Unique opportunities for new insight in the outer surfaces and interfaces by High Sensitiviy Low Energy Ion Scattering (HS-LEIS)

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March 23, 2011
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Outline

- **Introduction**
- **Principles and features of LEIS**
  - 1st atom, In – depth (0 – 10 nm), quantitative
- **Applications**
  - Organics (surface modific., anti-wetting, SAMs)
  - Catalysts (mixed oxides, coke, NP's, oxid. states)
  - Ceramics (SOFC, membranes)
  - ALD growth (high-k, inter-diffusion)
  - and many more ....

Why High-Sensitivity LEIS ?

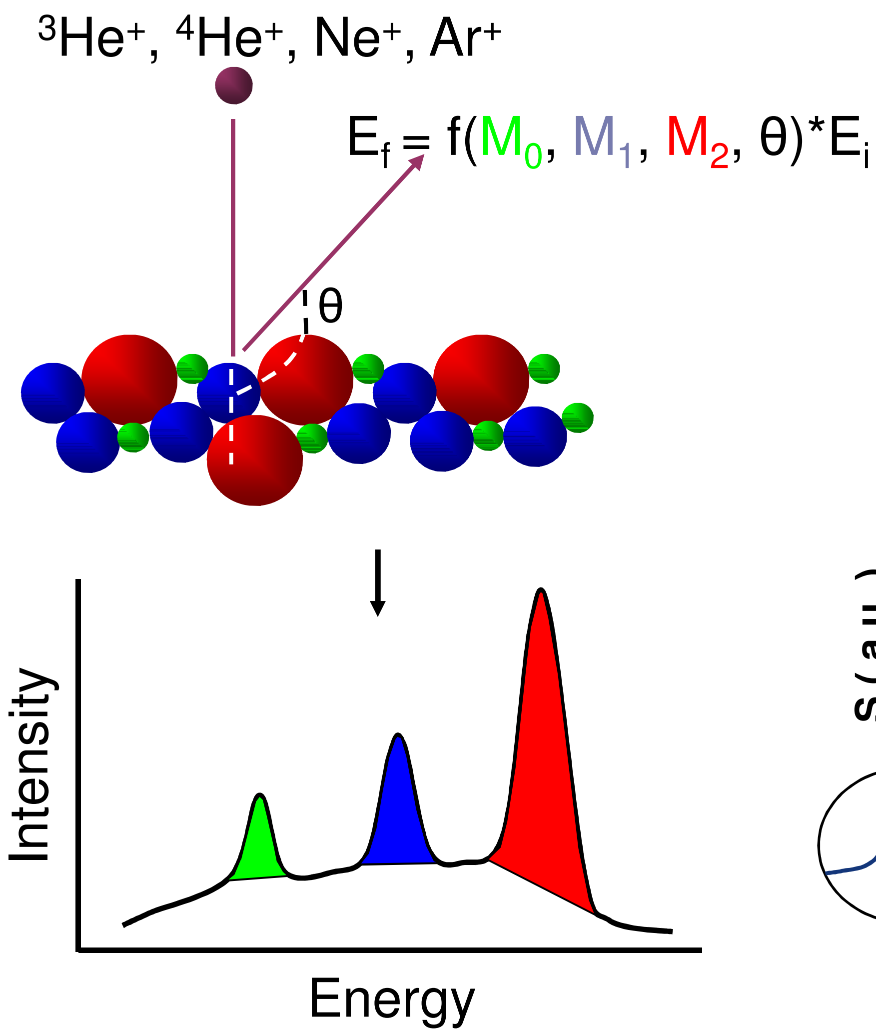
CONTROL at the ATOMIC LEVEL

requires

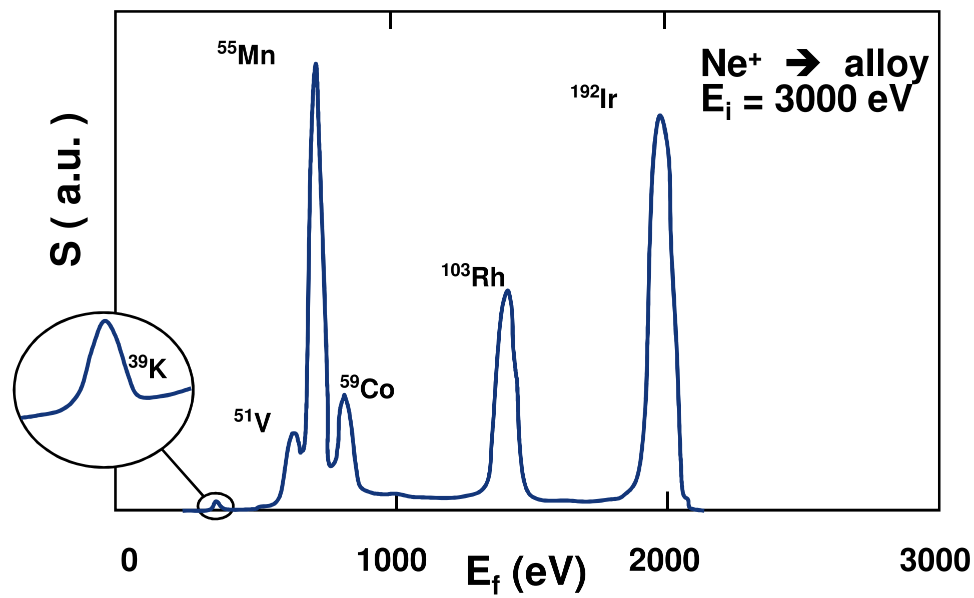
QUANTITATIVE ANALYSIS at the ATOMIC LEVEL

Low Energy Ion Scattering

Analytical Capabilities



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

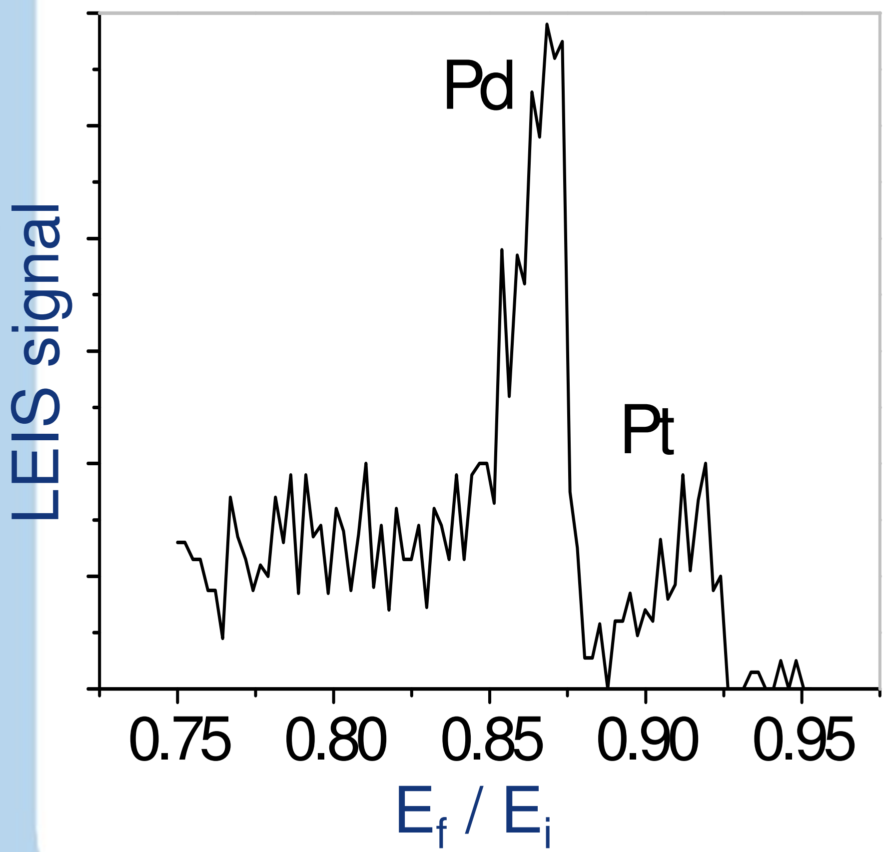


Conventional LEIS vs HS - LEIS

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

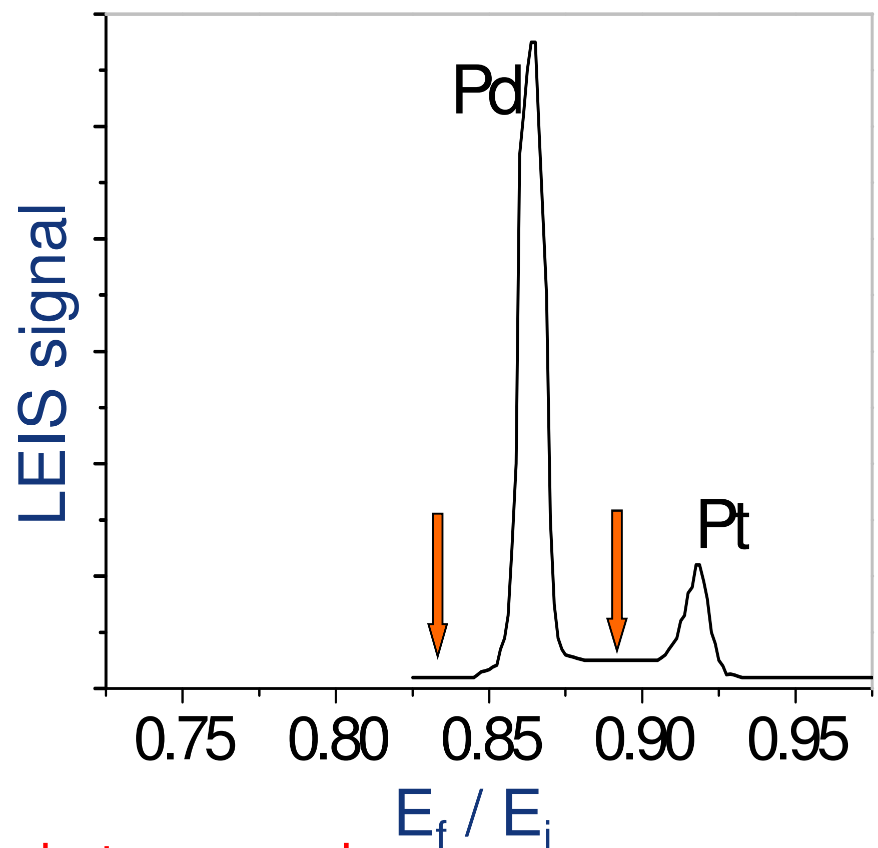
Conventional

^{4}He 10,000 nC



High-Sensitivity LEIS

^{4}He 5.4 nC



Promoters visible, but removed

NIM B 68 (1992) 207

Qtac : Unique new Analyser

High – Sensitivity LEIS

Energy image:

- parallel energy detection
- only low dose needed

↓

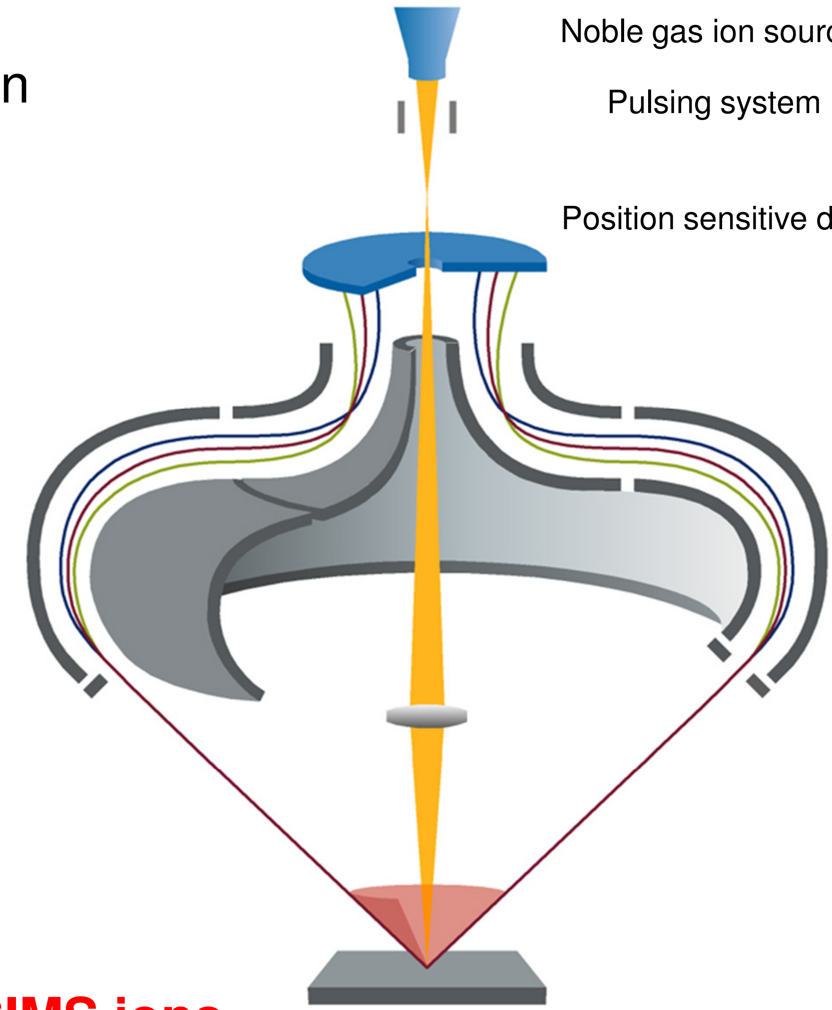
STATIC LEIS

" Analysis *before* Damage "

(Molecular Dynamics simulation)

" Hit same place only once "

ToF filtering eliminates SIMS ions



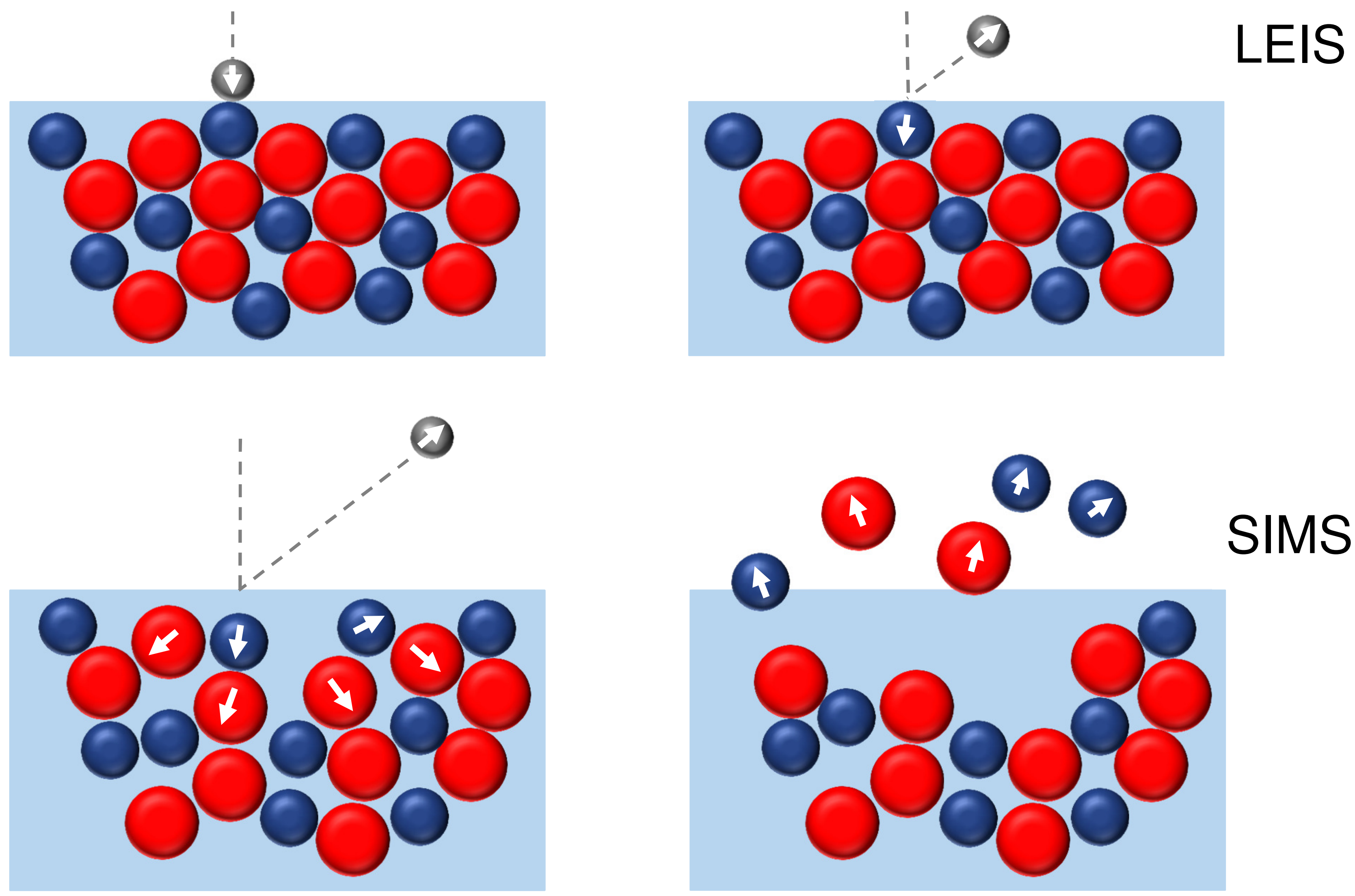
HS-LEIS: Principles and Key Features

- Analysis *before* damage (static)
- 1st Monolayer
- Quantitative (peak ⟶ concentration / coverage)
- Sensitivity
- Mass resolution
- ToF-filtered LEIS
- Imaging

- In-depth: Static (0 – 6 nm) *or* with sputtering

LEIS and SIMS

Time resolved: **LEIS analysis *before* damage !**



Quantification

Review:

Brongersma et al., Surf. Sci. Reports, 62 (2007) 63 – 109.

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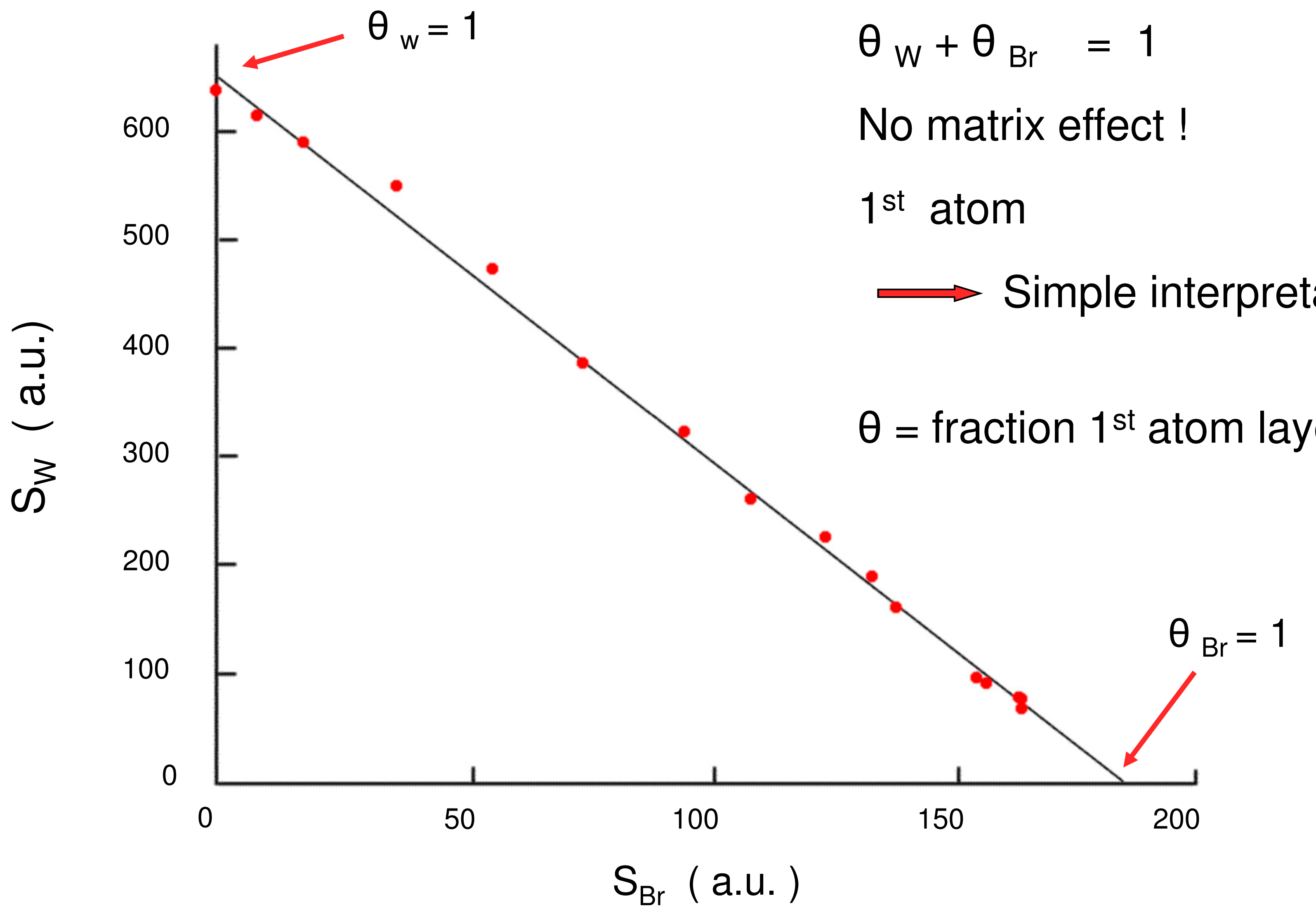
Quantification

Bromine adsorption on Tungsten



$\theta_W + \theta_{Br} = 1$

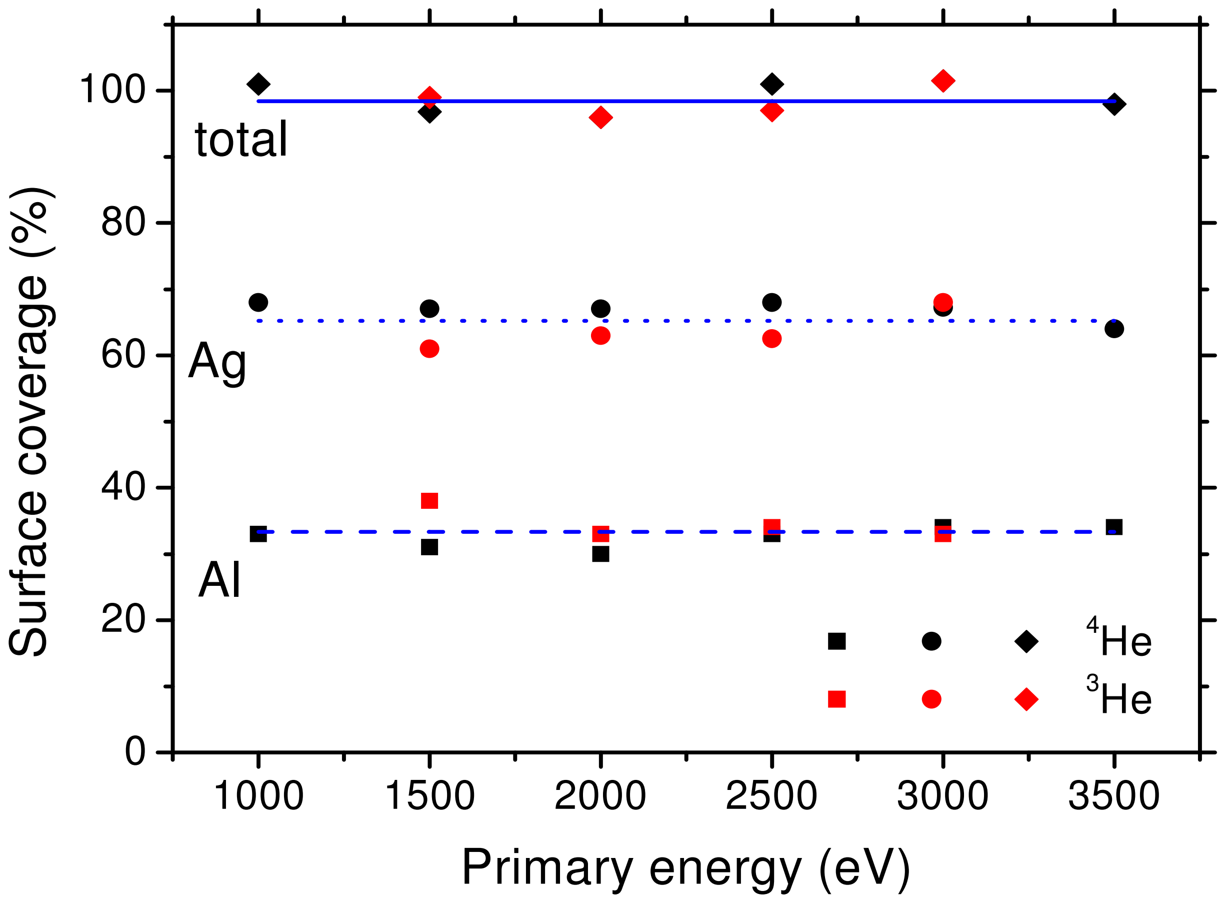
No matrix effect !

1st atom

→ Simple interpretation !!

θ = fraction 1st atom layer

Bulk Composition $Ag_{80} Al_{20}$



Surface Composition

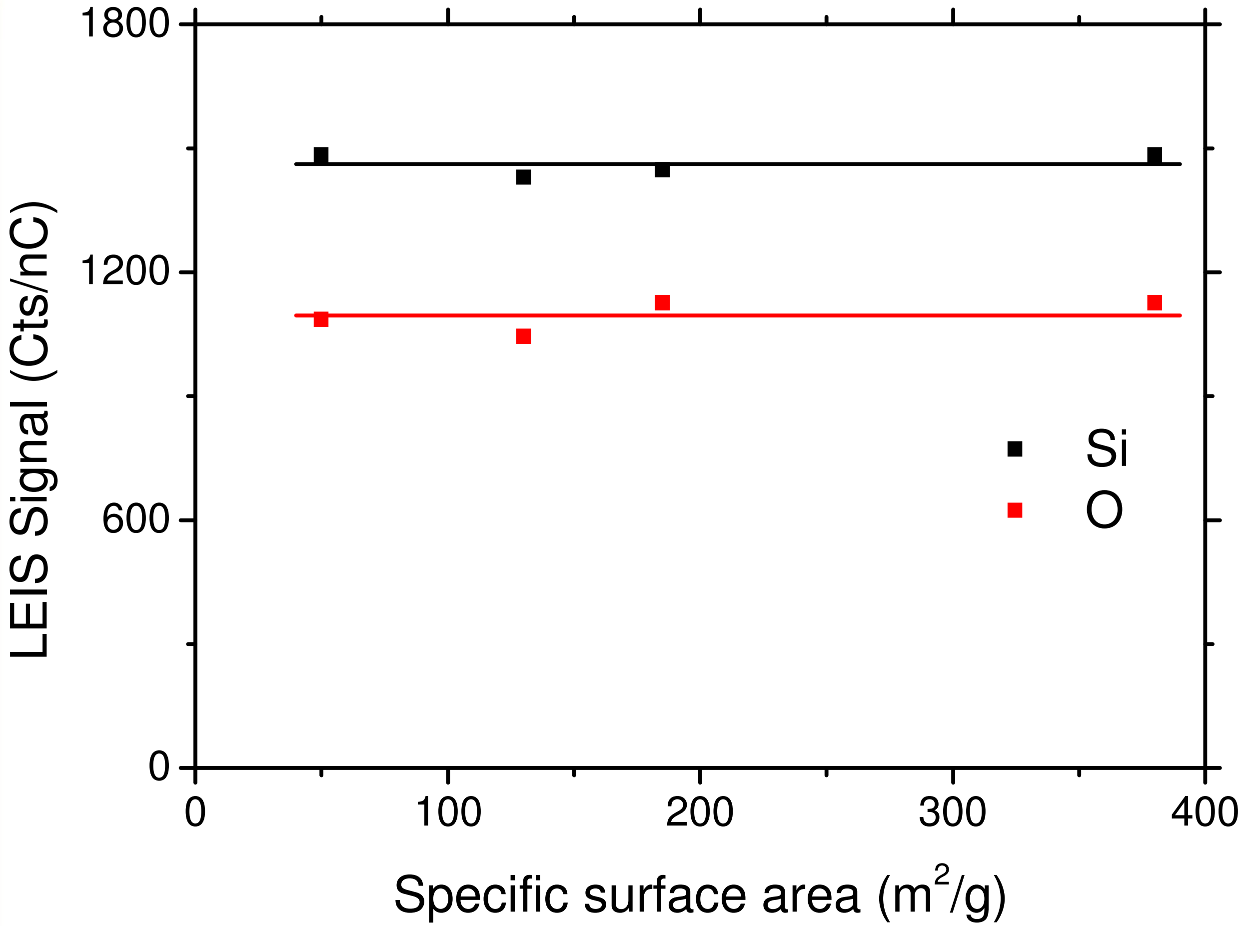
$Ag_{66} Al_{34}$

(independent of primary energy)

NO matrix effects

Rough silica: 50 – 380 m^2/g

HS-LEIS: Insensitive to roughness

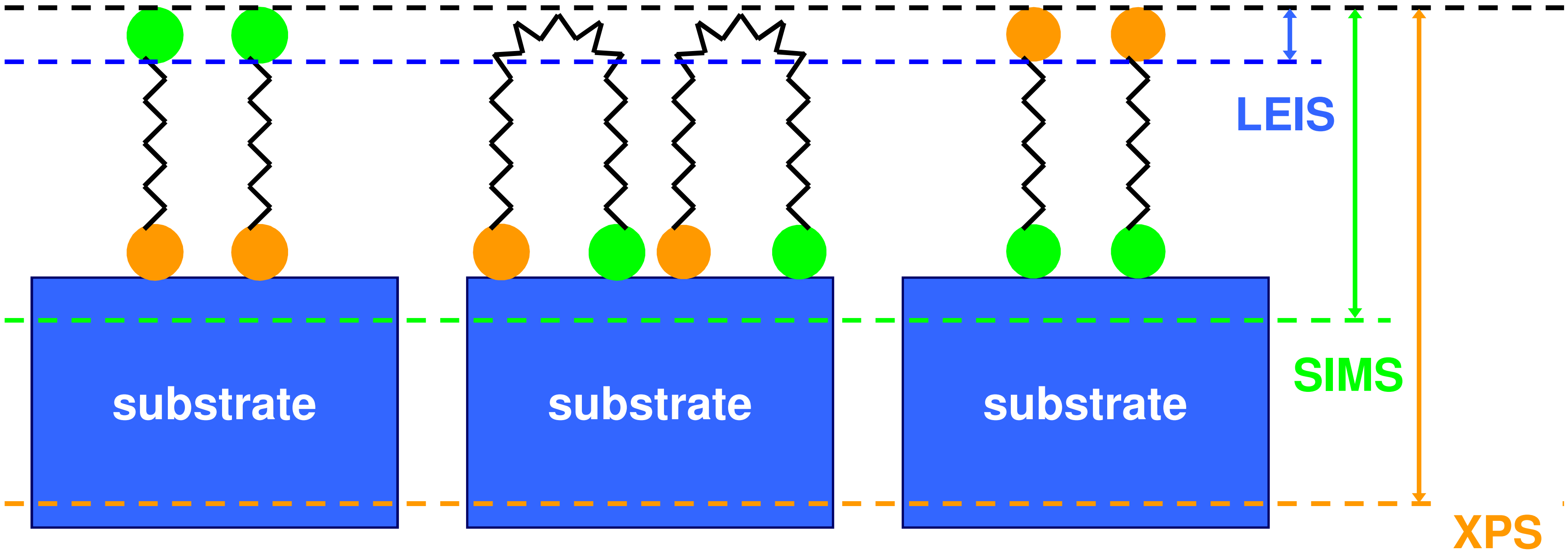


LEIS Signals:

rough silica about 77% of flat silica (quartz)

W.P.A. Jansen et al., *SIA* **36** (2004) 1469 - 1478.

Monolayer sensitivity



LEIS 1st atom and in-depth; quantitative, sensitive

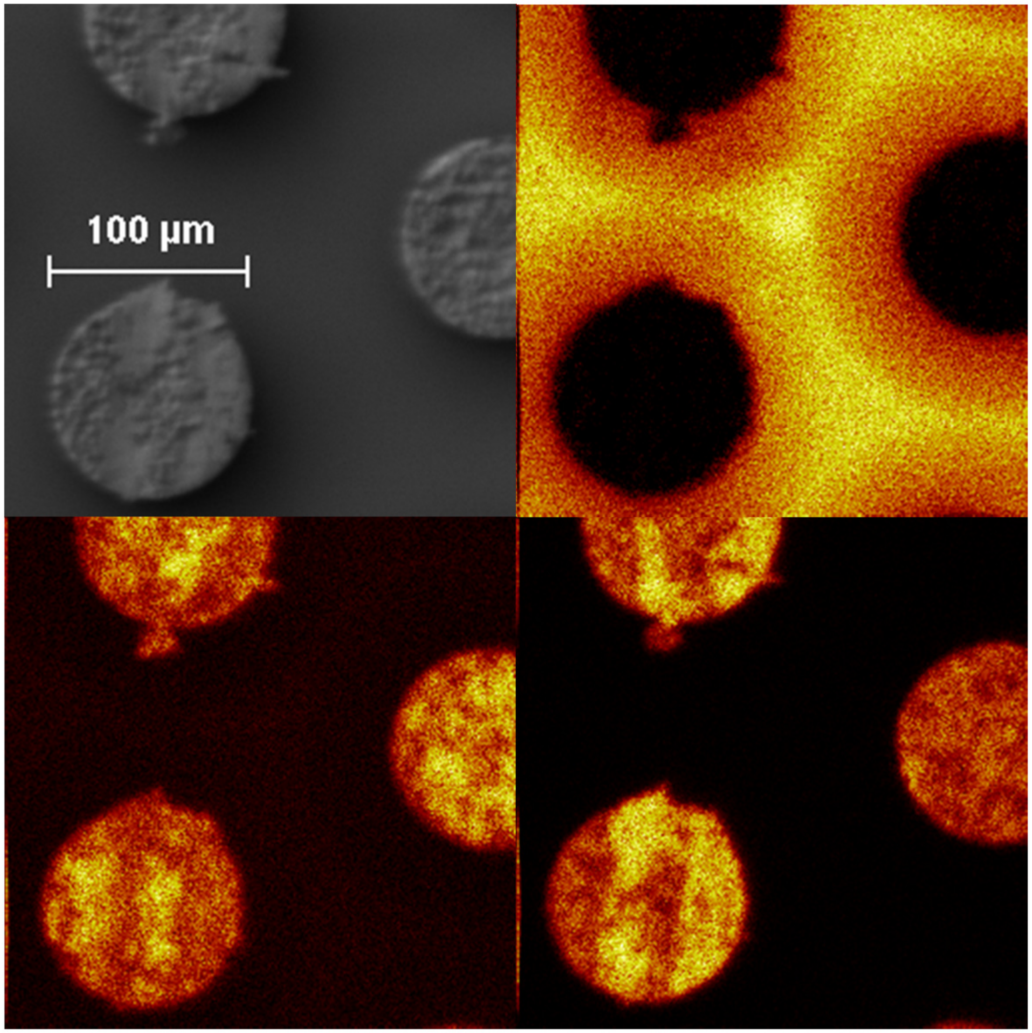
SIMS not quantitative for near-surface / interface

XPS average over 3 – 10 nm; chemical info

Elemental mapping by LEIS and SE Image

Solder bumps

SE image



Ti

Sn

Pb

LEIS and Microelectronics

Depth info for

Ultra thin layers and interfaces

In – Depth profiling

Two possibilities:

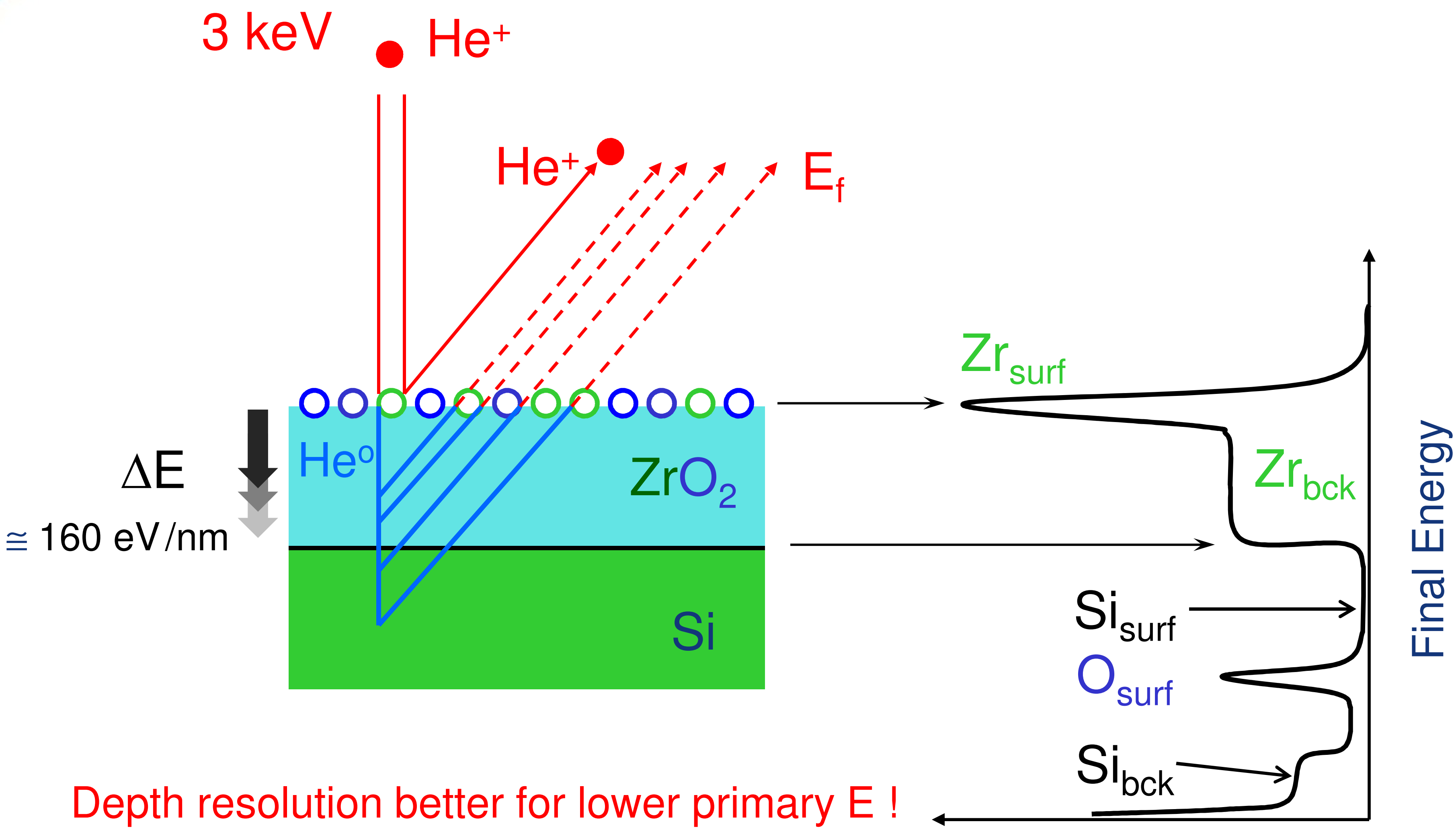
1. Static LEIS + sputter depth profiling with dual ion beam

   (advantage of quantification, depth resolution LEIS)

2. Static LEIS

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

Depth info

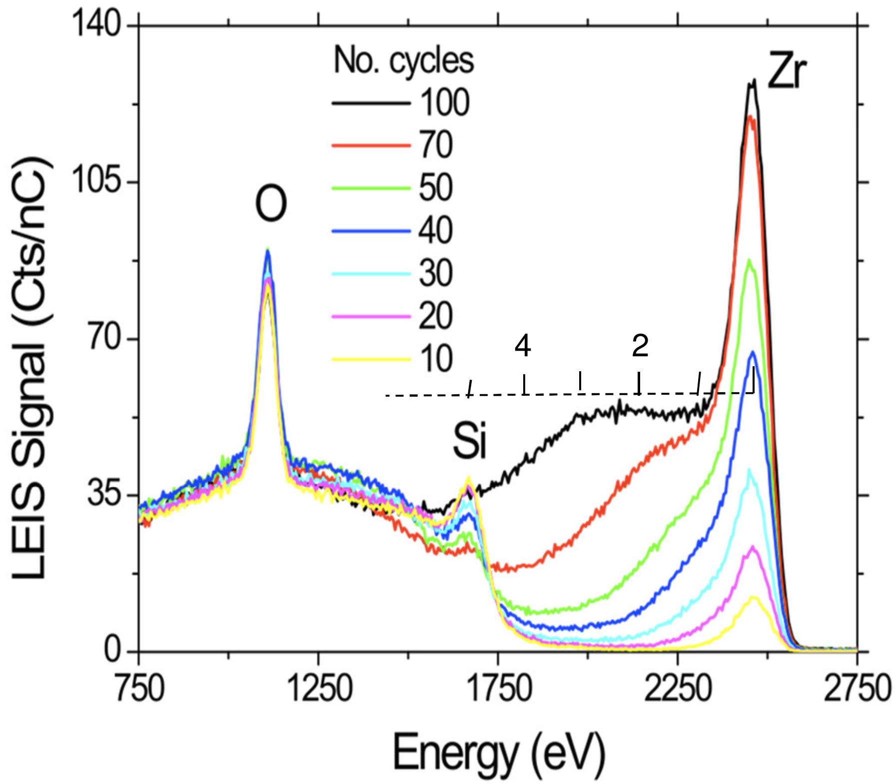


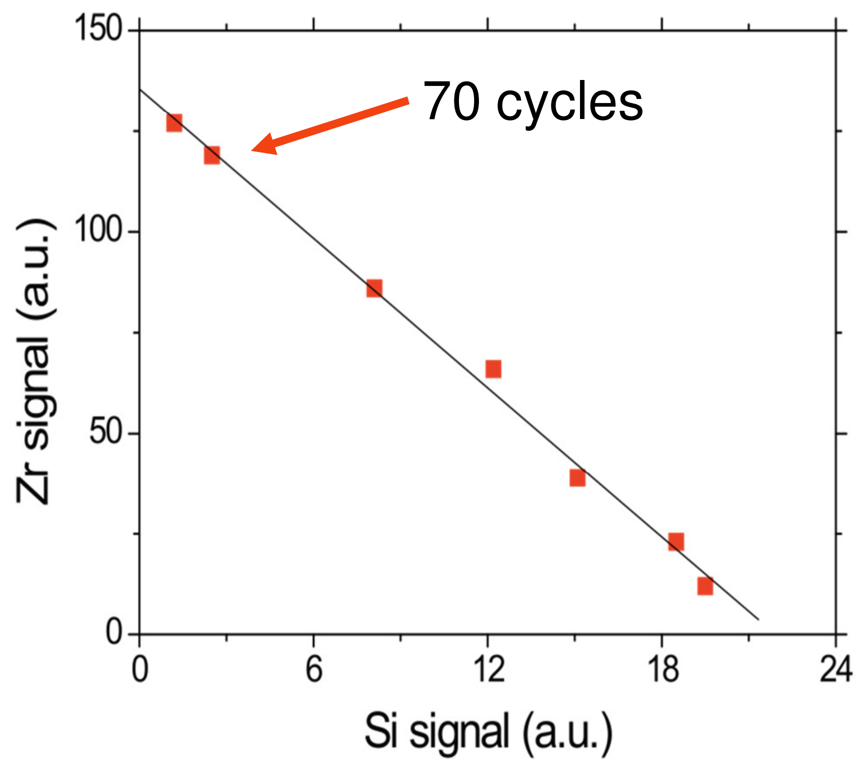
Depth resolution better for lower primary E !

1st atom and Static Depth Profile

ZrO_2 Atomic Layer Deposition on Silicon

- Closure / 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





INFO from LEIS spectra

In LEIS only backscattered *ions* are detected

Peaks: Ions backscattered from 1st atom.
(*one well-defined* collision)

Tails: Backscattering in deeper layers + reionization
(Scattering by oxygen atoms: efficient reionization)

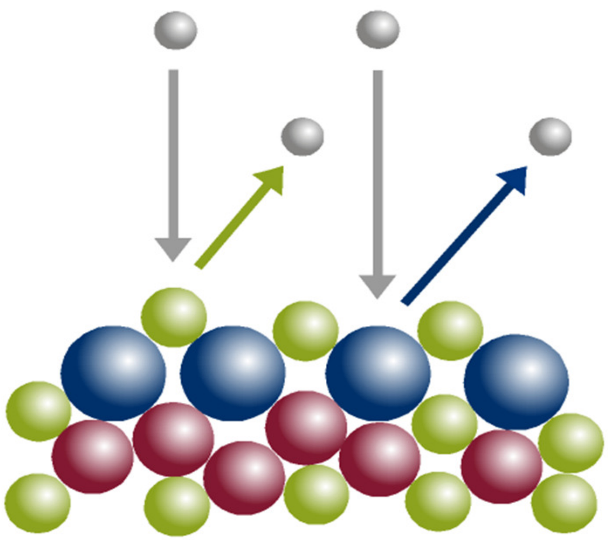
→ Shape: f (in-depth distribution Zr)

Intensity: f (oxygen concentration in 1st atomic layer)

LEIS Technique

Features of Low Energy Ion Scattering (LEIS)

He+, Ne+, Ar+, Kr+
1 - 8 keV



LEIS Features

Ultra-high surface sensitivity, ***top atomic layer*** analysis

Static depth profiling information (up to 10 nm)

Reliable and straight-forward ***quantification***

Detection of all elements ***> He***

Detection limits:

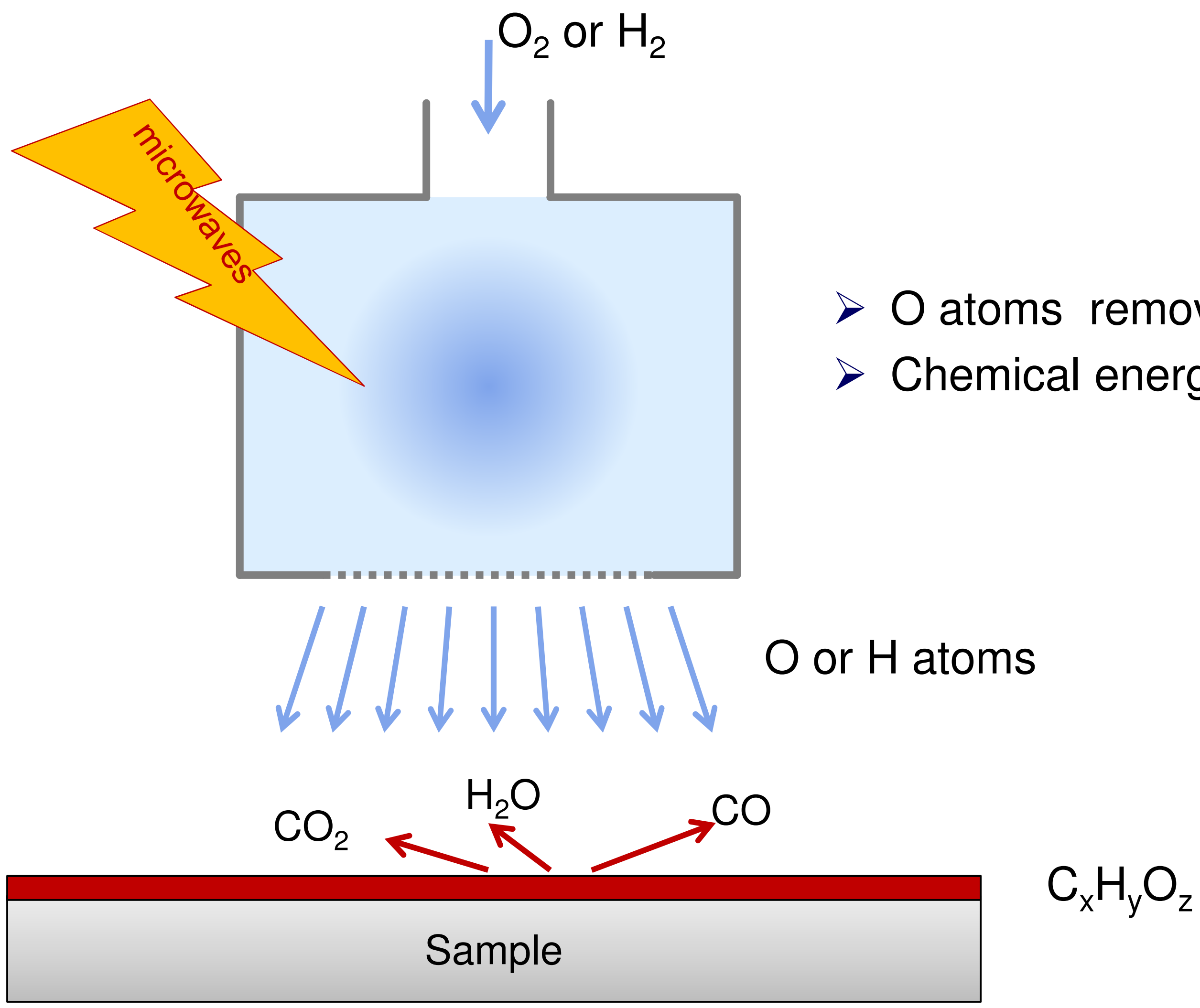
Li - O ≥ 1 % of 1 ML

F - Cl 1 % - 0.05 % of 1 ML

K - U 500 ppm - 10 ppm of 1 ML

Sample Treatment

Atom Source for Surface Cleaning



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

Organics

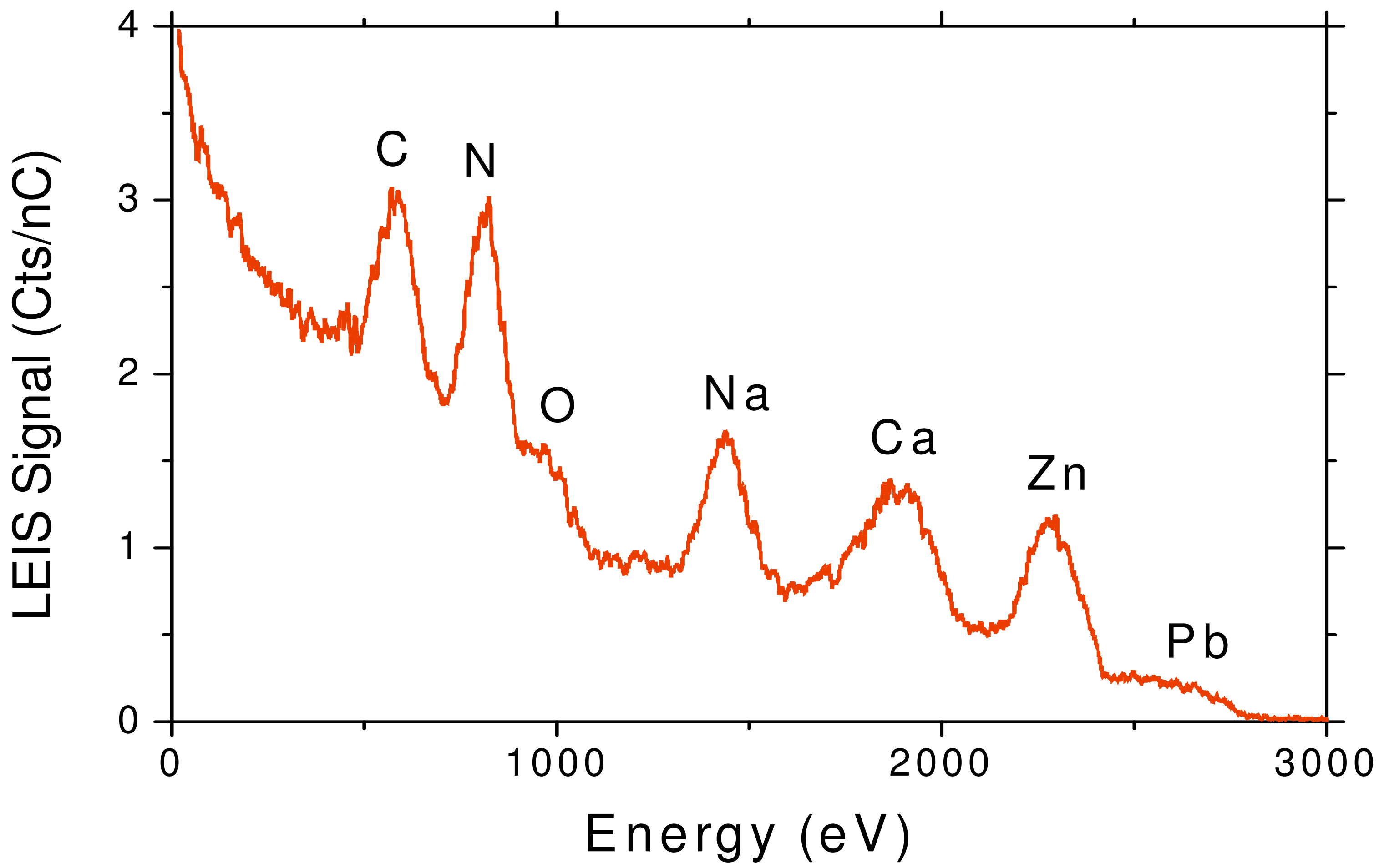
- Surface segregation
- Dendrimers
- Antiwetting
- Surface modification
- Metal / polymer interface
- SAMs

Polymers, SAMs, ...

- Inter - molecular segregation
  - Segregation impurities, additives (0.1 s - days - ..; up to 10^8 x !!)
- Intra - molecular segregation (0.1 s - days - ..)
  - Aging plasma oxidized PE
- Anti - wetting layers
- Metal diffusion in polymers
- SAM’s

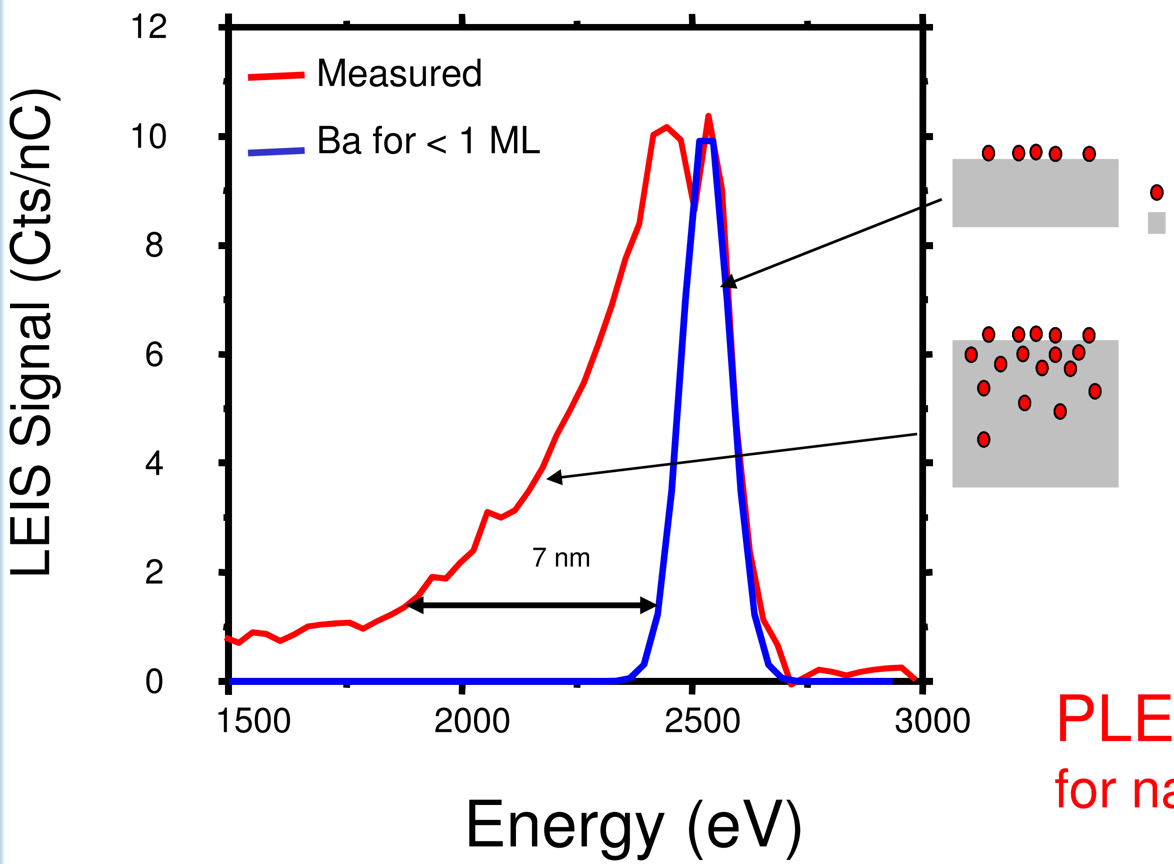
Acrylonitrile-Butadiene-Styrene (ABS)

Surface segregation of additives



Metal - polymer interface in ultra - thin layers

PLED: Ba evaporation on PPV



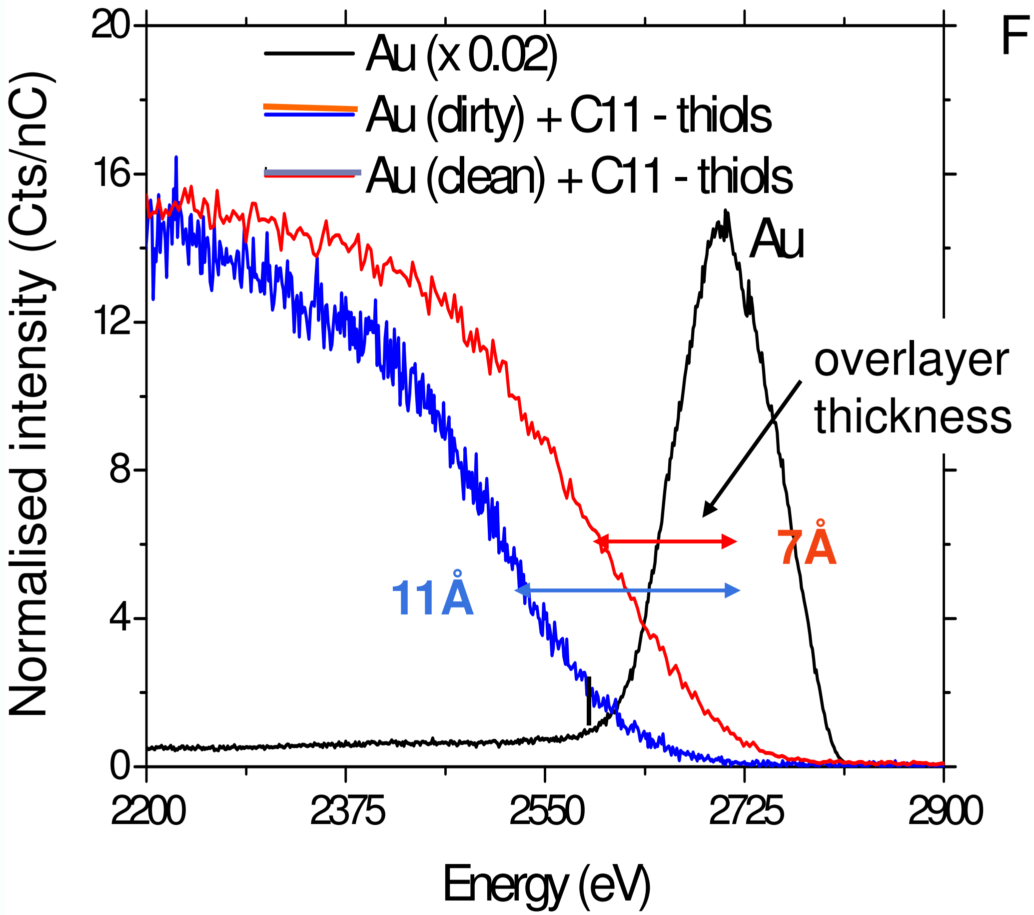
During evaporation of barium on PPV, most of the Ba diffuses into the PPV.

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

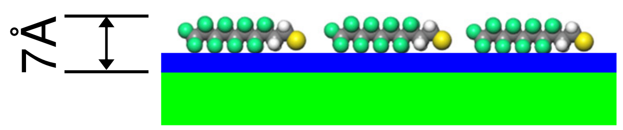
Peak shape ↔ depth distribution

PLED: higher light output for narrow depth distribution

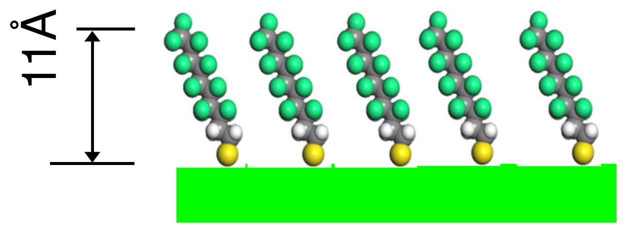
High-energy edge of SAMs on Au



Fluorinated thiol on dirty Au surface

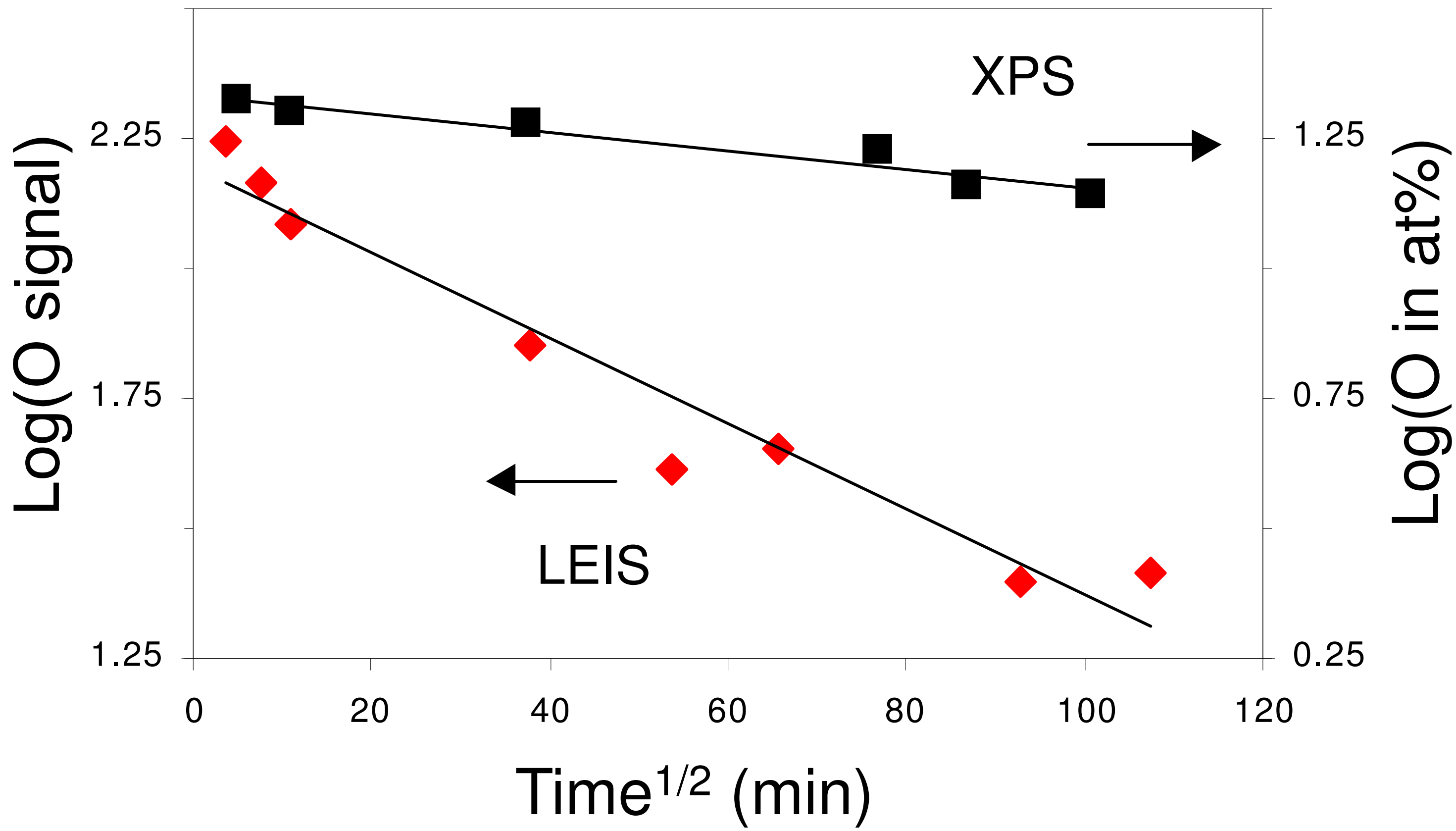


Fluorinated thiol on clean Au surface



Aging of plasma oxidized HDPE

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



HS – LEIS and Catalysis, Ceramics

Selection of examples:

- Pt/Au
- Mixed oxides
- γ-alumina
- Poison (Coke on TWC)
- Poison (oxygen membranes, SOFC)
- Use of probe molecules
- NP's , core/shell
- Oxidation state 1st atom

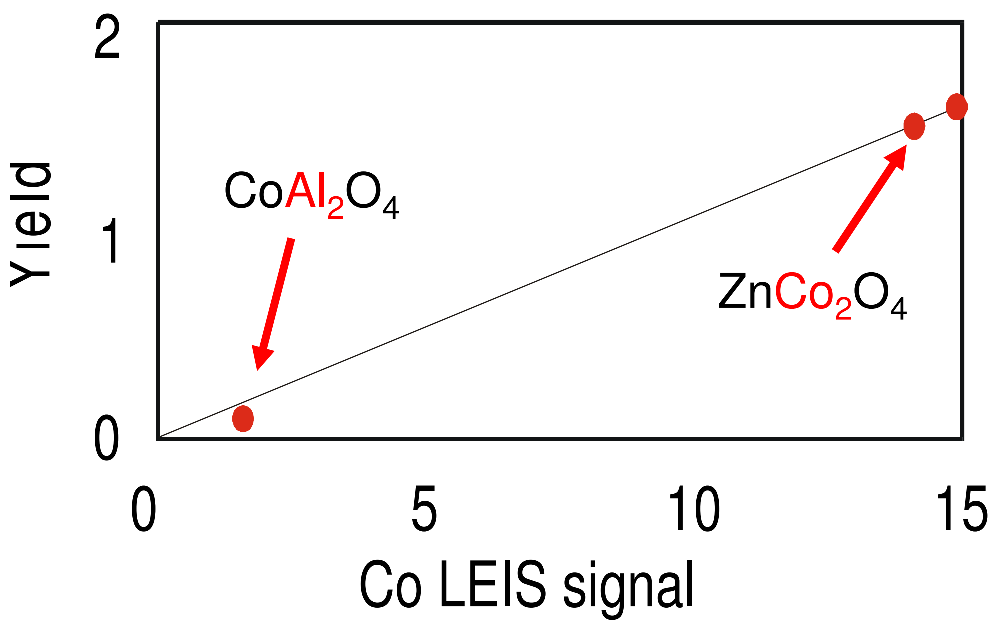
Important / unique applications for catalysis

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

Fuel Cells and Membranes

Importance of the outer surface

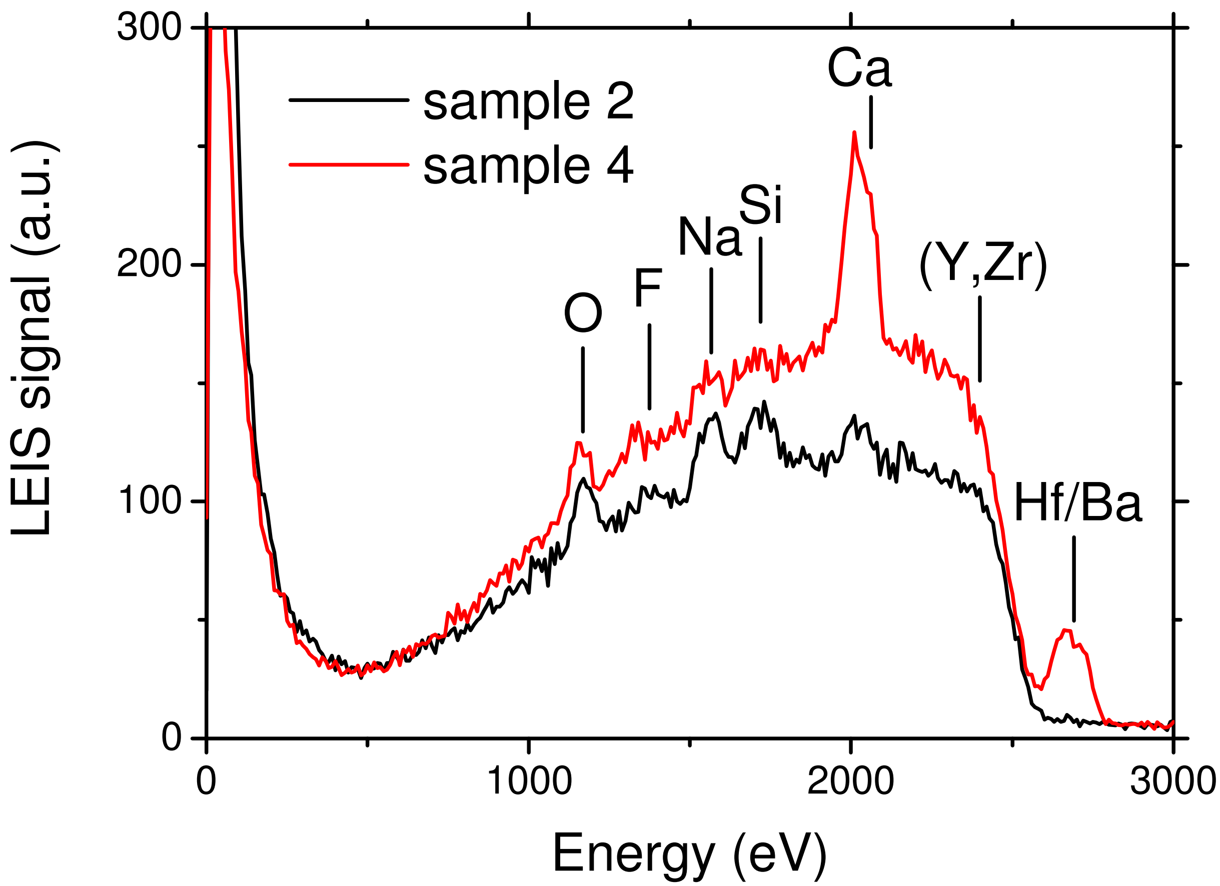
- Performance relies on oxygen transport
- Performance: “ Hampered by the surface ”
- Why ? What is the surface ??

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

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

Fuel Cells

Yttria stabilized Zirconia (YSZ) after calcination



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

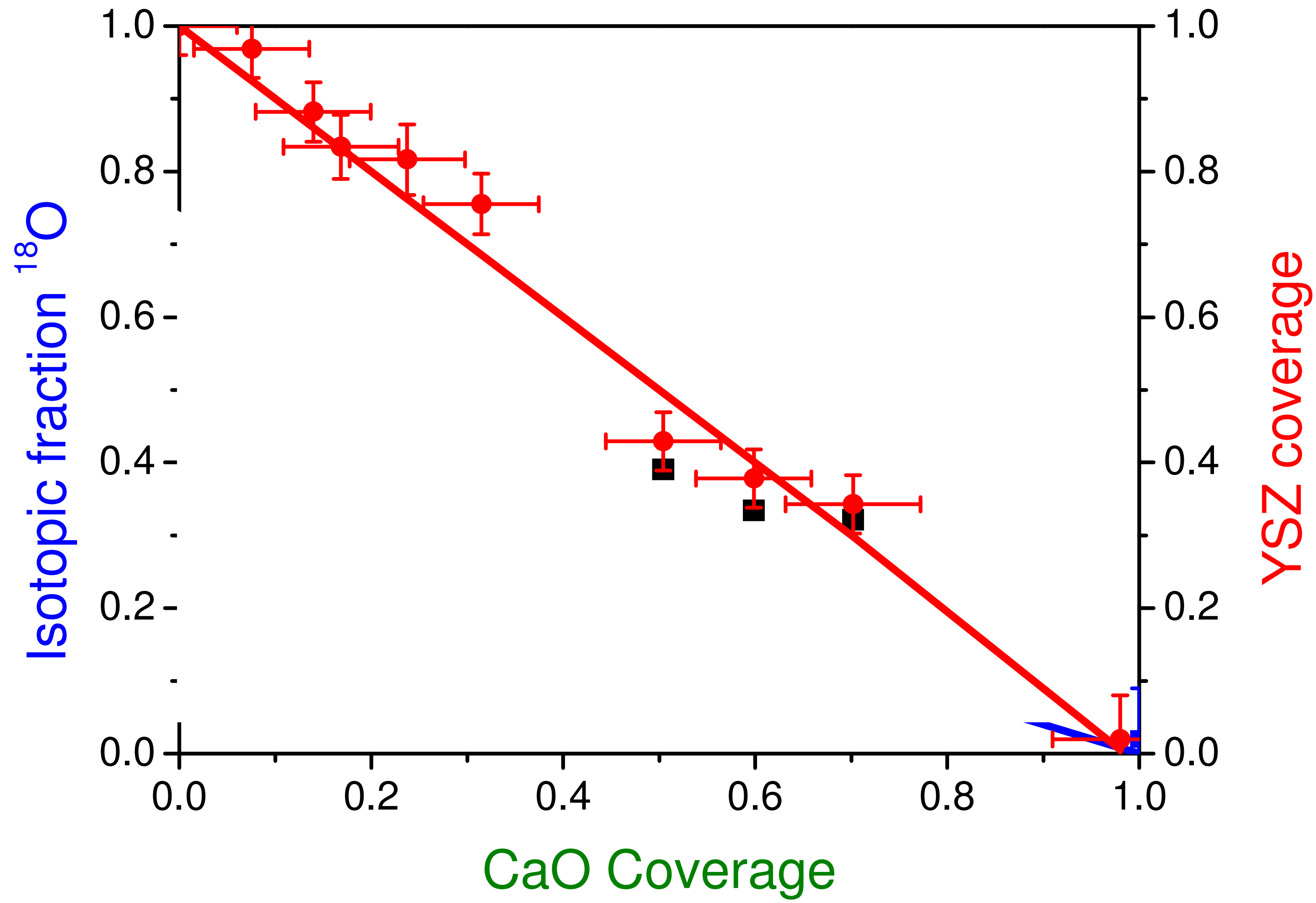
Segregation of monolayer of impurities

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

XPS: Ca not visible (↔ Zr)

Fuel Cells

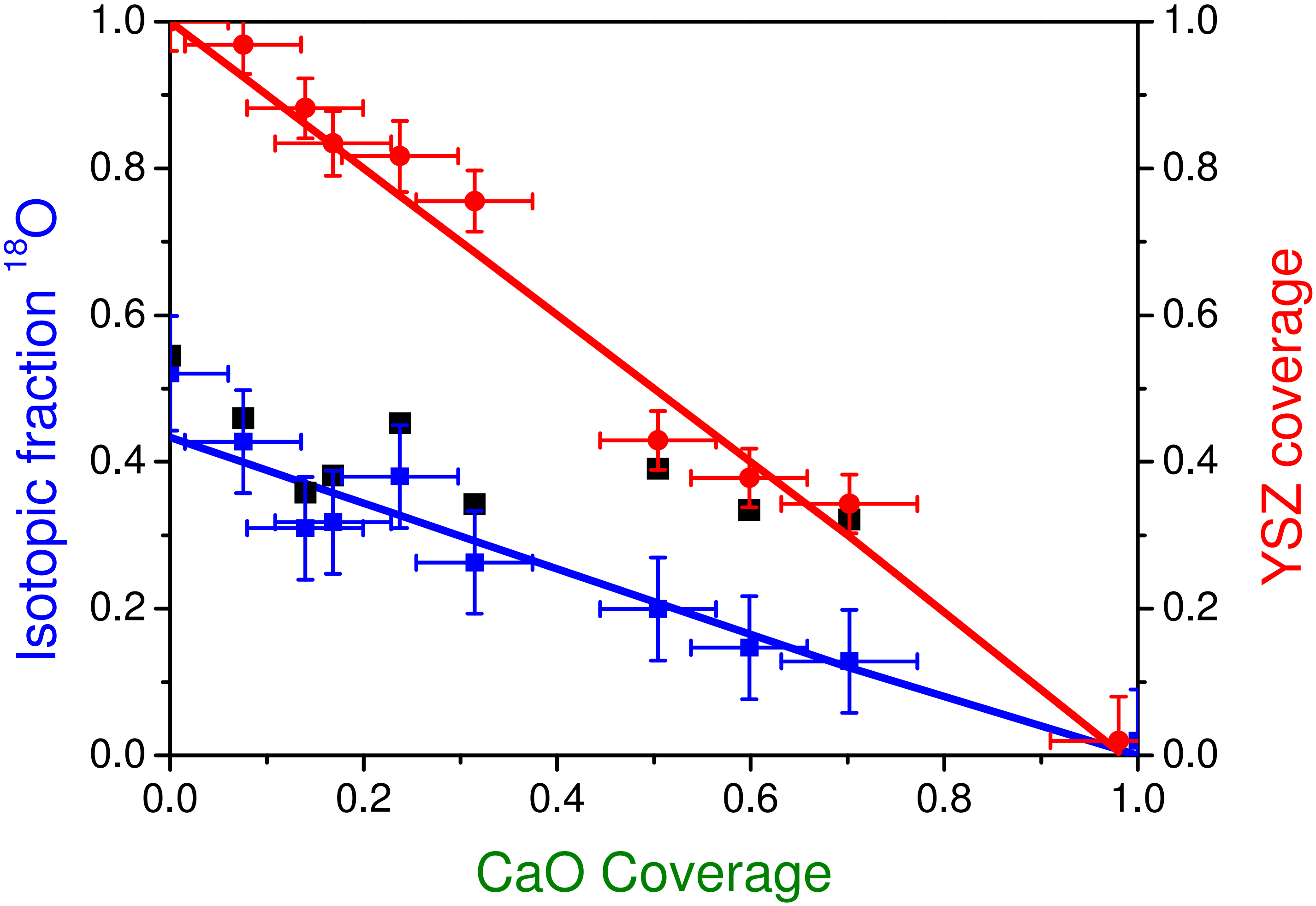
CaO coverage blocks $^{16}O - ^{18}O$ exchange



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

Fuel Cells

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



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

Coke Formation on Commercial TWC

iONTOF

Three Way Catalyst (TWC) (Pt, Rh / CeO_2 / $\gamma - Al_2O_3$)

Cold start: 50% loss of Pt signal — *sintering or coke formation ?*

Room temperature oxidation with atomic oxygen gives complete recovery of Pt signal ⟶ *loss is due to coke.*

Detection of C with "any" surface technique.
But: WHERE is the coke ??!

LEIS determines which fraction of Pt is covered by coke !

Applications:

- Number of Pt atoms available for catalysis.

  Quality control of catalysts !

- Detection of nucleation site for coke (active phase, support, binder, ...)

J.M.A. Harmsen, et al., Catal. *Lett.* **74** (2001) 133 – 137.

Particle Size on Supported Catalysts

iONTOF

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:

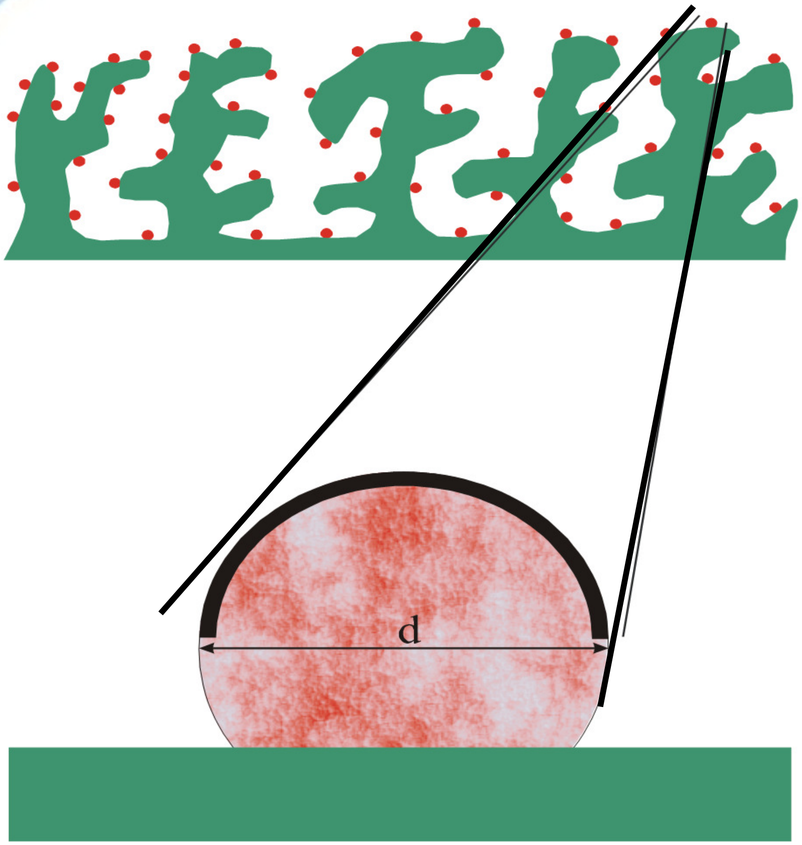
- new technique; any material; clusters: 1 atom - 10 nm

Comparison: → Richard A. P. Smith (J&M), 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)

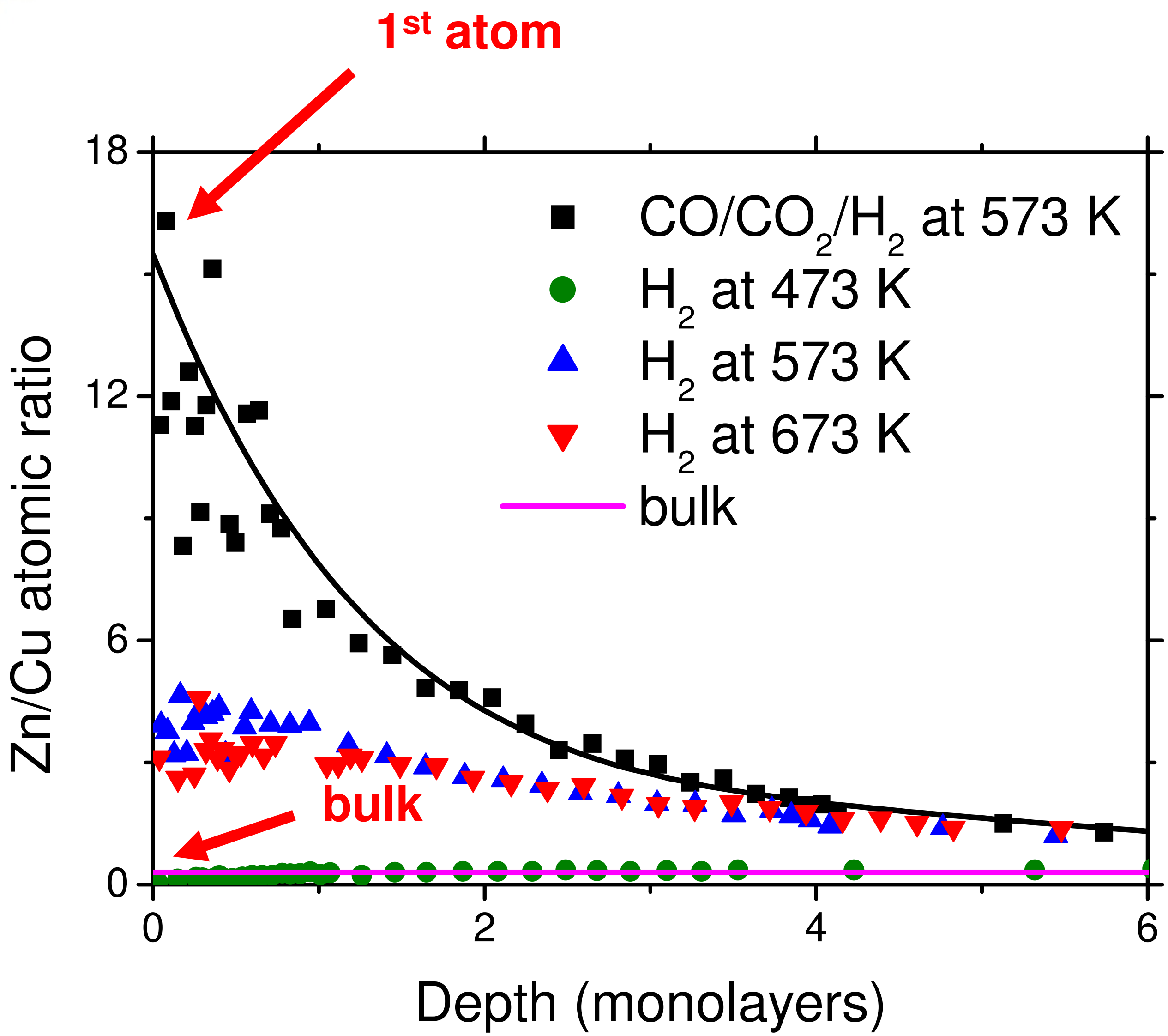
Accurate for d < 10 nm

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)

Cu / ZnO / SiO_2 Catalysts

Synthesis of Methanol, Fatty Acids



Strong Zn(O) segregation

Zn(O) on top of Cu is thermodynamically favorable

Oxidation states Cu and Zn in outer surface ?

LEIS + chemical titration !

XPS:

Oxidation states, BUT averaged over 10 – 20 atomic layers.

LEIS:

Elemental composition outer atomic layer, BUT no chemical info
Oxidation of metallic Cu, Zn gives shielding by oxygen.
Signal decrease: factor 5 resp. 3.7.

Chemical titration:

Information on oxidation states, BUT not only the outer surface (?)

→ **? ? ?**

Oxidation states Cu and Zn in outer surface ?

LEIS + chemical titration !

XPS:

Oxidation states, BUT averaged over 10 – 20 atomic layers.

LEIS:

Elemental composition outer atomic layer, BUT no chemical info
Oxidation of metallic Cu, Zn gives shielding by oxygen.
Signal decrease: factor 5 resp. 3.7.

Chemical titration:

Information on oxidation states, BUT not only the outer surface (?)

LEIS + Chemical titration: → **oxidation states in the outer surface !**

- N_2O for oxidation
- LEIS for detection increase in shielding after N_2O treatment

Cu / ZnO / SiO2 - Catalyst

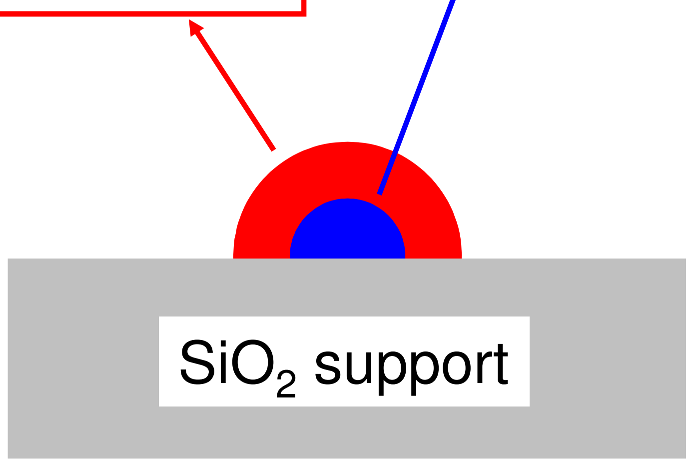
Determination of cluster size and oxidation states by LEIS

Cu/Zn/SiO_2 reduced at 473 K

Outermost atomic layer:

ZnO	0.42
Cu^{1+}	0.54
Zn^0	0.02
Cu^0	0.02

Subsurface: Cu: Zn = 9

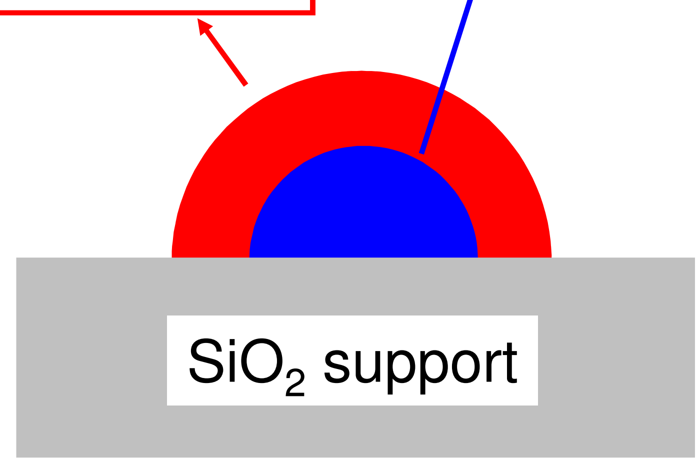


Cu/Zn/SiO_2 reduced at 673 K

Outermost atomic layer:

ZnO	0.77
Cu^{1+}	0.03
Zn^0	0.19
Cu^0	0.01

Subsurface: Cu: Zn = 9



LEIS and Microelectronics

Atomic Layer Deposition (ALD)

" Growth with Digital Accuracy "

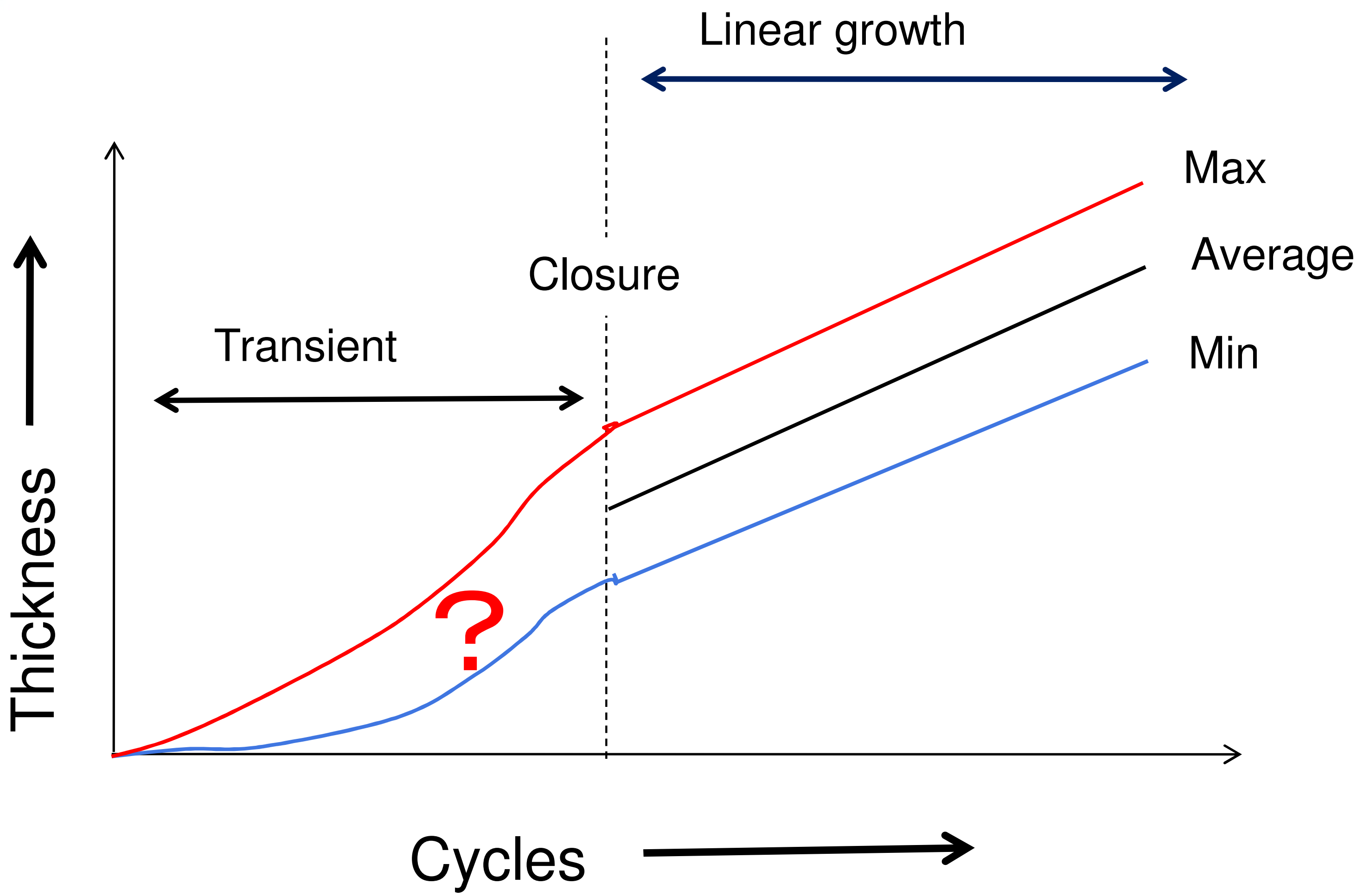
How many cycles for Closure ?

ALD cartoons: (often) show closed layer after 1 cycle
In practice: closure after a few up to > 100 cycles !

Typical examples (depending on ALD conditions !):

- 6 cycles CrOx / Al_2O_3
- 6-9 cycles HfO_2 / Si
- ~ 15 cycles ALN / SiO_2
- ~ 40 cycles Al_2O_3 / Si
- ~ 70 cycles Fe_2O_3 / ZrO_2
- ~ 150 cycles TiN / SiO_2

Layer thickness versus cycle



The transient regime determines closure and uniformity

Characterization of MOCVD vs. ALD HfO_2 layer closure and growth mode on Silicon: a new model for preferential deposition

M.J.P. Hopstaken[1], M.S. Gordon[1], J. Schaeffer[2], H. Jagannathan[1], T. Grehl[3], H.H. Brongersma[3,4], M. Copel[1], M.M. Frank[1], V. Narayanan[1], K. Choi[2], M. Fartmann[4], D. Breitenstein[4]

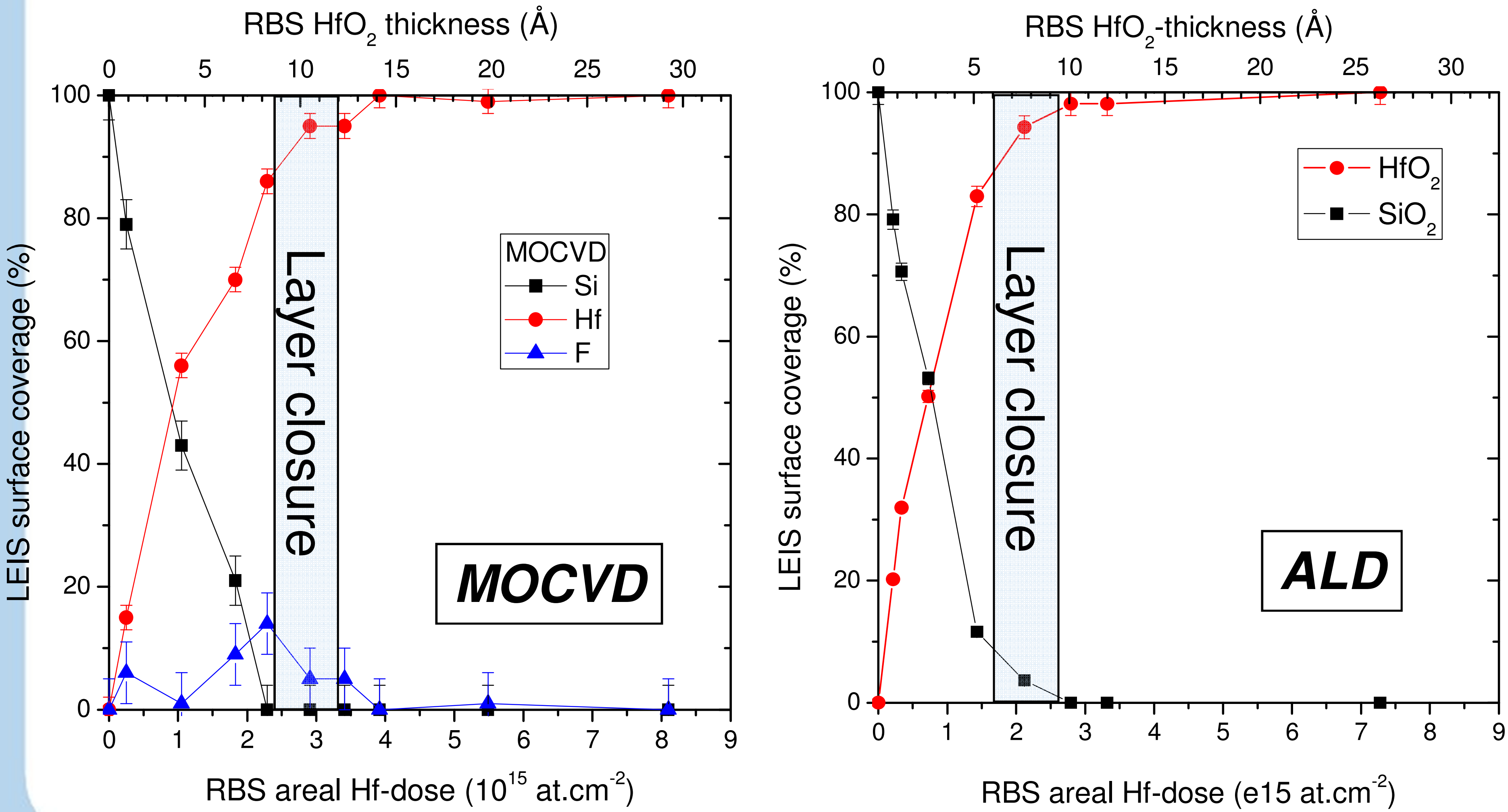
[1]IBM Research, [2]GLOBALFOUNDRIES, [3]ION -TOF, [4]Tascon

ALD 2010, June 21 – 23, 2010 Seoul, Korea

HfO_2 layer closure: MOCVD vs ALD

Surface fractions (LEIS) as function of coverage

→ Earlier layer closure for ALD-HfO_2



LEIS and Growth

- Initial growth; growth mode
- Poisoning, activation
- Closure, pinholes
- Thickness distribution

Conclusion IBM / Global Foundries / ION-TOF / Tascon study:

- Origin of the superior quality of the ALD grown layers revealed by HS-LEIS

  (other analytic tools have insufficient depth resolution)

Summary: Why do you need LEIS ?? !!

- Any material, any T
- Quantitative
- 1st atom and high-resolution in-depth !!

Unique applications of High Sensitivity LEIS (NOT's)

- Segregation, Anti-wetting
- Adhesion: " 5% vs 100% "
- Follow ultrathin growth
- Pinholes in ultrathin; Nano pinholes
- Metal / polymer in-depth diffusion
- Catalysis: poison, promoter, probe molecules, core-shell, ...
- Nanoclusters (diameter; outer atoms)
- Inorganics: oxidation states
- Improve cleaning strategies

Complementarity to XPS, ToF-SIMS, ...

Miscellaneous applications

- Microelectronics, polymers, ceramics, catalysis, sensors, ……..

But also:

- Pinholes in coatings
- Candy wrappers
- Gold mining
- F 16 Dome
- Bone tissue, implants, stents, ……
- Ageing of Linoleum (“ Linowonder”)
- Anti-wetting (watches, …..)
- Floor wax

Complementary Cutting Edge techniques

HS-LEIS + **HR-XPS**

Qtac^{100} **Scienta ESCA 300**

Lehigh University


qtac100
Thank you for your attention.