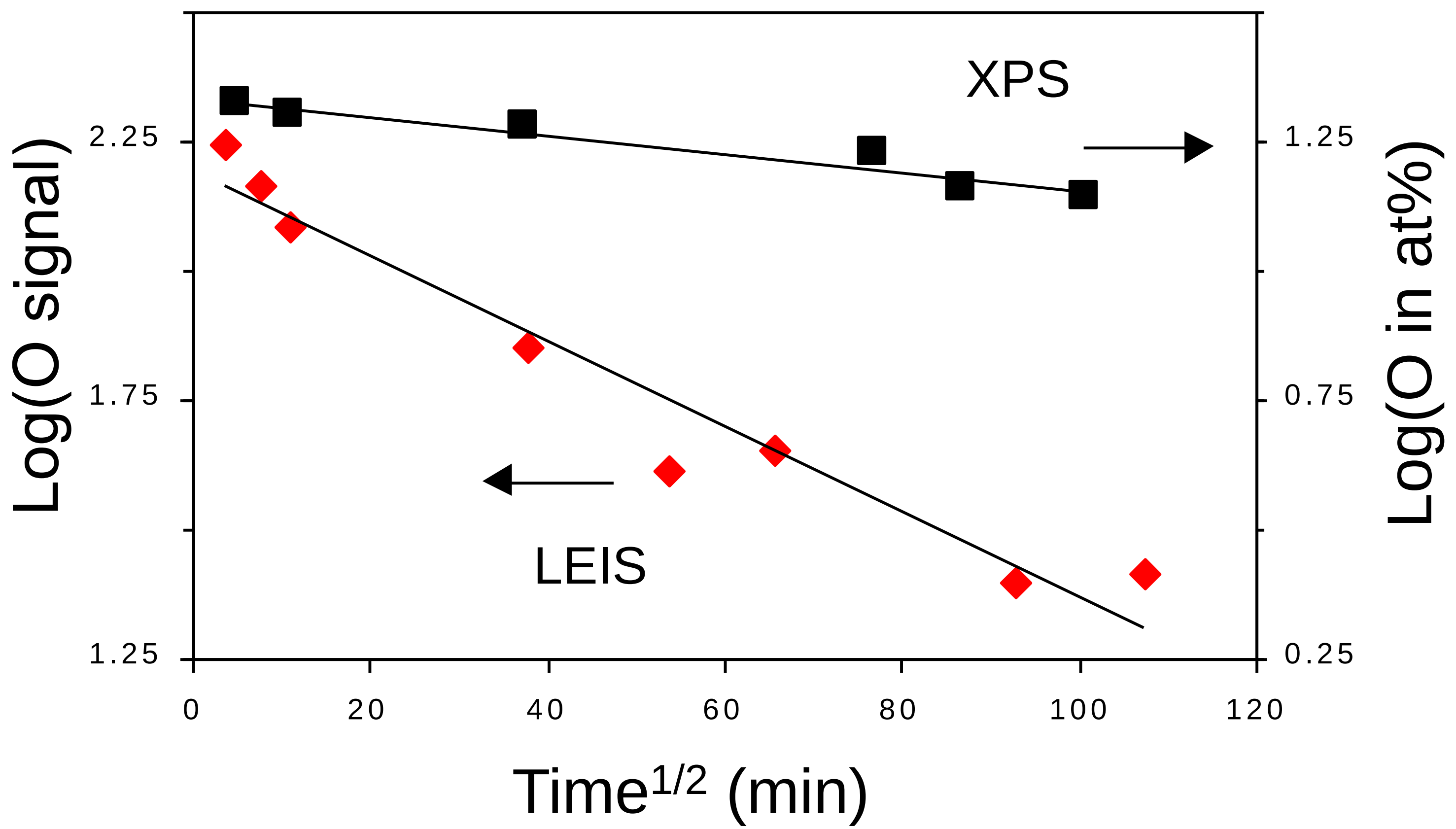
Peak shape ↔ depth distribution

PLED: higher light output for narrow depth distribution

Surface modification

Aging of plasma oxidized HDPE

- Aging (LEIS) faster than aging (XPS) !
- "Straight line" → diffusion process



Nano particles (supported catalyst)

- Average size
- Core / Shell

Particle Size on Supported Catalysts

Diameter ⟷ TON; size often related to failure

TEM:

- excellent catalyst characterisation
- detailed info, but local
- contrast required (high Z cluster on low Z support)

Chemisorption:

- requires known probe / surface interaction

HS - LEIS:

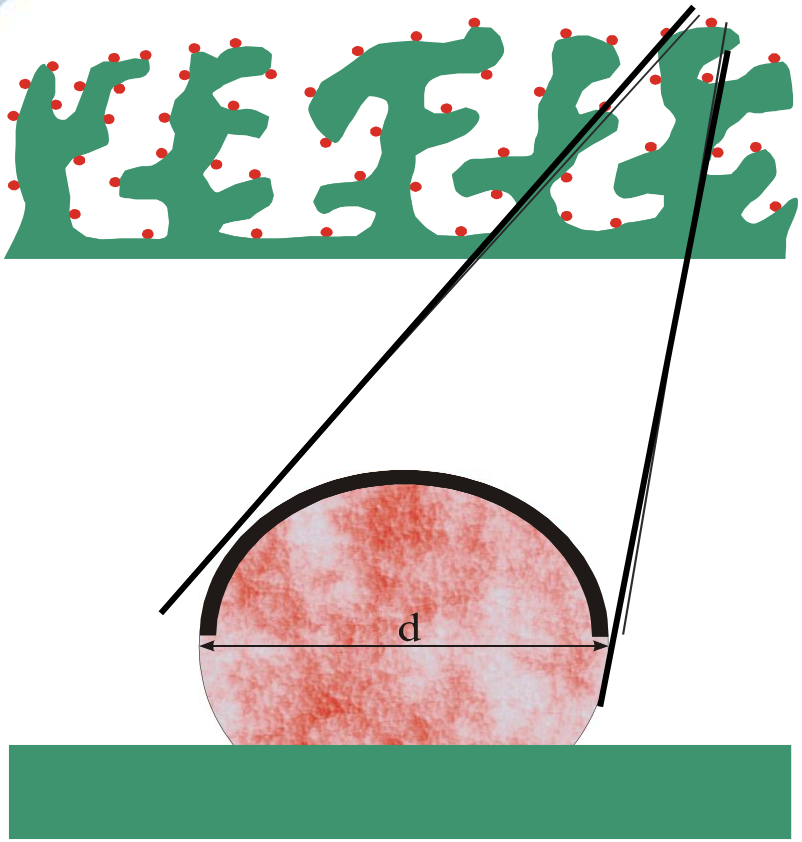
- new technique; any material; clusters: 1 atom - 10 nm

Comparison: → Richard A. P. Smith (J&M) et al., ECASIA 2009

→ T. Tanabe et al. (Toyota), Appl. Catal. A370 (2009) 108

Important / unique applications for catalysis

4. Nanoclusters



- Average diameter nanoclusters
- Surface segregation in alloy clusters
- Core/shell particles

  (verification, closure, thickness shell)

Example: Three-Way catalyst (exhaust)

Pt clusters on CeO_2/ …../ γ-alumina

Loading = 0.004 g Pt / γ-alumina

Cluster diameter: 1.6 nm (average)

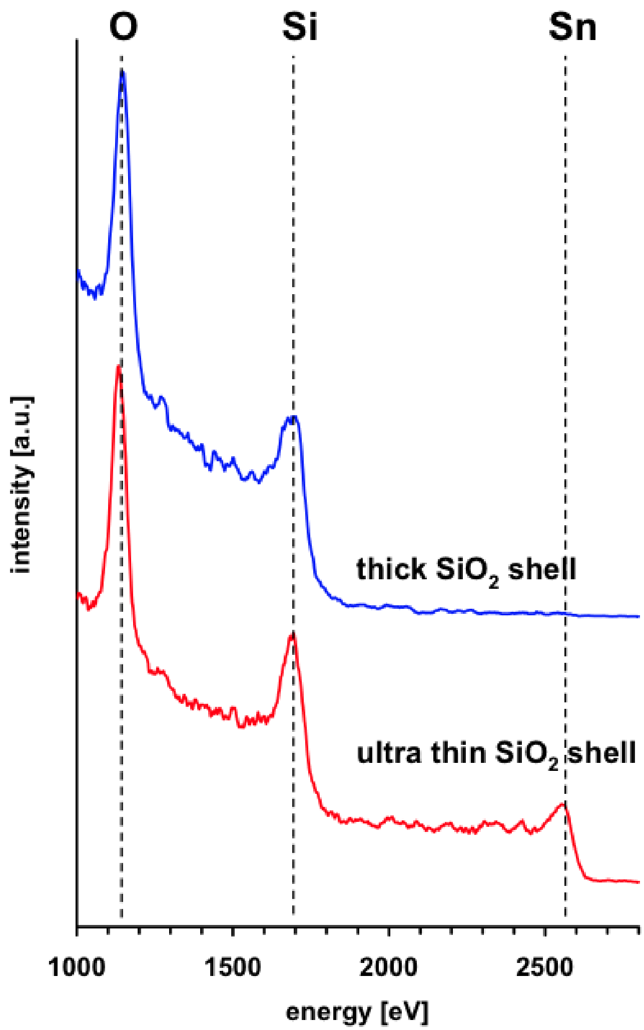
Accurate for d < 10 nm

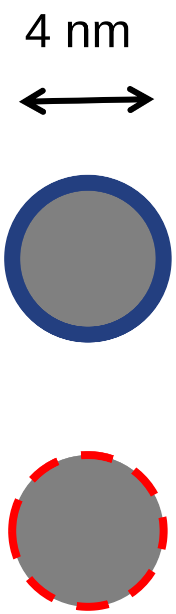
The diameter is derived from the ratio of the bulk loading (volume) to the LEIS signal (surface area)

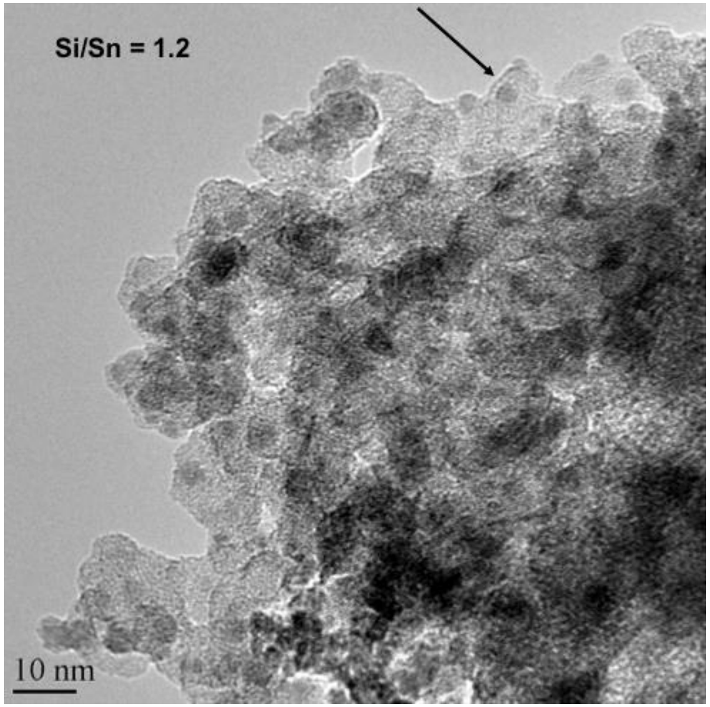
This method is possible where TEM fails (d ≤ 2 nm; high Z support)

Low Energy Ion Scattering

Characterisation of Functionalised Core/Shell Nanoparticles







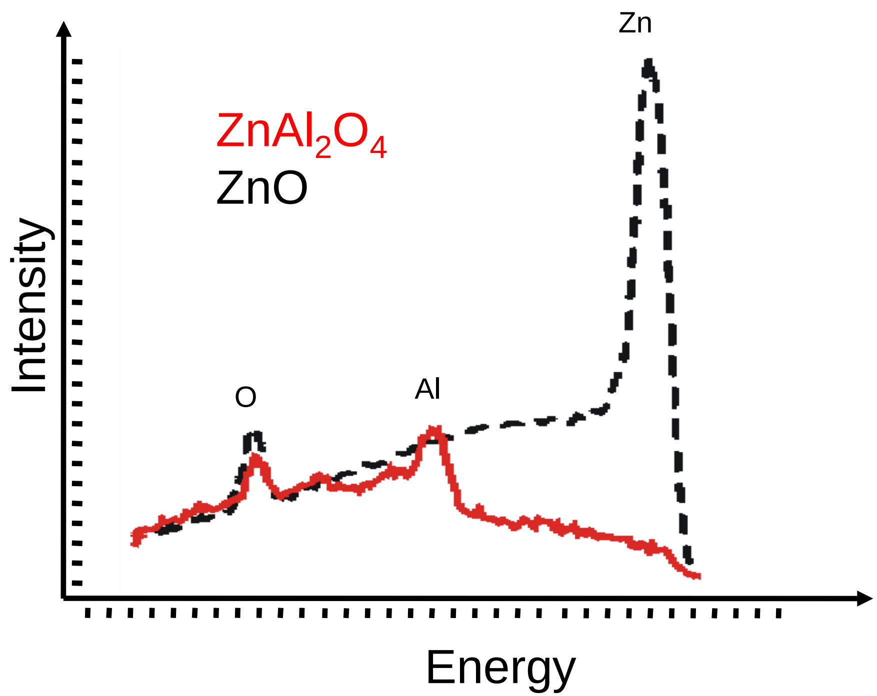
M. Fuchs et al., Surf. Interface Anal. **42** (2010) 1131

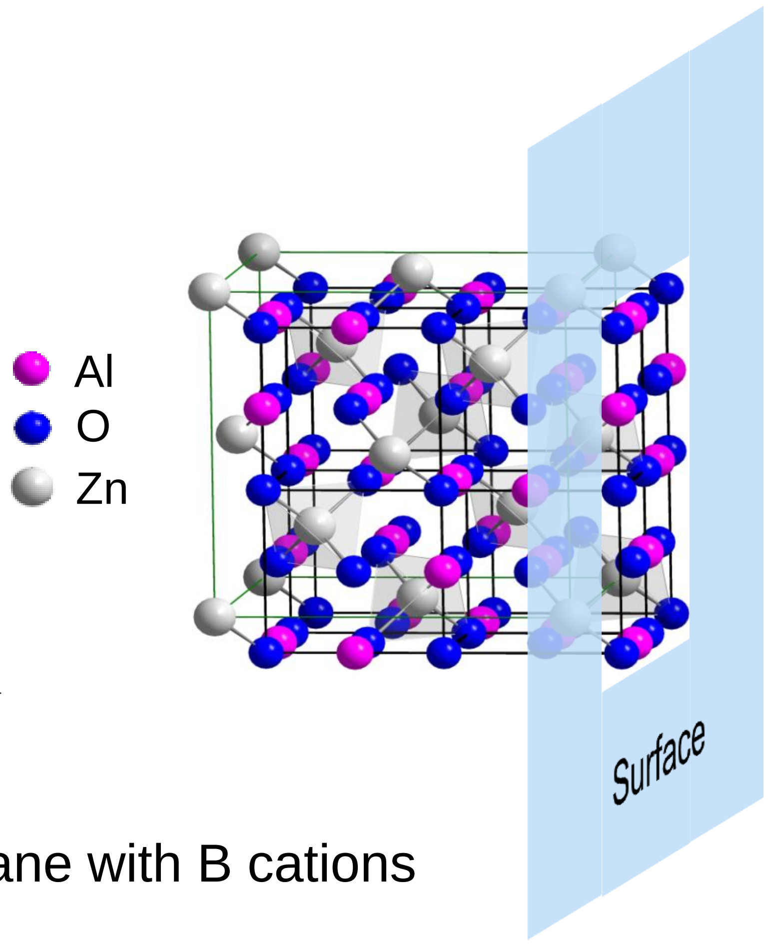
Courtesy of Karlsruhe Institute of Technology

The outer surface
of
mixed oxides

LEIS of spinels AB_2O_4

LEIS reveals surface composition powders





Powders: preferential exposure plane with B cations (octahedral sites)

→ Zn in tetrahedral site below surface

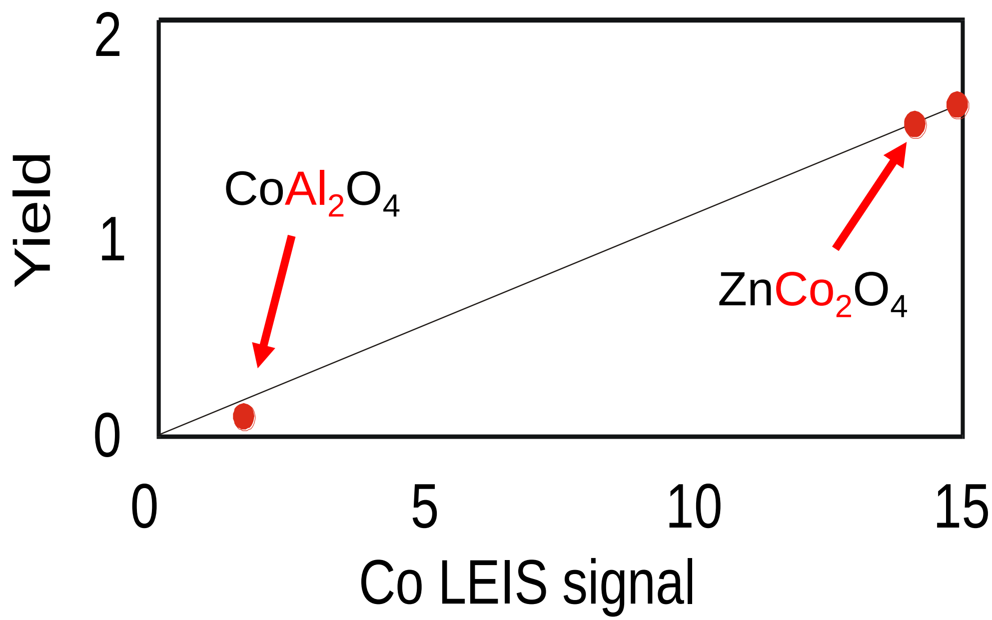
Important / unique applications for catalysis

Mixed oxides and catalysis

The atomic composition of the 1st atom layer controls catalysis.

In a spinel (AB_2O_4) only the B-cations (octahedral site) are catalytically active and visible for LEIS (1st at.).

The A-cations (tetrahedral sites) are in 2nd layer (not active, no LEIS peak).



$Co_3O_4 = CoCo_2O_4$

Test reaction:

only Co catalytically active

Co signals:

XPS:	1 :	2 :	3
LEIS:	0.3 :	1.9 :	2.0

LEIS ⟷ **Catalysis** ⟷̸ **XPS**

Spinels (AB_2O_4)
LEIS and chemistry

Cations in octahedral sites at surface (B in normal spinel)

⇒ LEIS
⇒ Chemistry
} **1 : 1 !**

Cations in tetrahedral sites below surface (A in normal spinel)

⇏ Chemistry
⇏ LEIS

Perovskites, other oxides: more complicated !
Kilner et al.: LaSrCo oxides ….

Alumina: difference α – γ !

Fuel Cells and Oxygen Membranes

Importance of the outer surface

- Performance relies on oxygen transport
- Performance: “ Hampered by the surface ”
- Why ? What is the surface ??

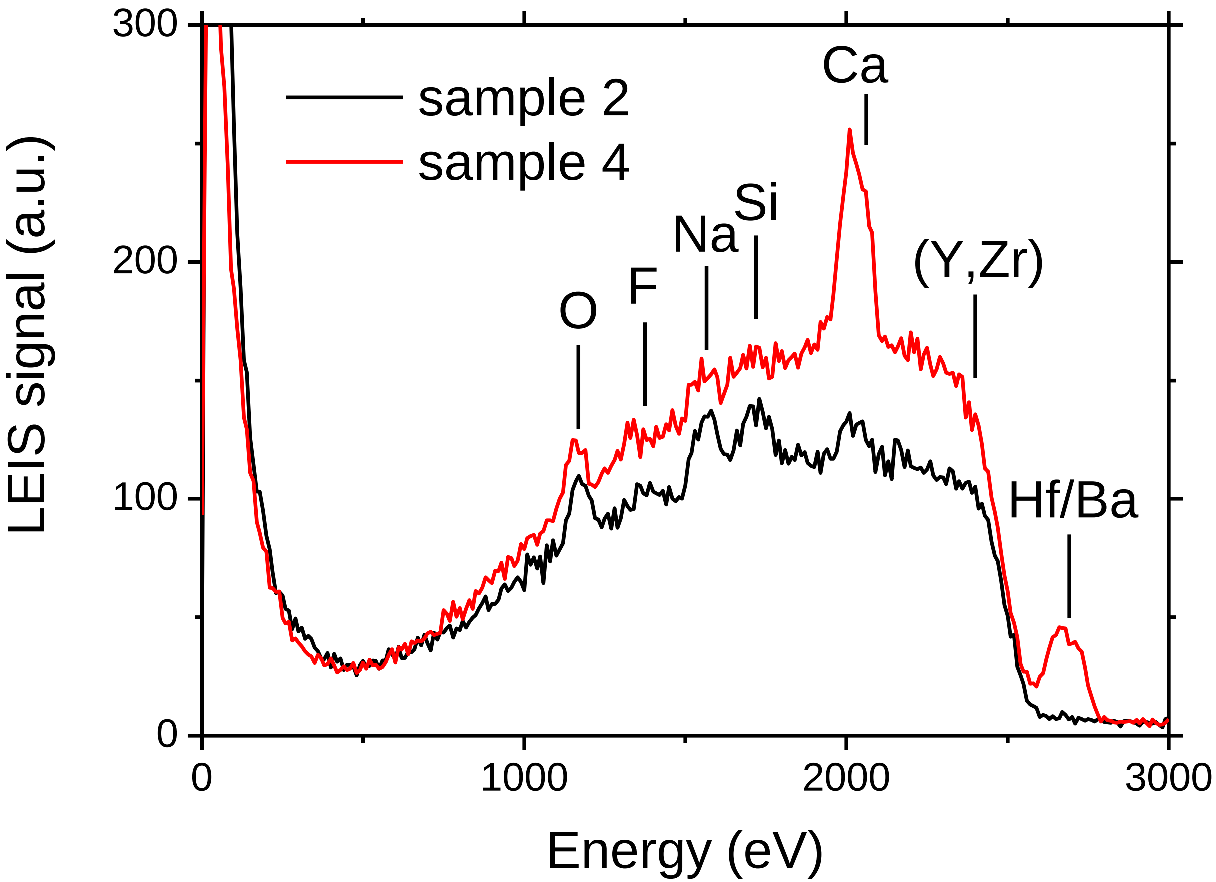
M. de Ridder et al., J. Appl. Phys. 92 (2002) 3056 - 3064

M. de Ridder et al., Solid State Ionics 156 (2003) 255 – 262

J.A. Kilner et al., J. Solid State Electrochem. 15 (2011) 861 - 876

Fuel Cells

Yttria stabilized Zirconia (YSZ) after calcination



Calcination for 5 hours at 1000 °C in an oxygen flow of 1.5 bar.

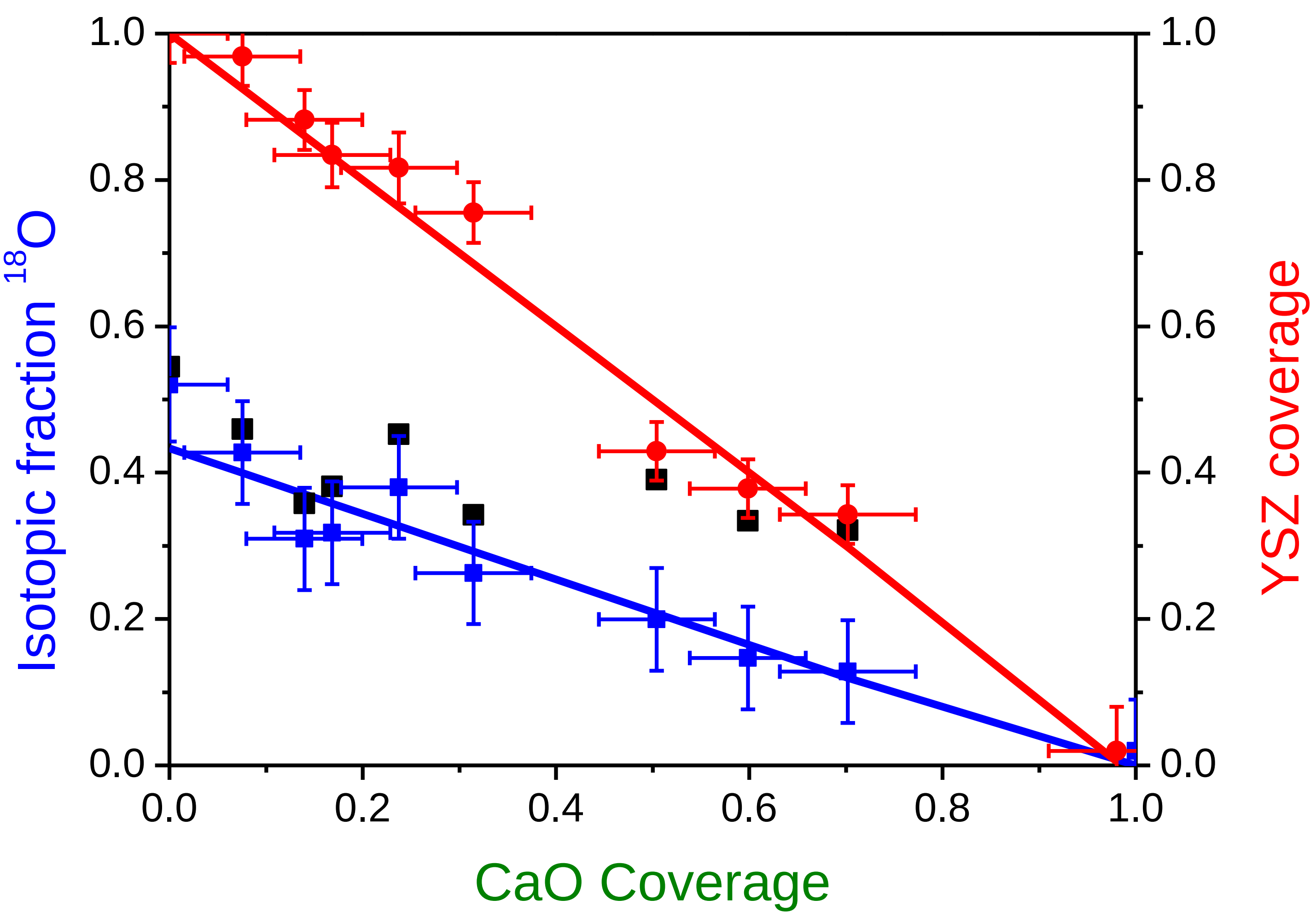
Segregation of monolayer of impurities

For T > 700 C: No Y, Zr in 1st atom !

XPS: Ca not visible (↔ Zr)

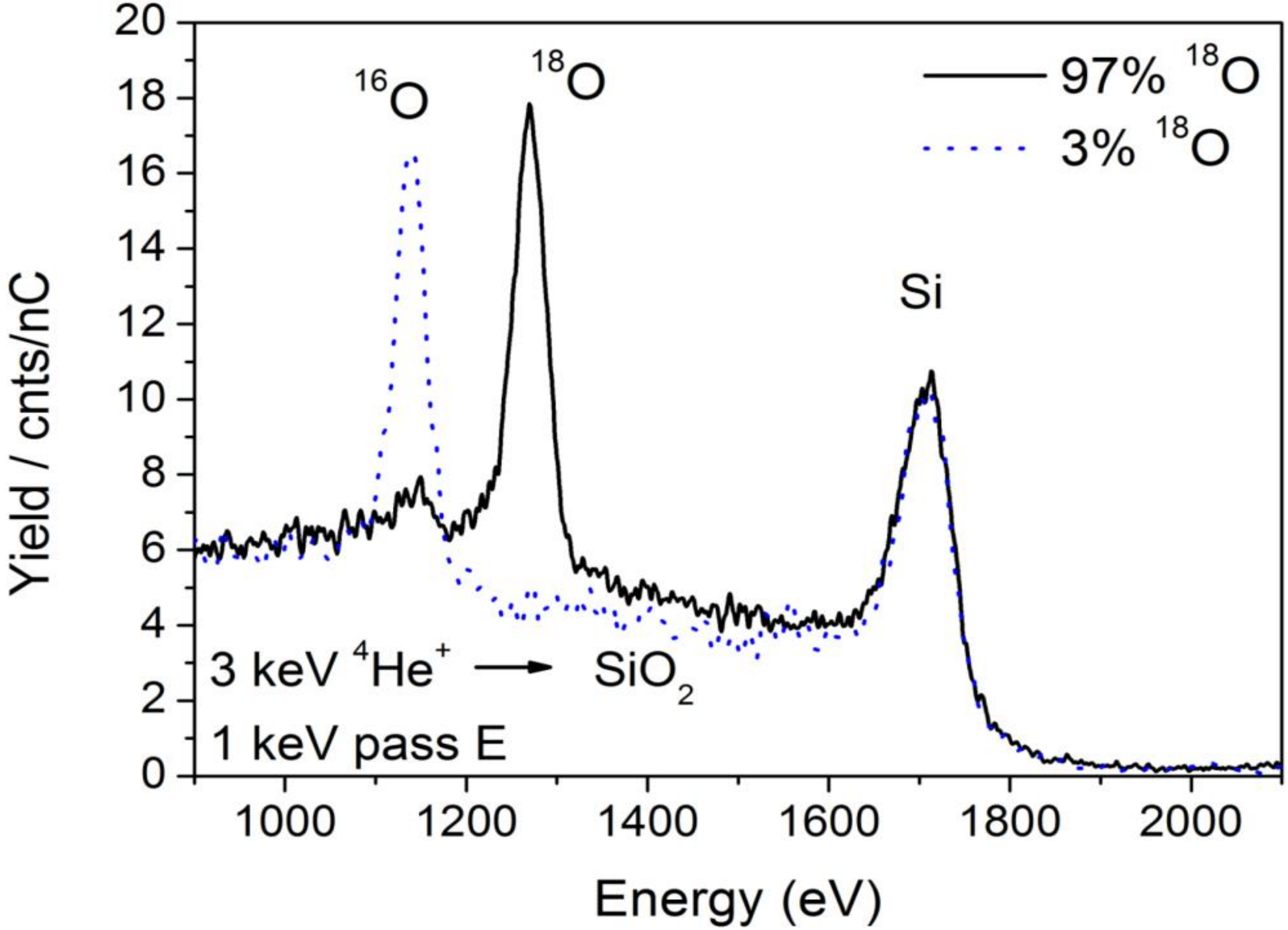
Fuel Cells

CaO coverage blocks ^{16}O – ^{18}O exchange



M. de Ridder et al., *Solid State Ionics* **156** (2003) 255 - 262

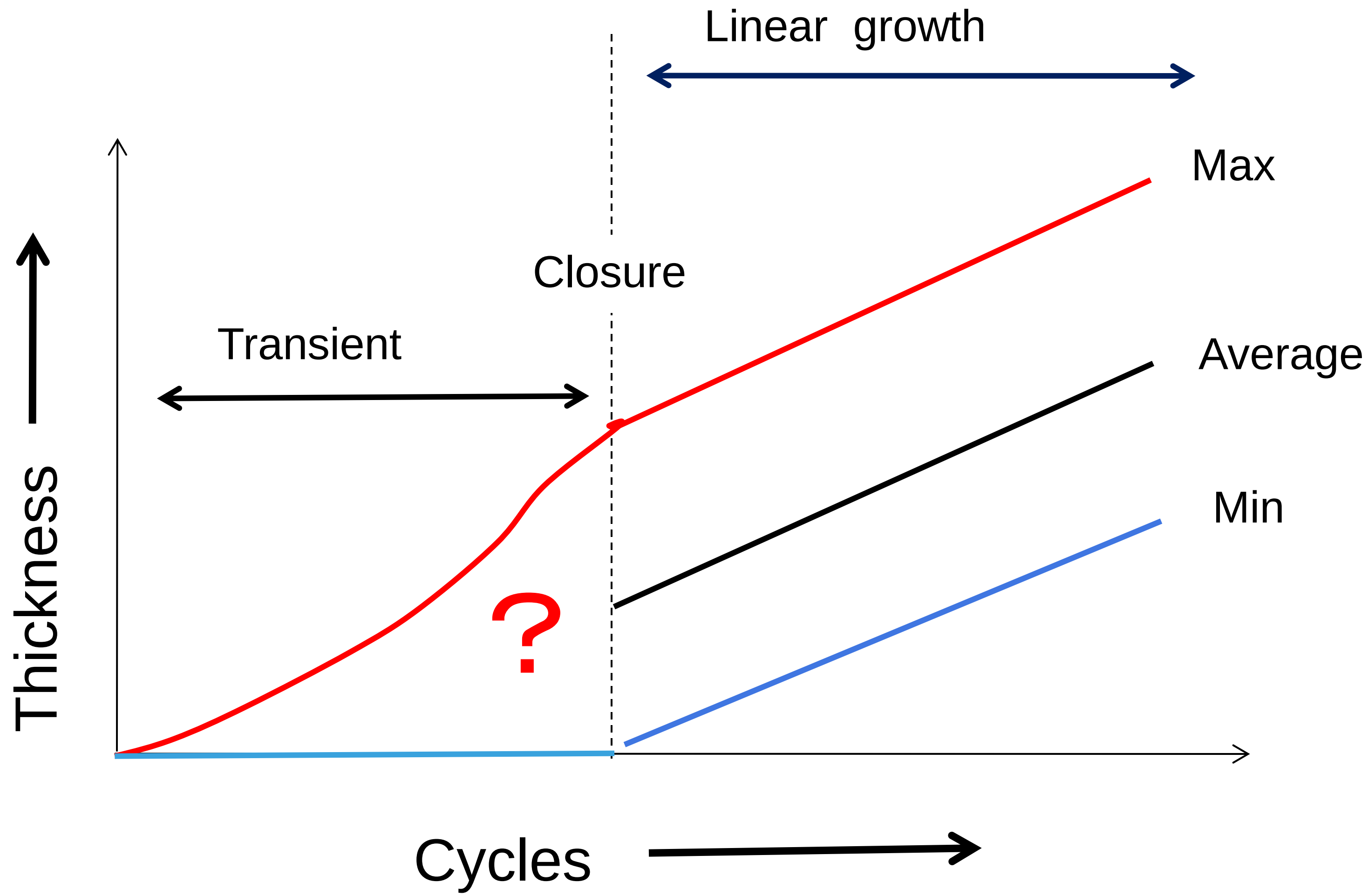
Isotopic exchange 16O – 18O



H. Téllez, R. J. Chater, S. Fearn, E. Symianakis, H. H. Brongersma, J.A. Kilner
Appl. Phys. Lett. 101, 151602 (2012)

Growth of Ultra thin

Layer thickness versus cycle



The transient regime determines the uniformity of the layer

Transient regime (growth before closure)
(6 up to > 150 cycles !)

IONTOF

Width of the transient regime depends on nucleation of ALD reaction, precursors and growth mode

- **2D growth:** Preferential growth on substrate

  CrOx/Al_2O_3, ZrO_2/SiO_2, HfO_2/Si

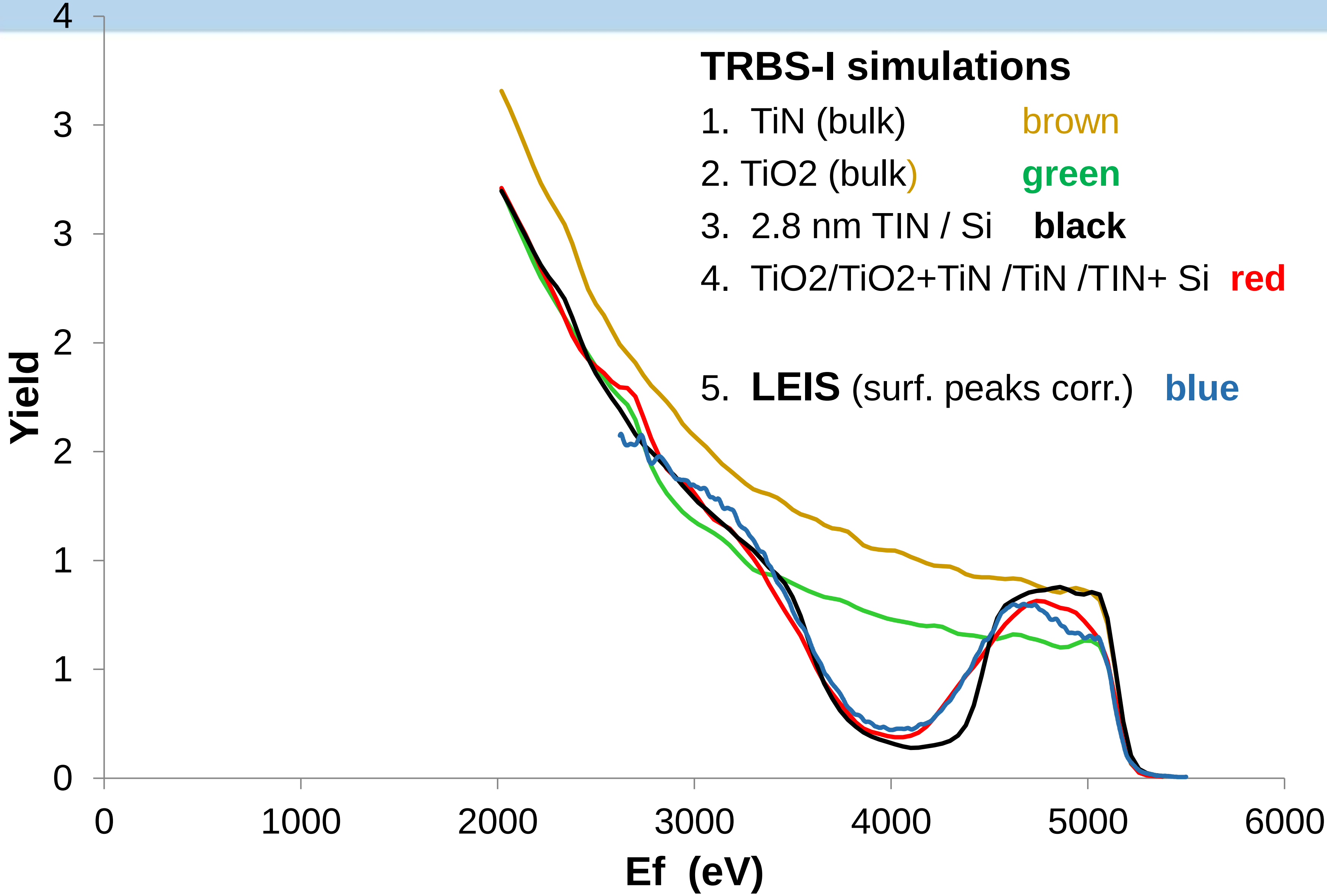
- **Random growth** AlN/Al_2O_3, AlN/SiO_2, Fe_2O_3/ZrO_2

- **3D growth:** Preferential growth on pre-deposited matter

  Ni/Al_2O_3, HfO_2/Ge, WNC/SiO_2/Si, Ta(CN)/SiO_2/Si, Ta(Si)/SiO_2/Si, TiN/SiO_2, Al_2O_3/Si-H, ZrO_2/Si-H

Controlling the transient regime is fundamental for continuity of ultrathin ALD films. **ALD + LEIS !!**

7 keV He+ LEIS
3.0 nm TiN / Si(100) nominal



Growth of Ultra-thin layers

LEIS: *1st atom + in-depth, quantitative, sensitive*

- Initial growth
- Poisoning, activation
- Pinholes
- Diffusion
- Thickness uniformity

- Use LEIS in the optimization of growth processes (ALD!)

Summary

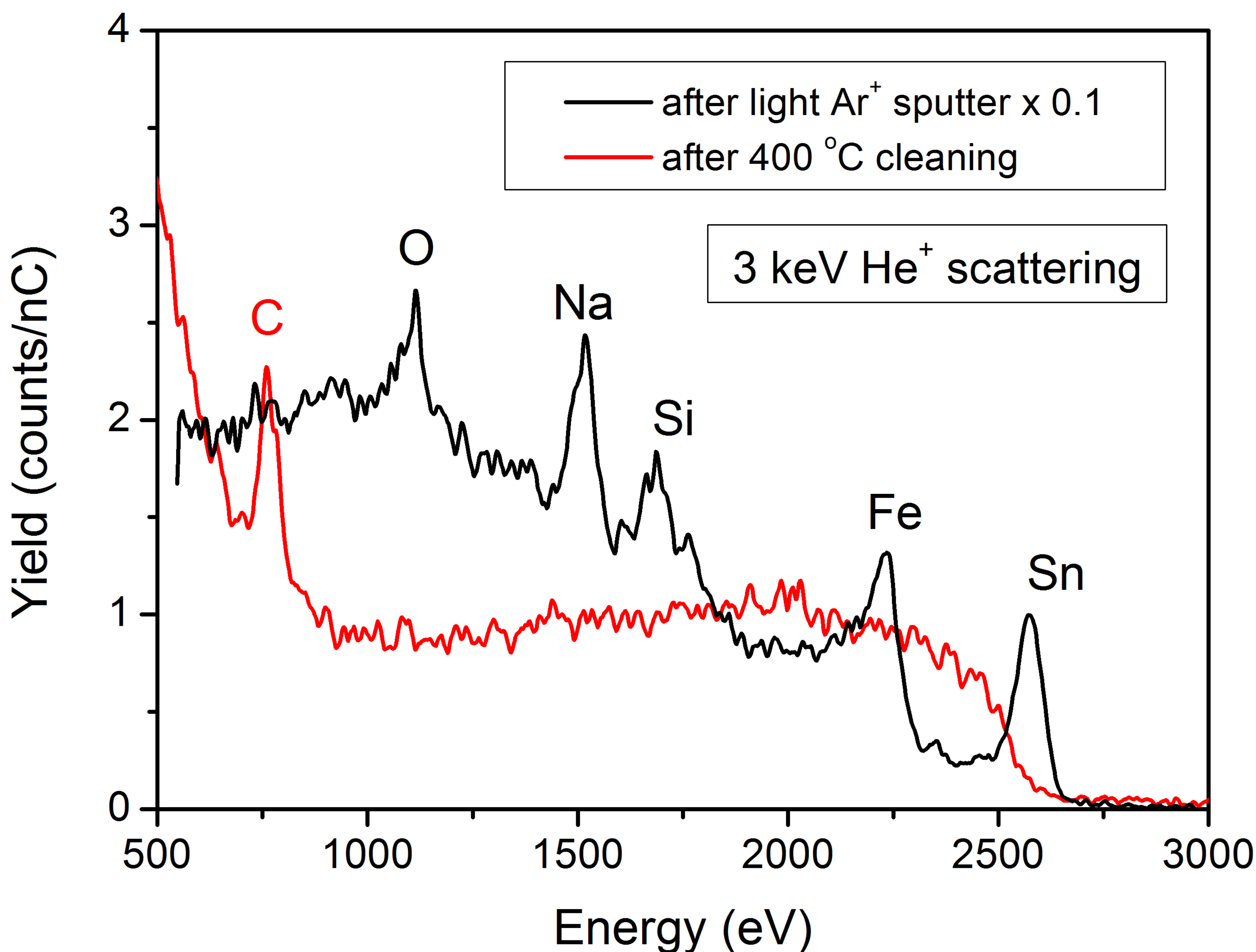
- Sensitivity
- 1st atom + in-depth
- Surf. segr. / anti wetting / M – polymer / surf. Modific. / NPs / graphene
- Outer surface of oxides
- SOFC , membranes
- ALD growth

Miscellaneous applications

- **Catalysts, microelectronics, polymers, (bio-) sensors, ...**

But also:

- Candy wrappers
- F 16 dome, windows of planes
- Bone tissue, dental implants, stents, ……
- Aging of linoleum (“ Linowonder”)
- Anti-wetting (watches, diapers, …..)
- Floor wax



after light Ar+ sputter x 0.1
after 400 °C cleaning
3 keV He+ scattering
C
O
Na
Si
Fe
Sn
0
1
2
3
4
500
1000
1500
2000
2500
3000
Yield (counts/nC)
Energy (eV)

Graphene analysis with LEIS ??

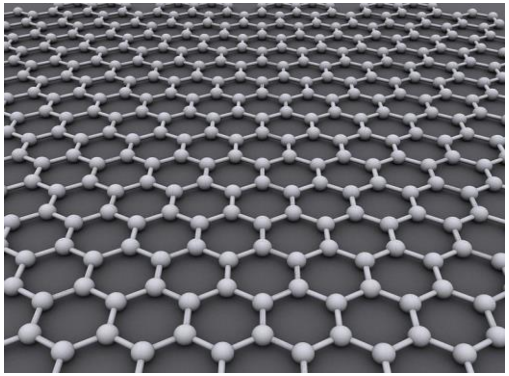
Wishes:

- Determination layer thickness, layer integrity
- Distinguish and Quantify carbon allotropes
- Detection contaminants / dopants *on/in* and *below* the film (intercalation)

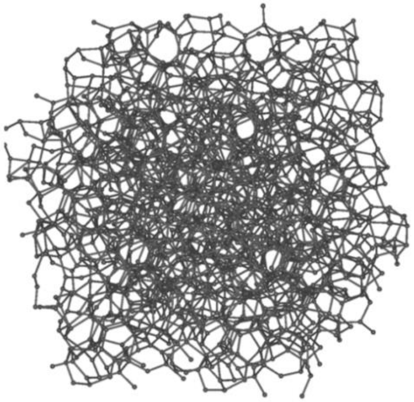
LEIS ??

- Carbon: low Z ⟹ Low sensitivity
- Monolayer depth info? Carbon atoms very small
- Distinguish allotropes ? No matrix effects (in general)

LEIS seems useless for studying graphene, but : ....



Author: AlexanderAlUS, wikipedia

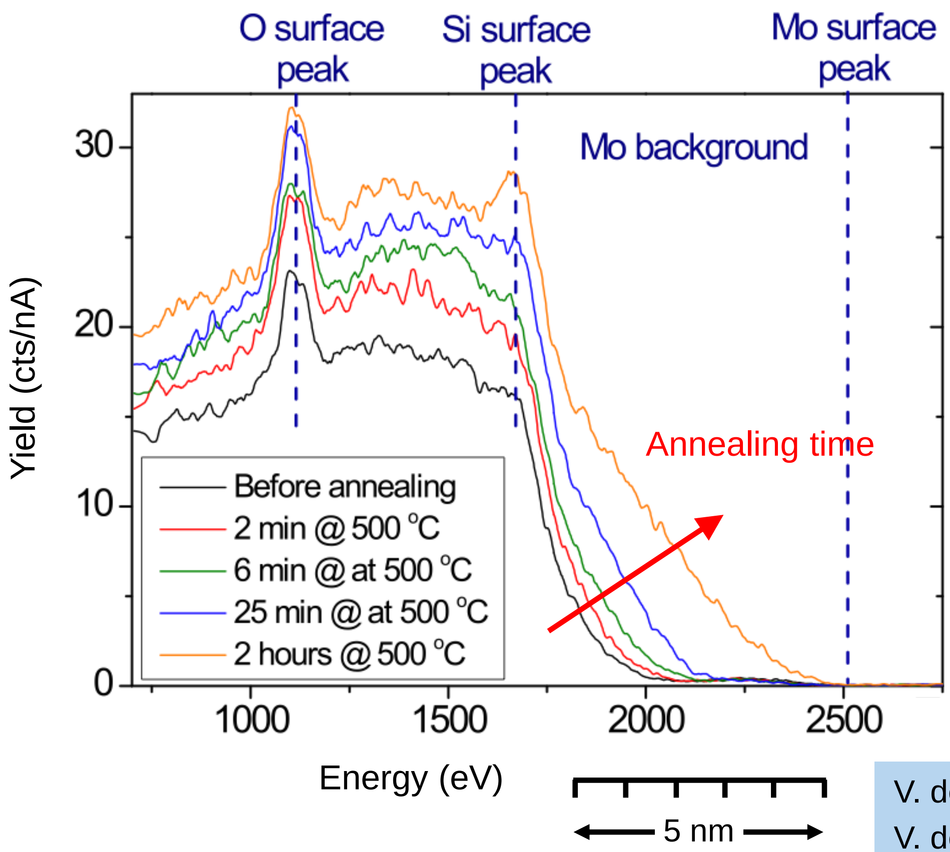


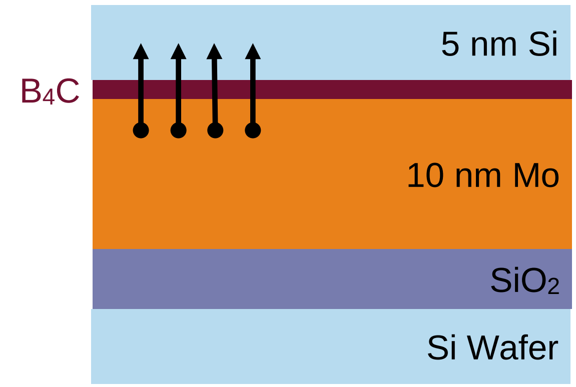
Author: Mstroeck, wikipedia

Diffusion study with in-situ heating

Mo/Si layer – quantification of diffusion constant

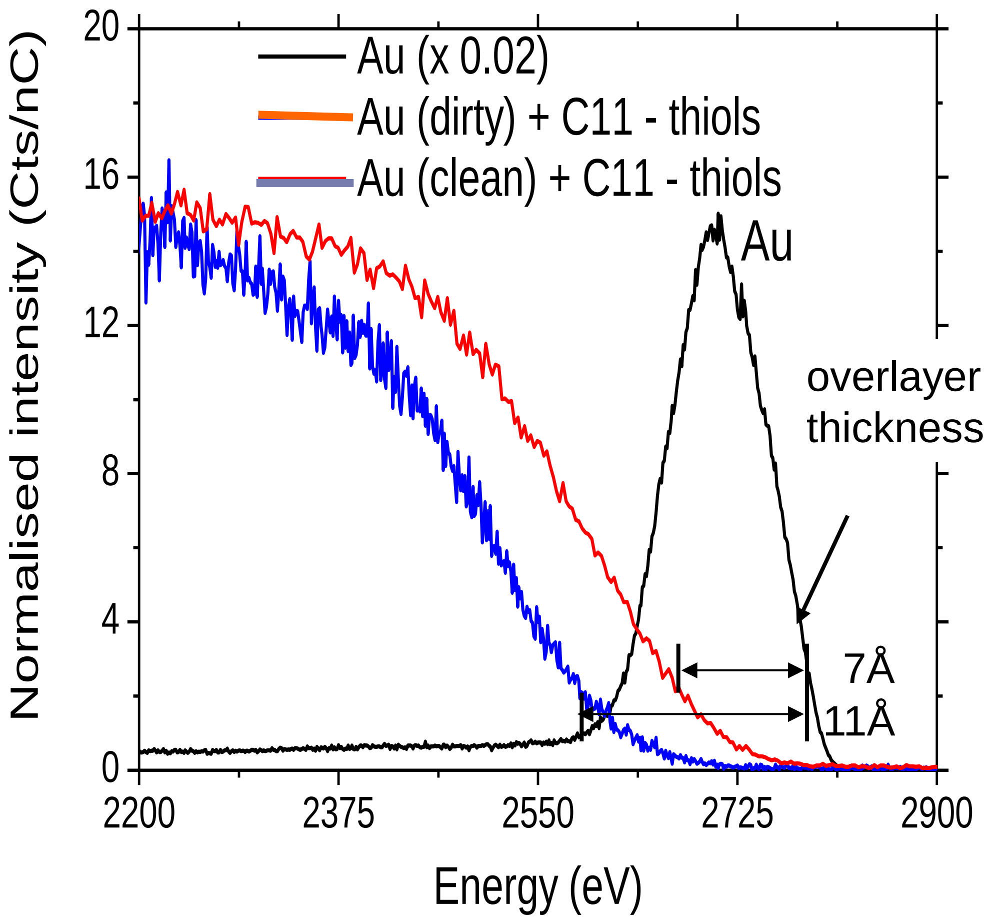
- 5 nm Si / 1.6 nm B_4C / 10 nm Mo, annealing @ 500 deg. C
- Diffusion coefficient without B_4C : $(8 \pm 2) \cdot 10^{-20}$ m^2/s
- Diffusion coefficient with 1.6 nm B_4C: $(4 \pm 1) \cdot 10^{-21}$ m^2/s



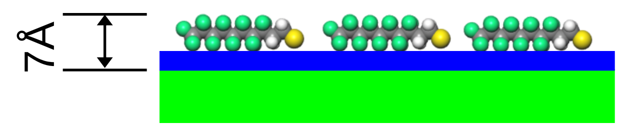


V. de Rooij-Lohmann, *Appl. Phys. Lett.* **94** 063107 (2009)
V. de Rooij-Lohmann, *J. Appl. Phys.* **108** 014314 (2010)

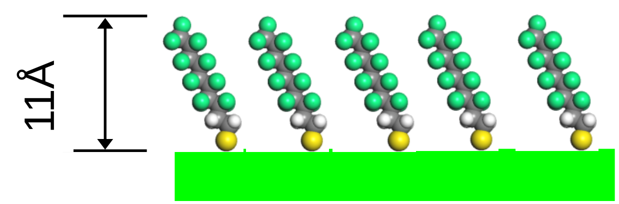
High-energy edge of SAMs on Au



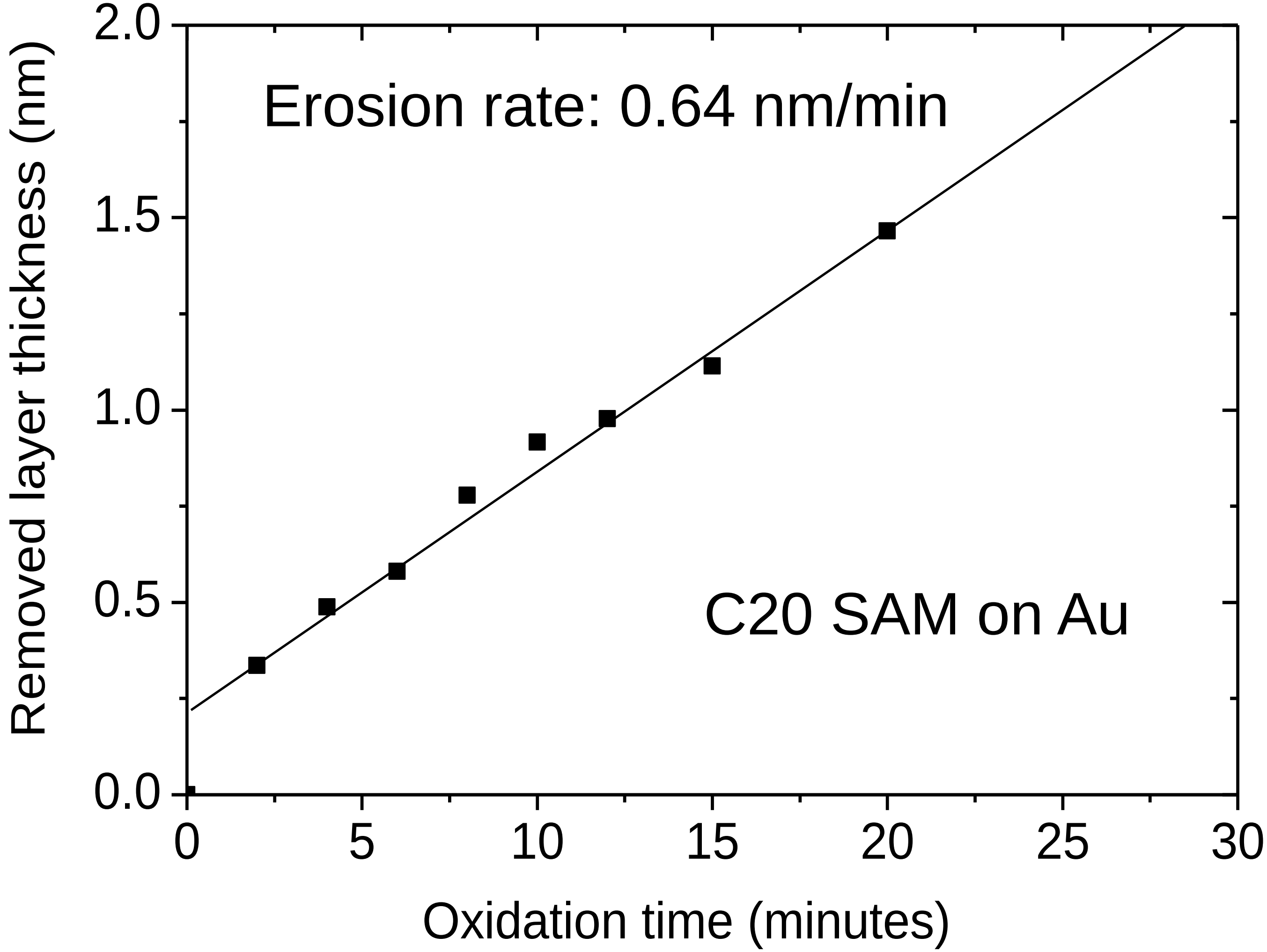
Fluorinated thiol on dirty Au surface



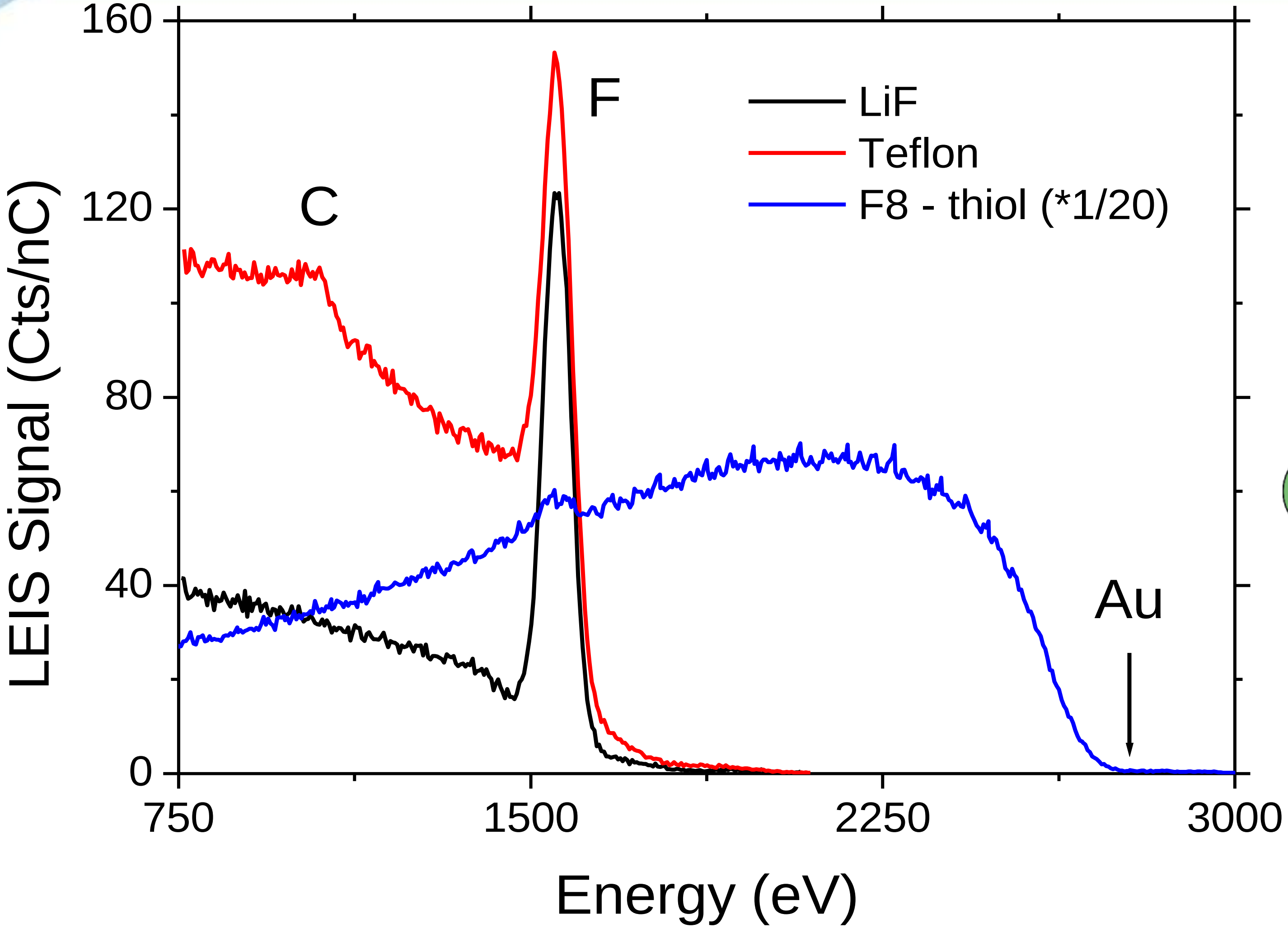
Fluorinated thiol on clean Au surface

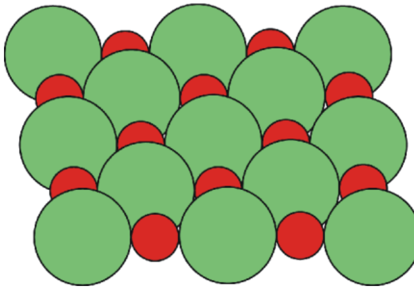


Erosion rate for atomic oxygen treatment



Quantification of F with LiF(100)





LiF (100)

LiF(100) : Teflon : s.-a. ML = 1.23 : 1.24 : 1.48 *10^{15} at./cm^2

Outer and Near surface of Perovskites by LEIS (for Fuel Cells and Oxygen Membranes)

iONTOF

Outer surface: **A-site** termination (LEIS: no other cations)

Subsurface: Layered oxide (LEIS depth profiling)

Examples:	*Structure*
$La_{0.6}$ $\mathbf{Sr_{0.4}}$ $Co_{0.2}$ $Fe_{0.8}$ $O_{3-\delta}$	Perovskite
Gd **Ba** Co_2 $O_{5-\delta}$	Double Perovskite
$\mathbf{La_2}$ Ni $O_{4-\delta}$	Ruddlesden - Popper

John Druce, Helena Tellez, 2014