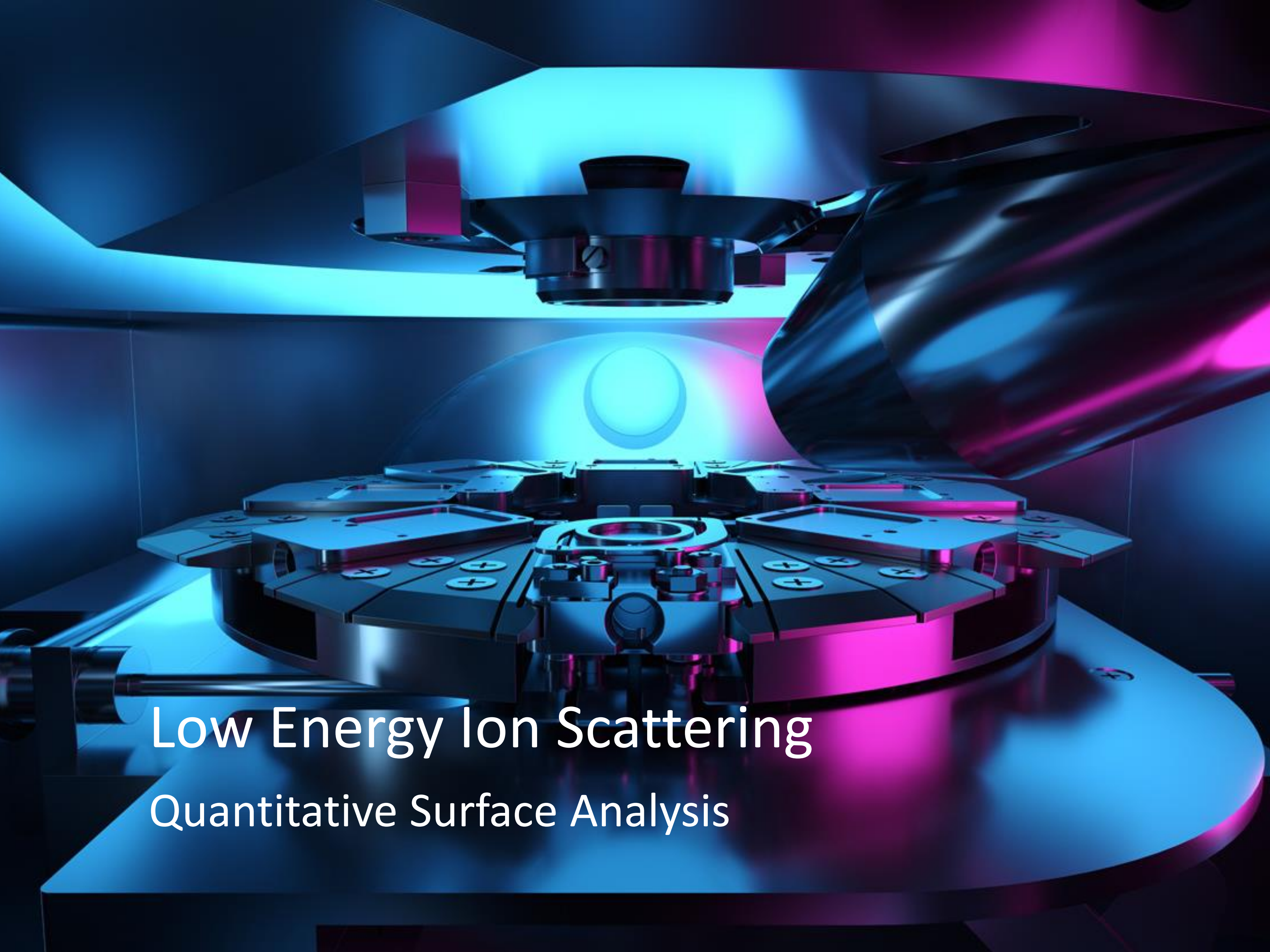
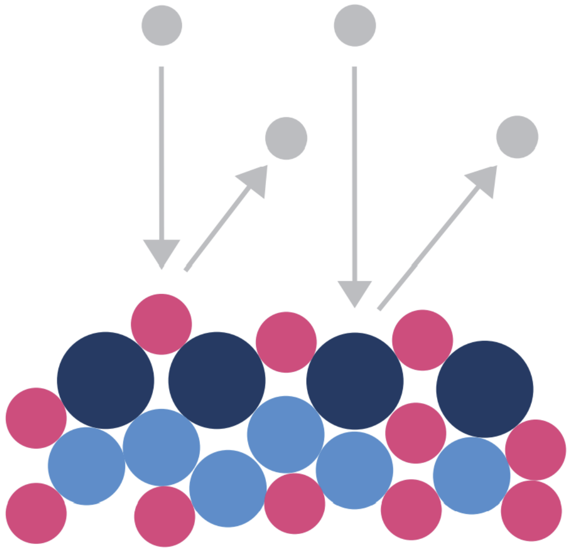


Low Energy Ion Scattering

Quantitative Surface Analysis

Principle of Low Energy Ion Scattering (LEIS)

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



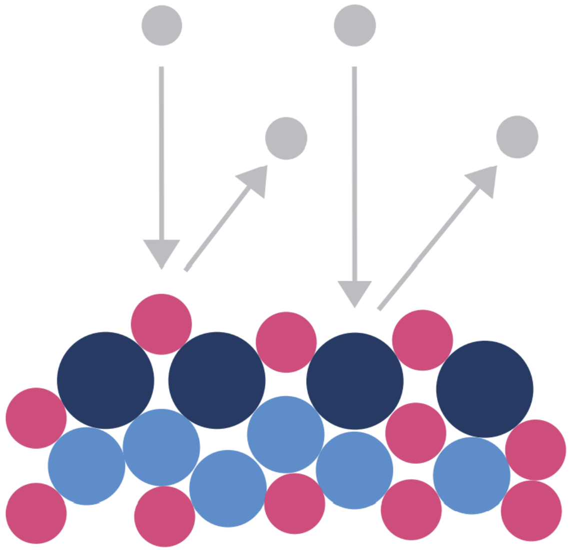
$$E_S = k \cdot E_P = \left(\frac{\cos\Theta + \sqrt{\left(\frac{M_S}{M_P}\right)^2 - \sin^2\Theta}}{1 + \frac{M_S}{M_P}} \right)^2 \cdot E_P$$

for $\frac{M_S}{M_P} \geq 1$

Energy of scattered ions (E_S) is following the laws of the ***conservation of energy and momentum***

Features of Low Energy Ion Scattering (LEIS)

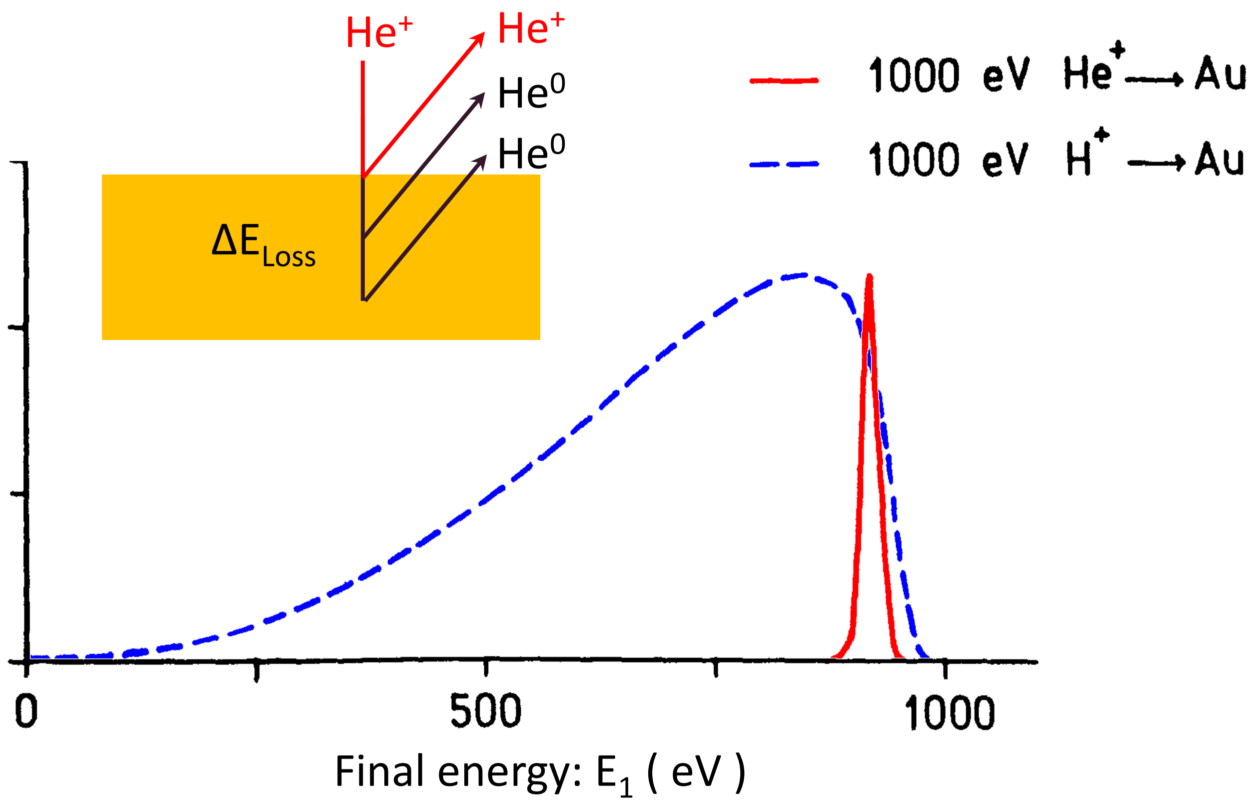
He^+, Ne^+, Ar^+, Kr^+
1 - 8 keV



- Ultra-high surface sensitivity, top atomic layer analysis
- Static depth profiling information (up to 10 nm)
- Reliable and straight-forward quantification
- Simple analysis of insulators and rough samples
- Detection of all elements > He
- Detection limits (of 1 ML):
  - Li - O ≥ 1 %
  - F - Cl 1 % - 0.05 %
  - K - U 500 ppm - 10 ppm

Brongersma et al., Surf. Sci. Rep. 62 (2007) 63
Brongersma, Low-Energy Ion Scattering, in: Characterization of Materials, Wiley (2012)

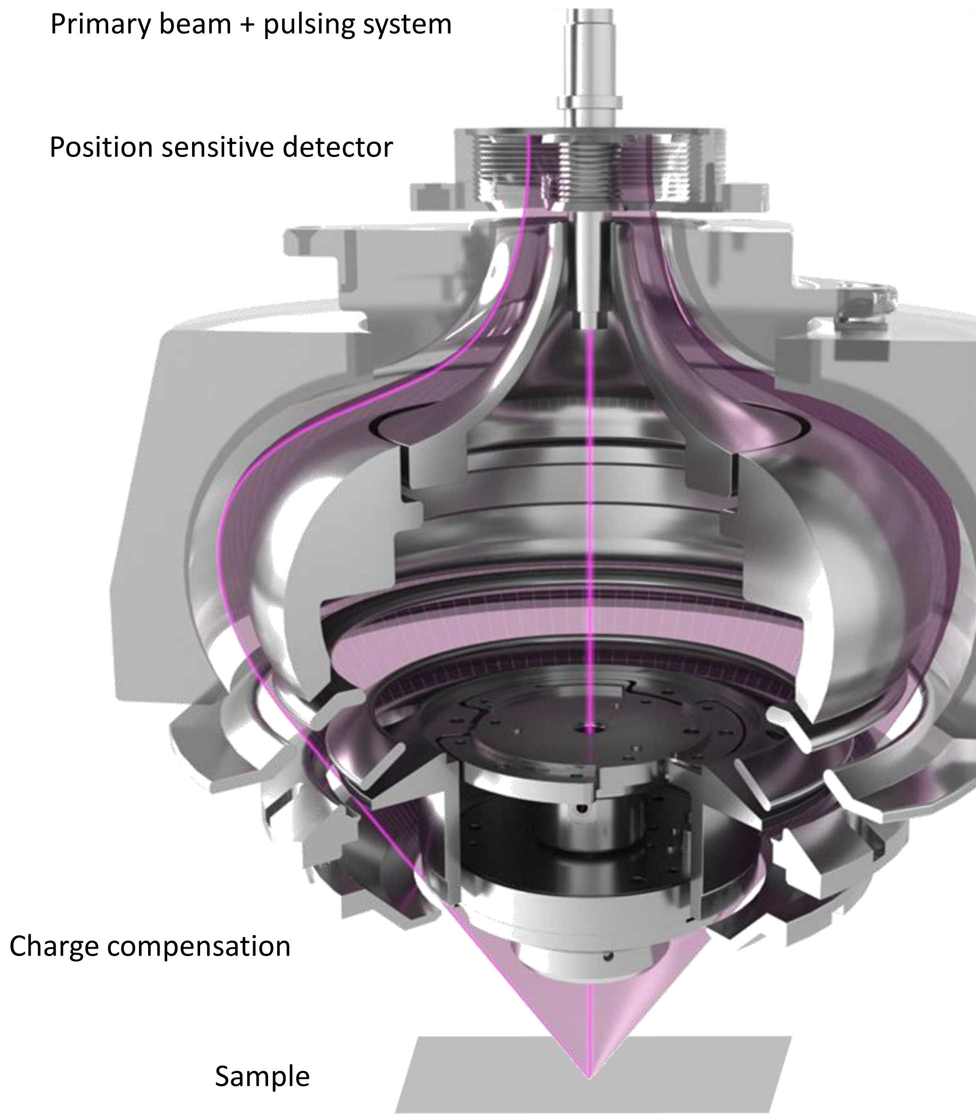
Extreme Surface Sensitivity using Noble Gas Ions



- Neutralization effect of noble gas ions when penetrating the surface allows for extreme surface sensitivity

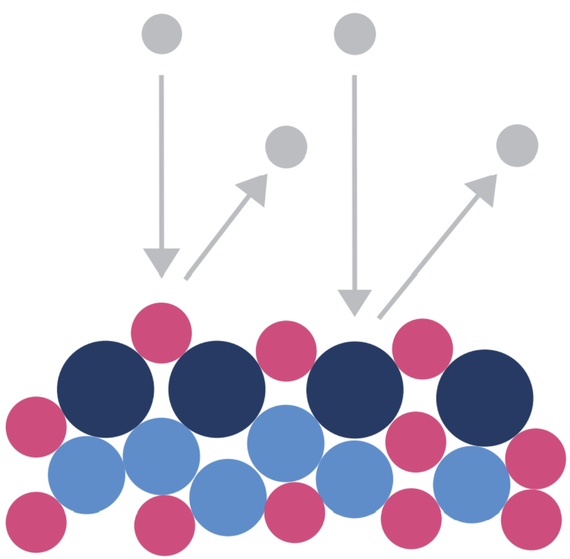
Double Toroidal Energy Analyzer

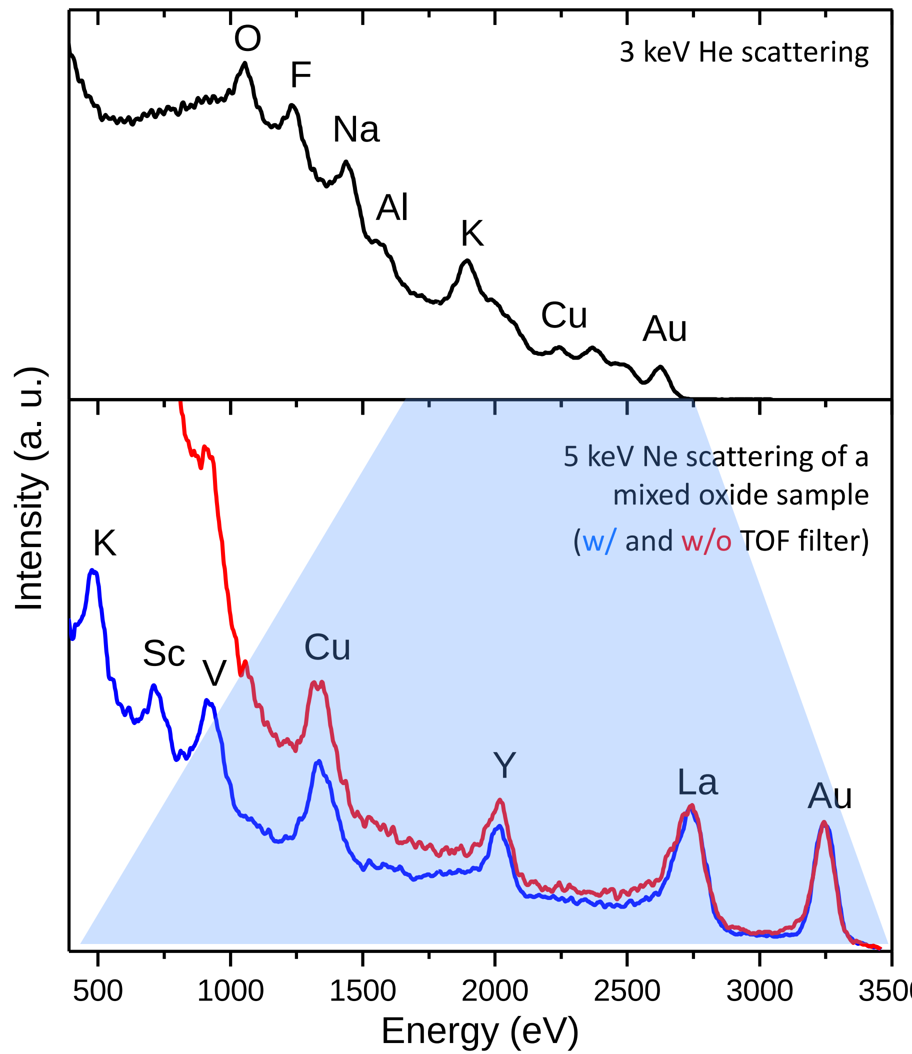
- Crucial for practical work:
  Analysis before destruction
- High sensitivity and high-resolution analyzer:
  - ✓ Parallel detection of energy
  - ✓ Parallel acceptance of angles (azimuth)
  - ✓ Well defined scattering angle for high mass resolution



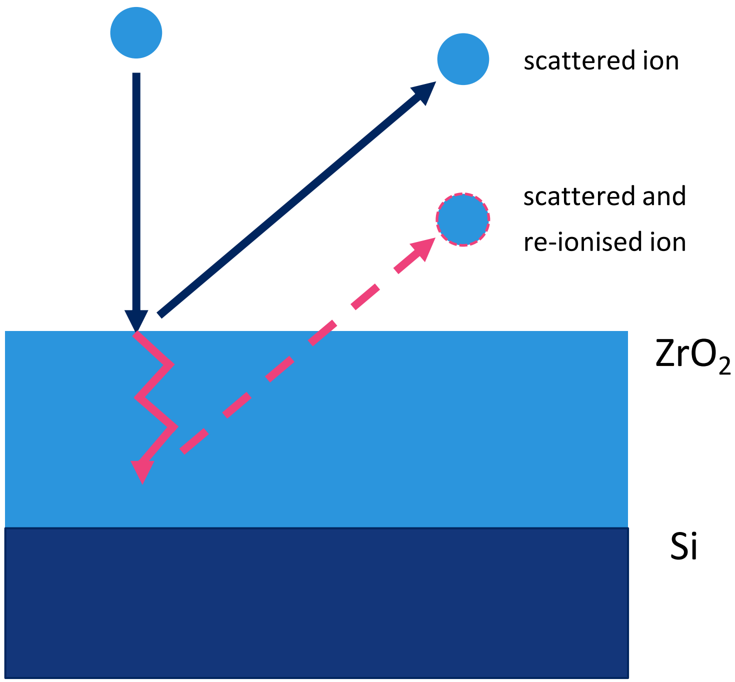
Detection of All Elements > He

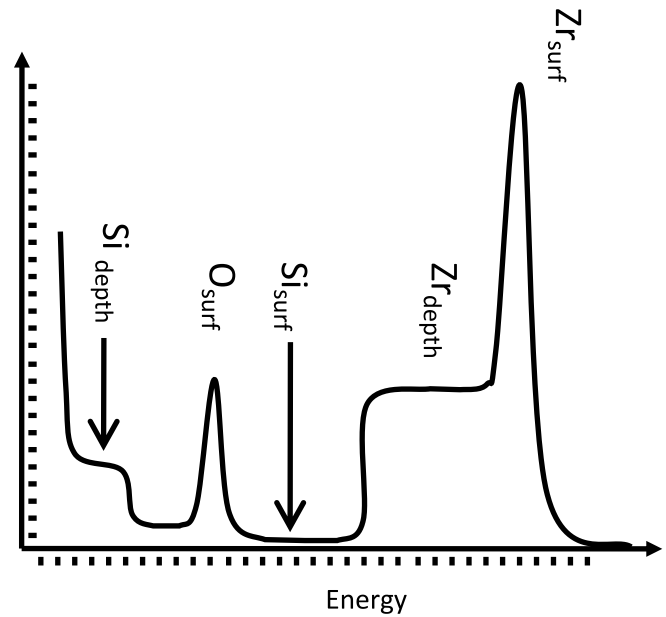
> Switching to Ne and Ar scattering expands mass scale for heavier elements





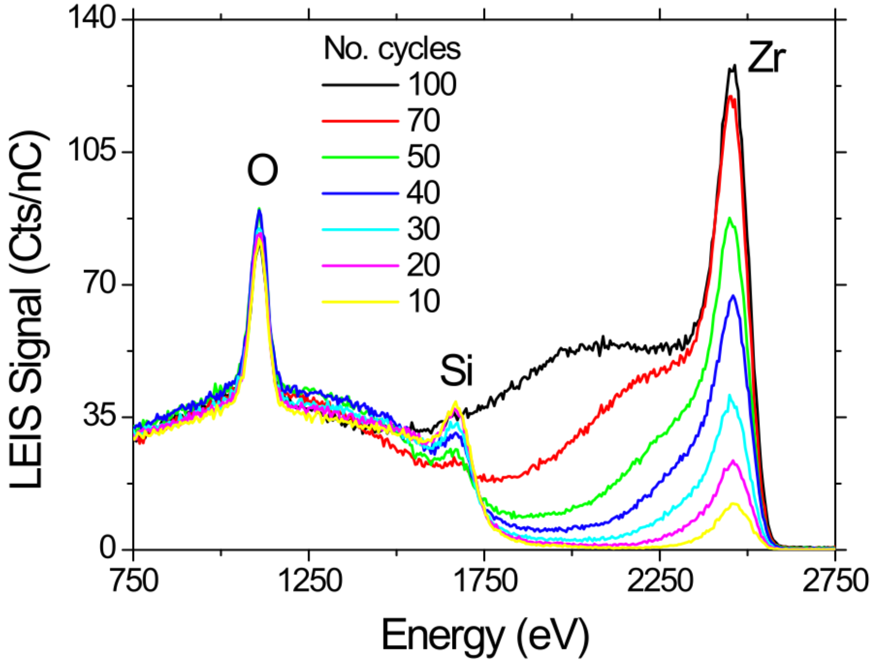
Spectroscopy and Static Depth Profiling

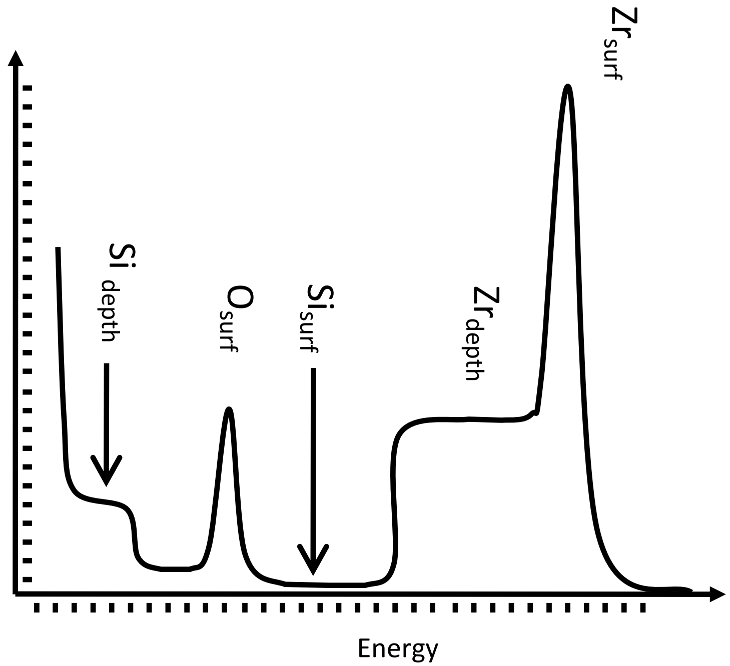




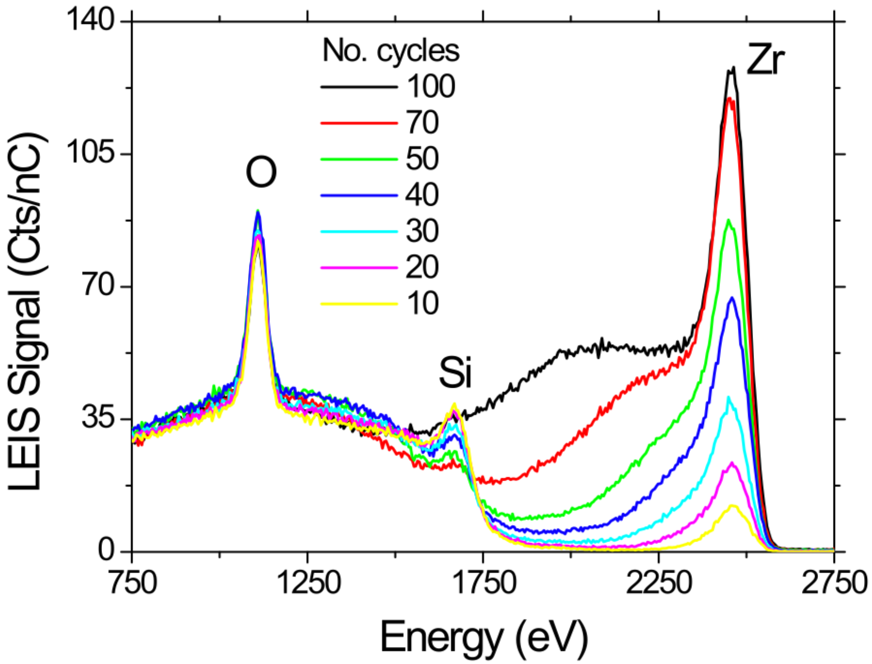
- Ions can be scattered at the surface, giving element specific surface peak
- Ions are also scattered in deeper layers, undergoing an additional energy loss proportional to the depth
- When scattered in the volume, a re-ionization at the surface is required for detection. This is promoted by some elements (e. g. oxygen) and gives tails to the left of the peaks
- Energy loss can be converted to depth

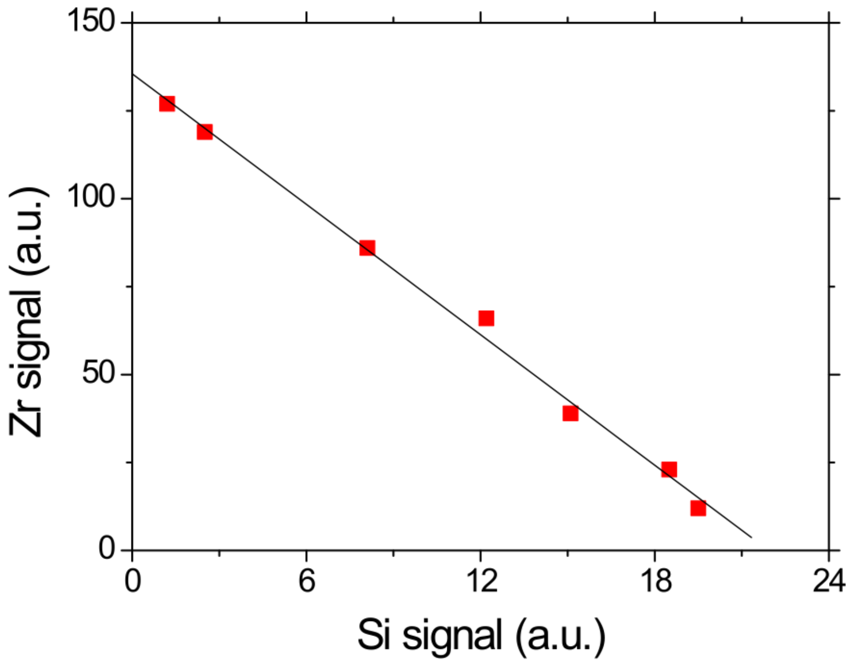
ZrO_2 Atomic Layer Deposition on Silicon





ZrO_2 Atomic Layer Deposition on Silicon

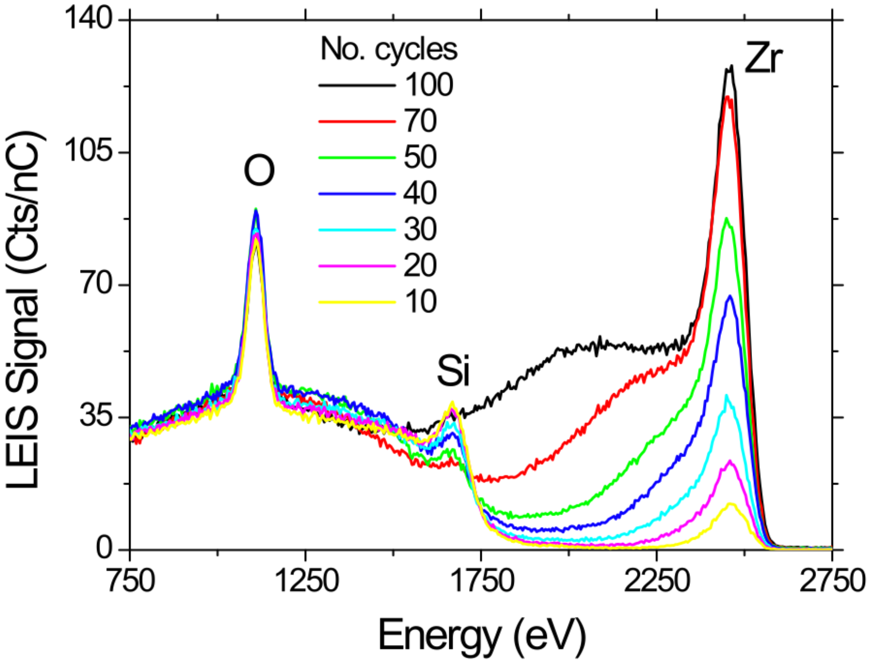


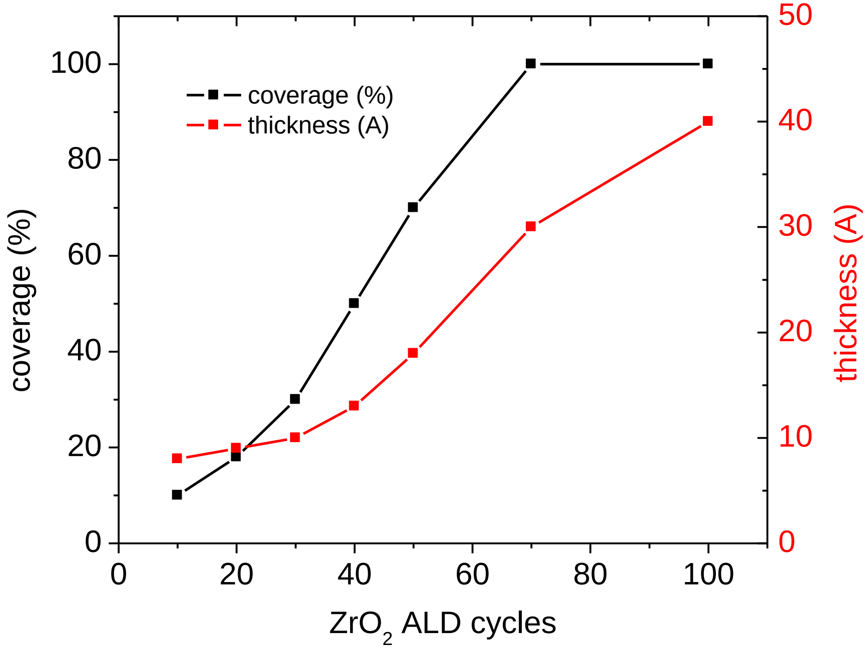


- Correlation plots: Extrapolation to both axes gives sensitivity factors for pure materials
- This allows reference free quantification in two component systems (and in many cases also with three components)

ZrO_2 on Si: A non-ideal ALD process

3 keV He^+ scattering from ZrO_2 layers on Si





- Zr peaks develops a tail long before reaching maximum intensity (= layer closure)
- Coverage and thickness can be measured independently

Catalysis

(Almost) No Influence of Surface Roughness

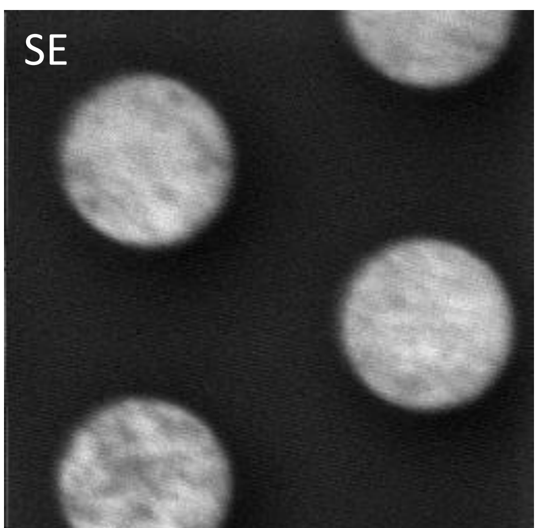
> Analysis of catalysts with huge surface area routinely done
> Depth of field of analyzer: approx. 500 µm

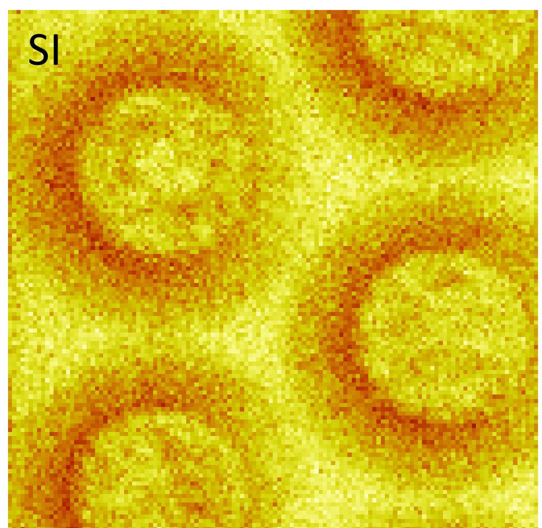
Table 2. Relative LEIS yields of a flat quartz sample and pressed silica powders (300 MPa) with specific surface areas of 50–380 $m^2\ g^{-1}$

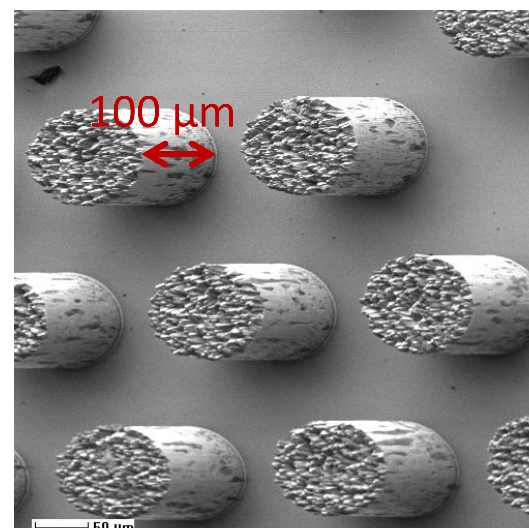
Sample	Specific surface area ($m^2\ g^{-1}$)	Si	O	Si/O ratio
Quartz	$\sim 10^{-4}$	1.00	1.00	1.00
Aerosil Ox-50	50	0.80	0.84	0.95
Aerosil 130	130	0.77	0.81	0.95
Akzo Düren	185	0.83	0.82	1.01
Aerosil 380	380	0.83	0.84	0.99

Jansen et al., Surf. Interface Anal. **36** (2004) 1469

FoV: 300 x 300 µm²







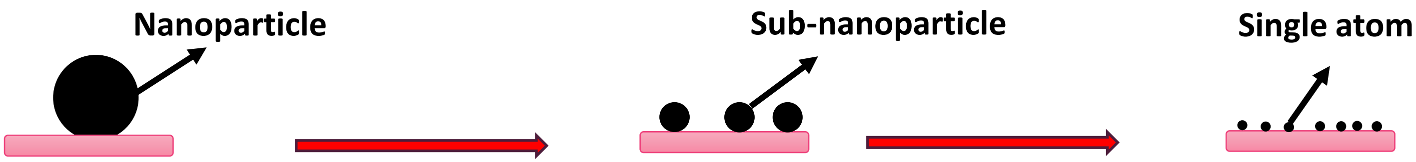
Surface Analysis of Catalysts

- Pressure gap
  - Pressure inside the reactor: ≈ 10 bar
  - Pressure inside the analysis chamber: ≈ 10^{-6} – 10^{-10} mbar
- Structure gap
  - Low loading, rough surfaces (1000 m^2/g) inside the reactor
  - High loading and flat surfaces inside the analysis chamber
- The Qtac bridges the structure gap but the pressure gap exists partially.
- Workaround
  - In-situ preparation of the catalyst with subsequent quenching

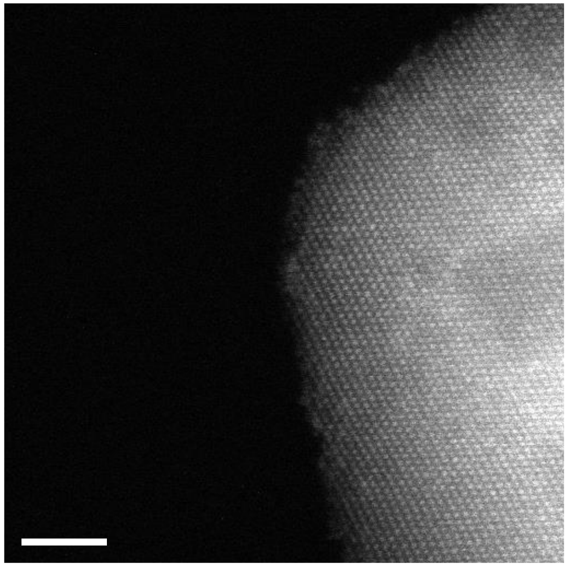
Single Atom Catalysts (SAC)

Single atom heterogeneous catalysis

> improved efficiency, higher reactivity, and better selectivity
> lower loading of precious metals



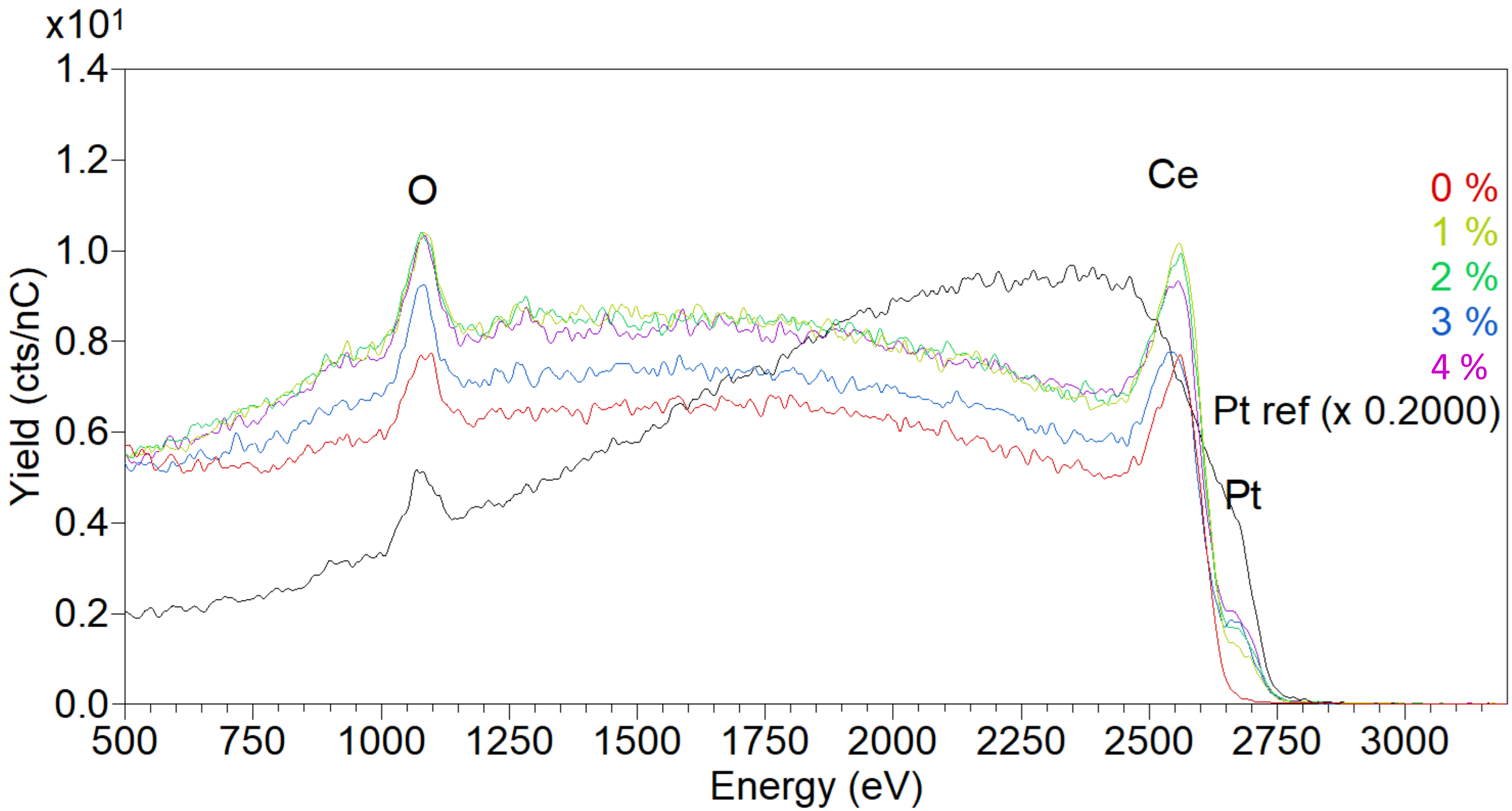
> Pt/CeO_2, prepared using atom trapping
> 1, 2, 3, 4 wt. % Pt, 10 h @ 800° C in air
> At higher loading, large Pt particles expected
> Small Pt particles are not stable at elevated T, evaporation of PtO_2
→ either single atoms or large particles



Jones et al., Science (2016)

SAC – 3 keV He^+ scattering

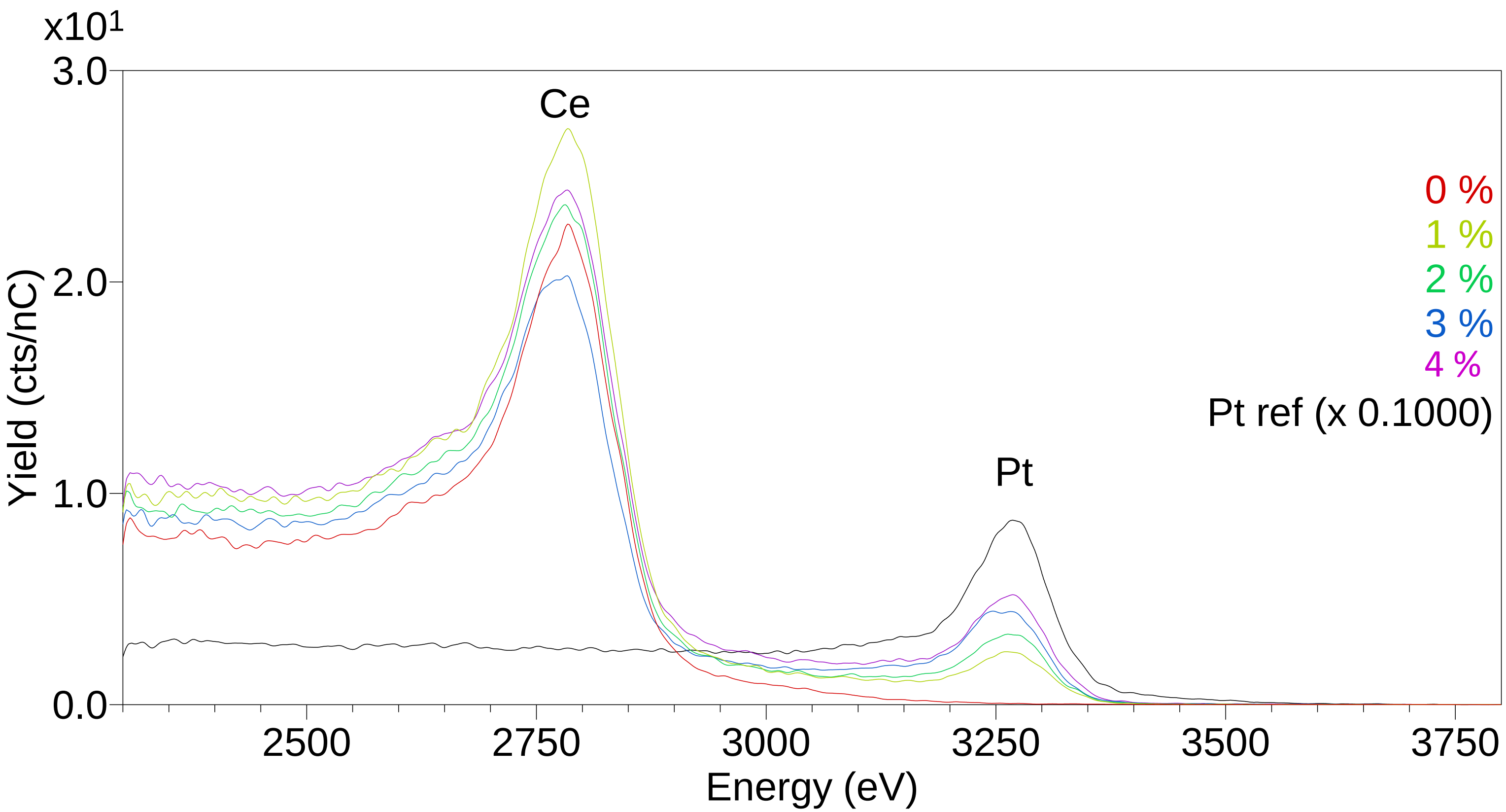
> Samples and Pt metal cleaned using atomic oxygen
  → no C, organics
> No unexpected elements at the surface
> Mass resolution not sufficient for Ce/Pt → Ne scattering



ACS Catalysis, 2019, DOI: 10.1021/acscatal.8b04885

SAC – 5 keV Ne^+ scattering

- Excellent mass resolution
- Quantification by comparison to Pt reference

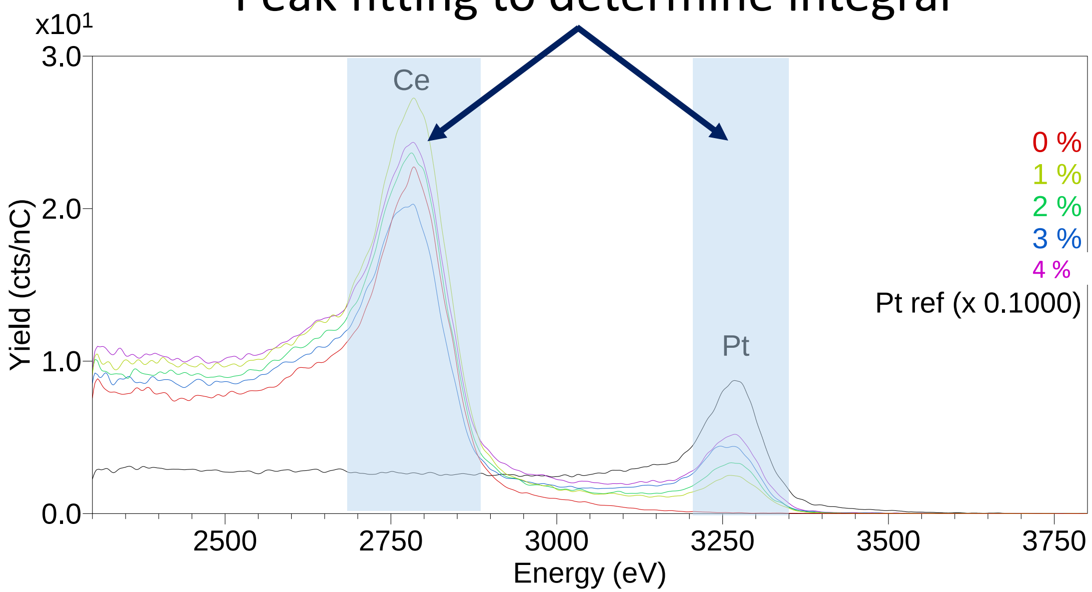


ACS Catalysis, 2019, DOI: 10.1021/acscatal.8b04885

SAC – quantification

- Determine LEIS signal for reference PtO_2 – 6820 cts/nC
- Calculate PtO_2 density of reference: 9.01 PtO_2/nm^2
- Calculate PtO_2 density of samples: $Y_{LEIS}/6820 * 9.01\ PtO_2/nm^2$
- Apply small roughness correction – catalyst and reference are very different

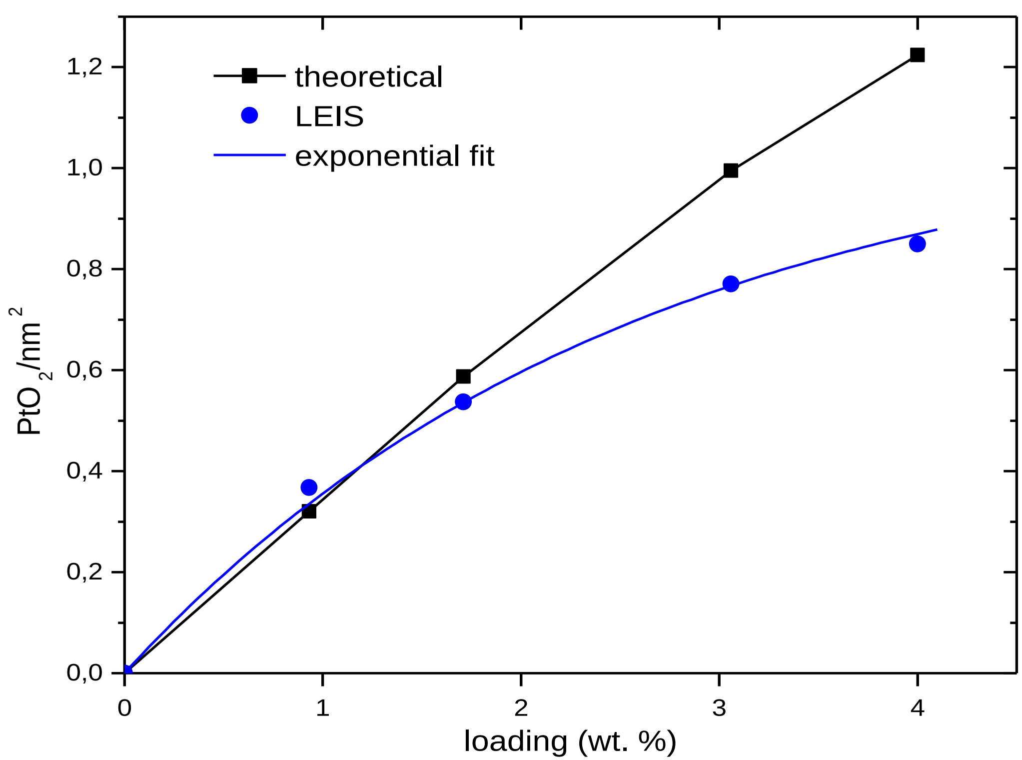
Peak fitting to determine integral



ACS Catalysis, 2019, DOI: 10.1021/acscatal.8b04885

SAC – surface fraction

> At 1 and 2 wt. %, Pt is present as single atom catalyst – quantitative agreement, no normalization
> At 3 % loading, 77 % of the atoms are detected in the outer layer
> At 4 % loading, 69 % of the atoms are in the outer layer
> As large particles only minimally contribute to the surface, their signal is weak in LEIS



ACS Catalysis, 2019, DOI: 10.1021/acscatal.8b04885

Coated particles

> Full picture from multiple techniques

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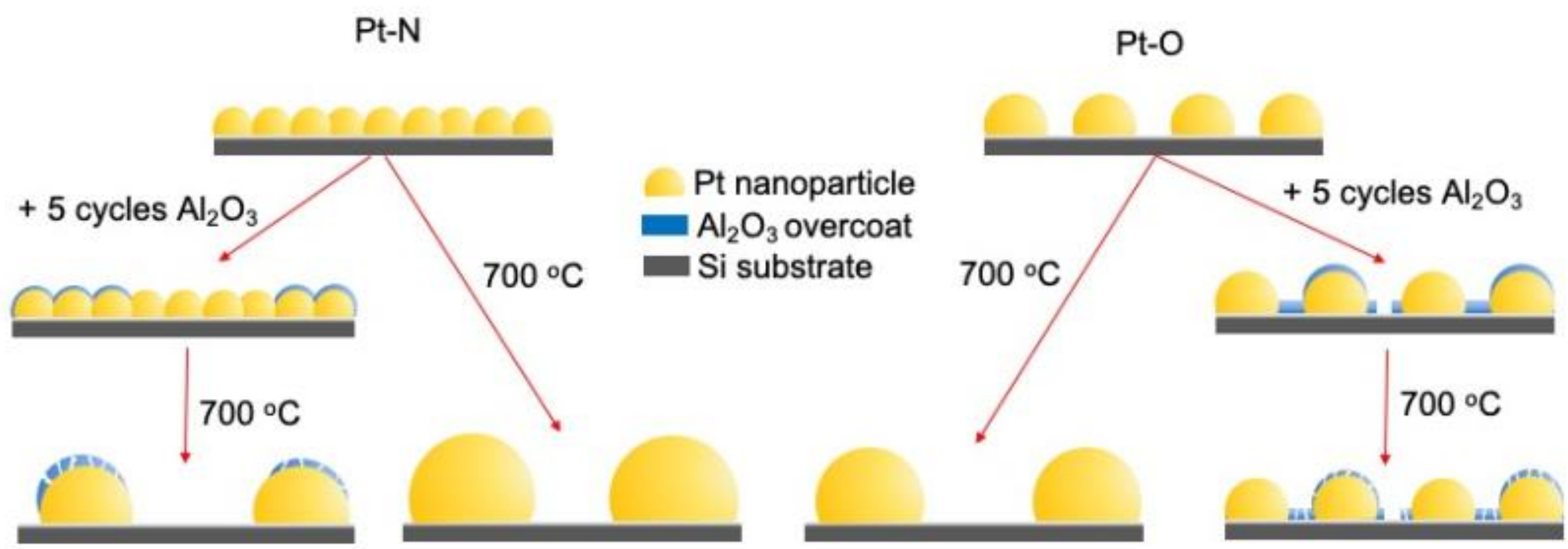
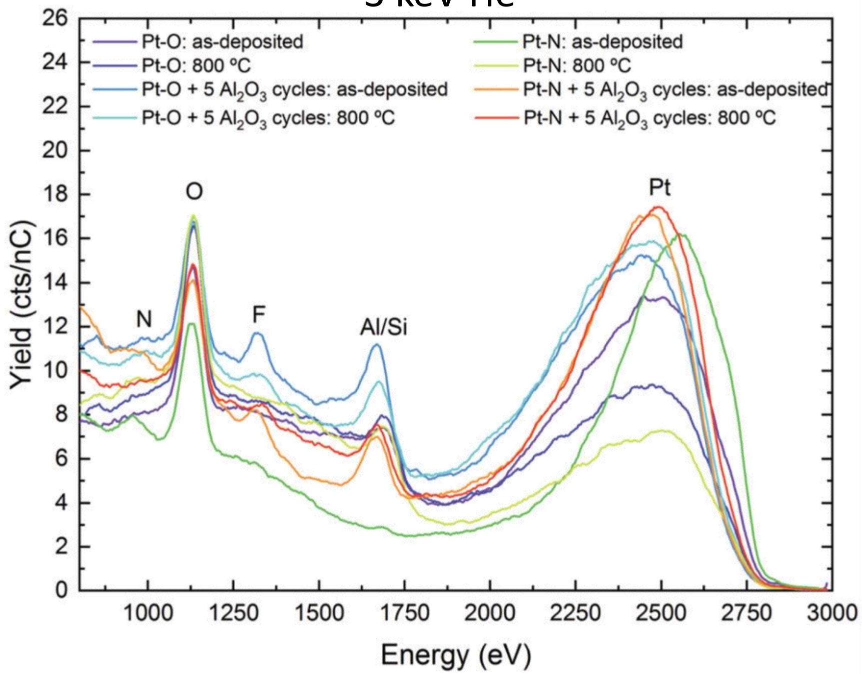


Solano, Dendooven et al. Nanoscale, 2020, 12, 11684–11693, DOI: 10.1039/d0nr02444a

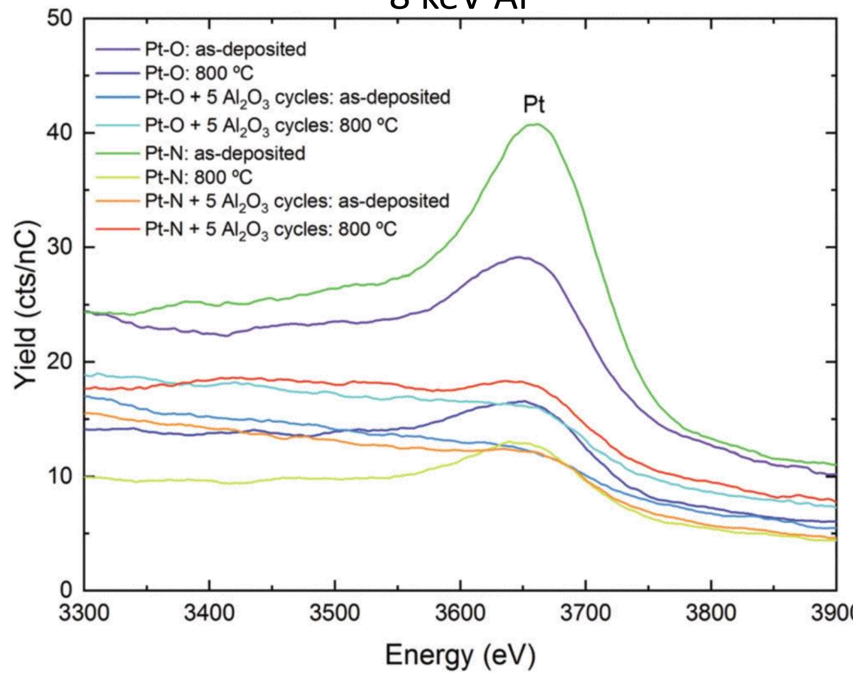
Pt + Al_2O_3 nanoparticles

- Nanoscale Pt particles are desirable for catalytic activity **and** efficiency
- Problem: Particle coarsening due to harsh thermal and chemical conditions during catalysis
- Idea: ALD Al_2O_3 overcoating to prevent particle coarsening

3 keV He



8 keV Ar



Solano, Dendooven et al. Nanoscale, 2020, 12, 11684–11693, DOI: 10.1039/d0nr02444a

Coated particles

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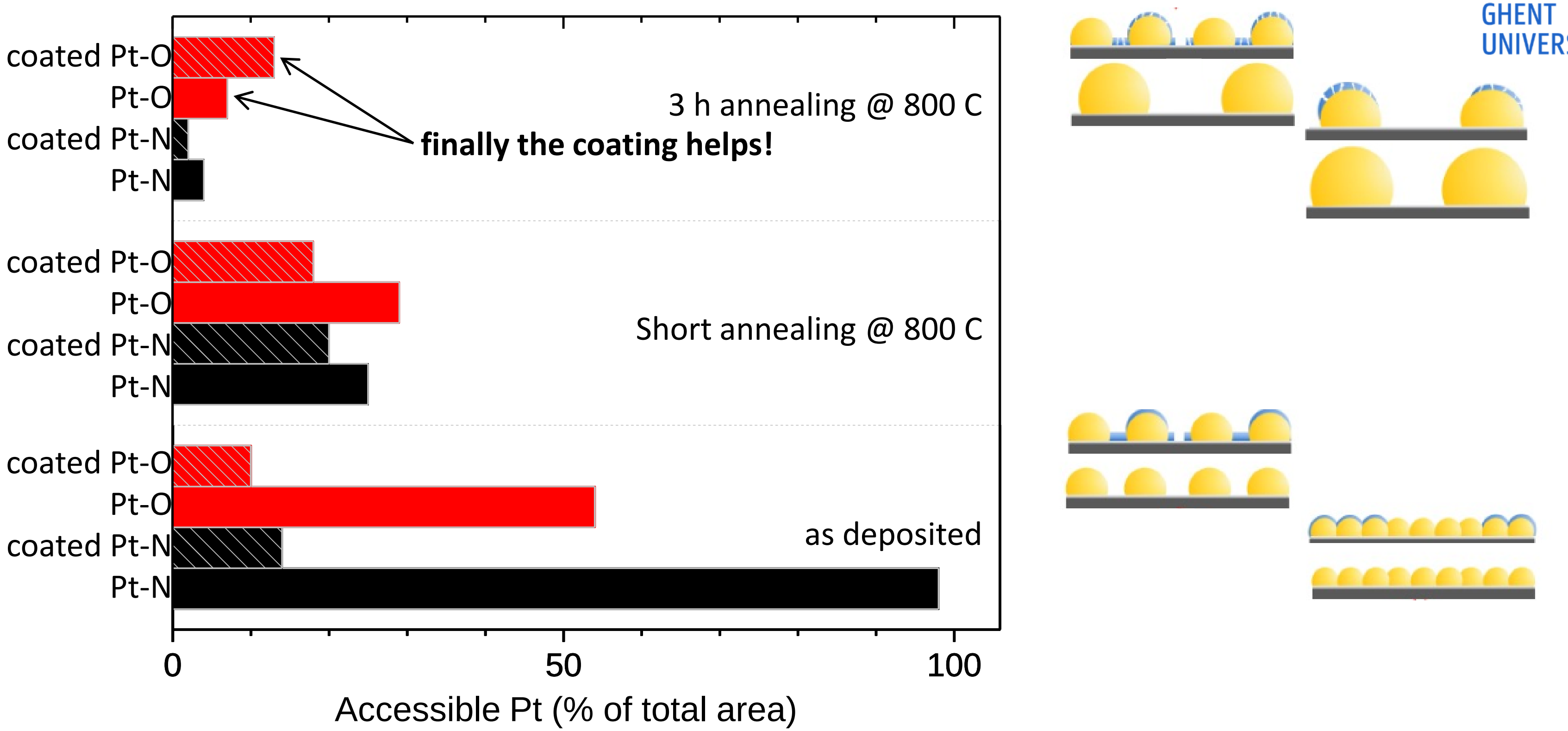
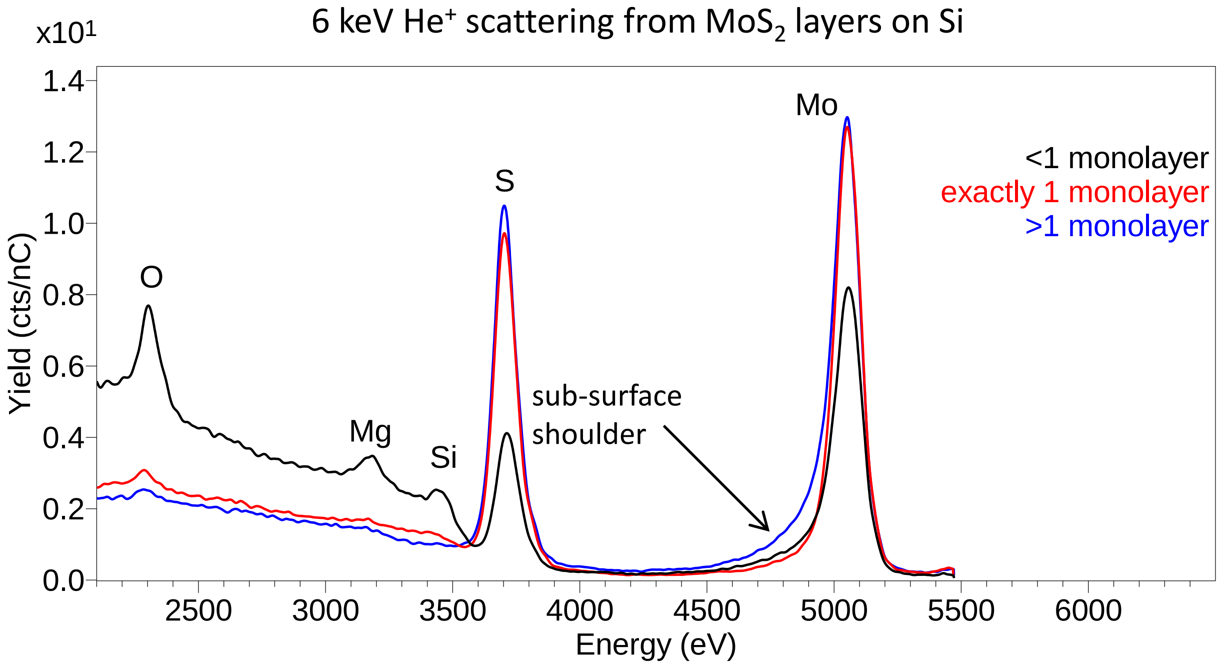


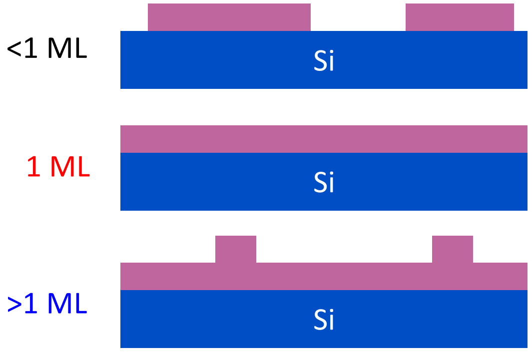
- XRF (RBS calibrated) quantifies total Pt amount
- in-situ GISAXS measures particles coarsening
- LEIS quantifies availability of Pt even after Al_2O_3 overcoat
- Key result: Isolated particles are required to prevent coarsening by ALD

Solano, Dendooven et al. Nanoscale, 2020, 12, 11684–11693, DOI: 10.1039/d0nr02444a

Ultra-thin films

MoS_2 on Si: An ideal ALD process





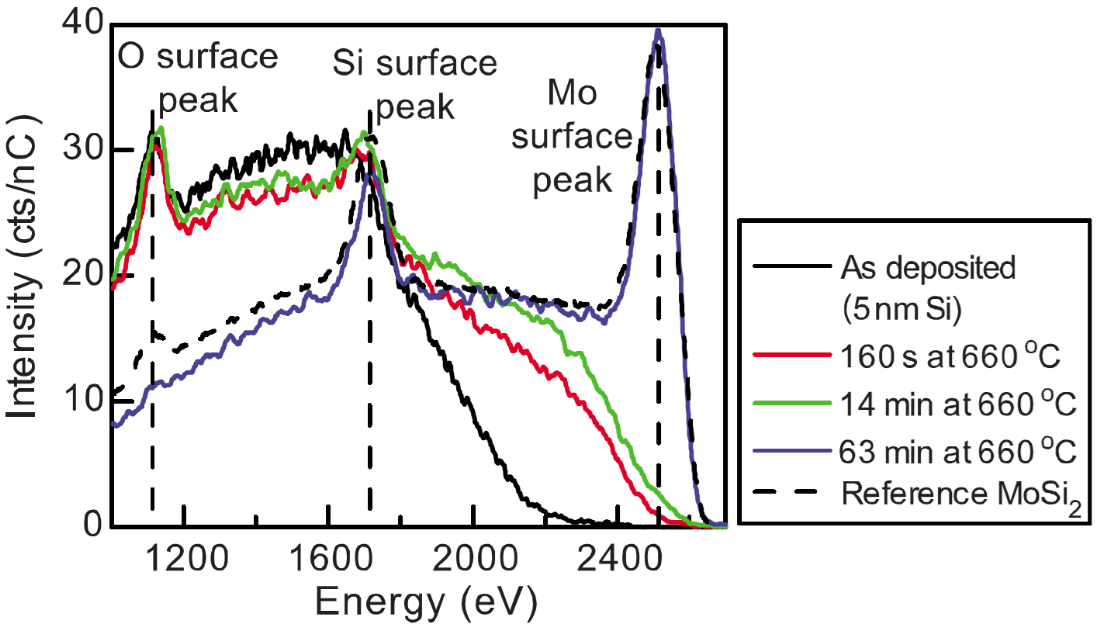
- Mo surface peak:
  - Symmetric Gaussian: (sub-)monolayer coverage
  - Peak integral proportional to fraction of surface covered
  - Tail for >1 monolayer developing

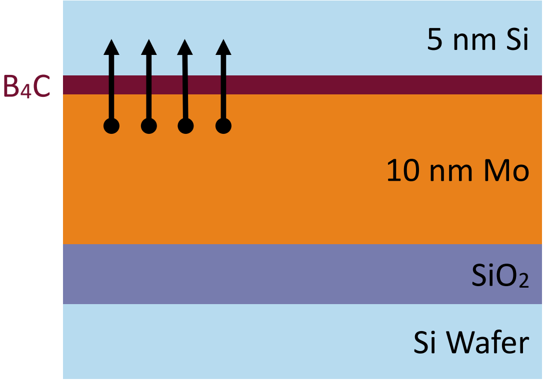
Samples courtesy of Jeong-Gyu Song

YONSEI UNIVERSITY

Diffusion study with in-situ heating – Mo/Si layers

> 5 nm Si / 1.6 nm B_4C / 10 nm Mo, annealing @ 660 deg. C

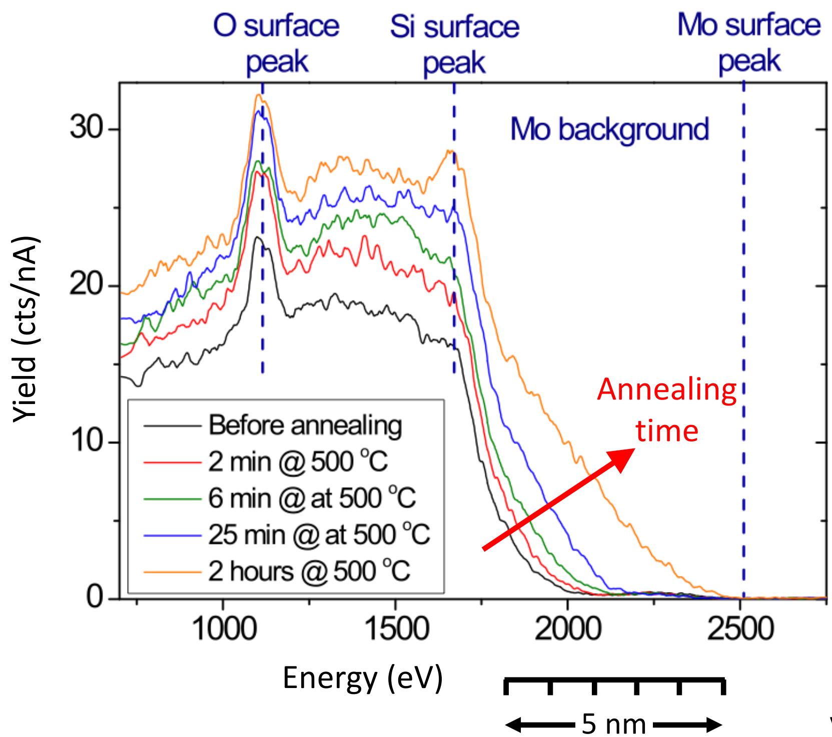


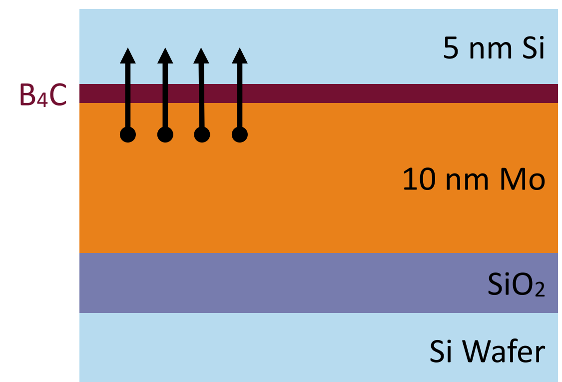


V. de Rooij-Lohmann, *Appl. Phys. Lett.* **94** 063107 (2009)
V. de Rooij-Lohmann, *J. Appl. Phys.* **108** 014314 (2010)

Diffusion study with In-situ Heating

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

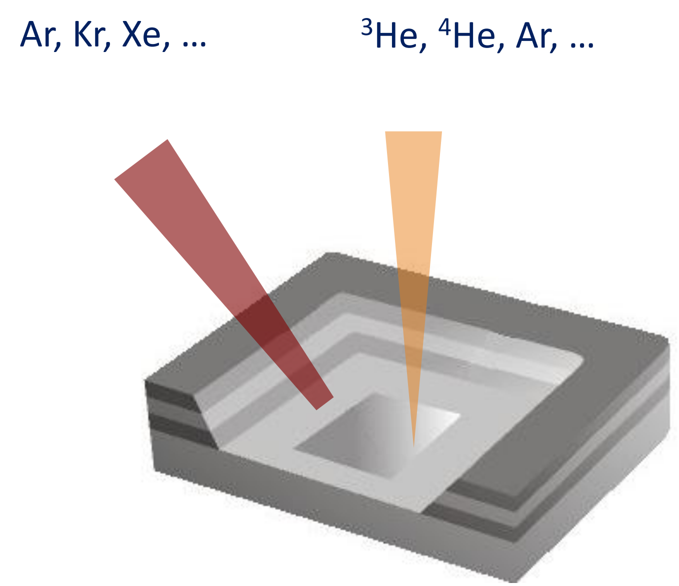




V. de Rooij-Lohmann, *Appl. Phys. Lett.* **94** 063107 (2009)
V. de Rooij-Lohmann, *J. Appl. Phys.* **108** 014314 (2010)

Sputter Depth Profiling

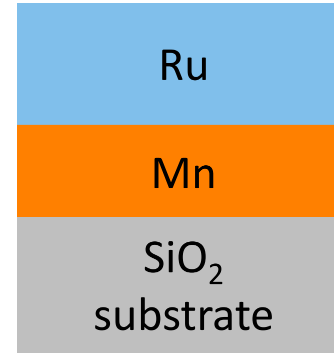
- Sputter and analysis beam conditions are optimised independently
- Sputtering using inert species (usually Ar) at low energy to assure high depth resolution
- Scattering using a noble gas ion beam selected for optimum sensitivity and mass resolution for the elements of interest

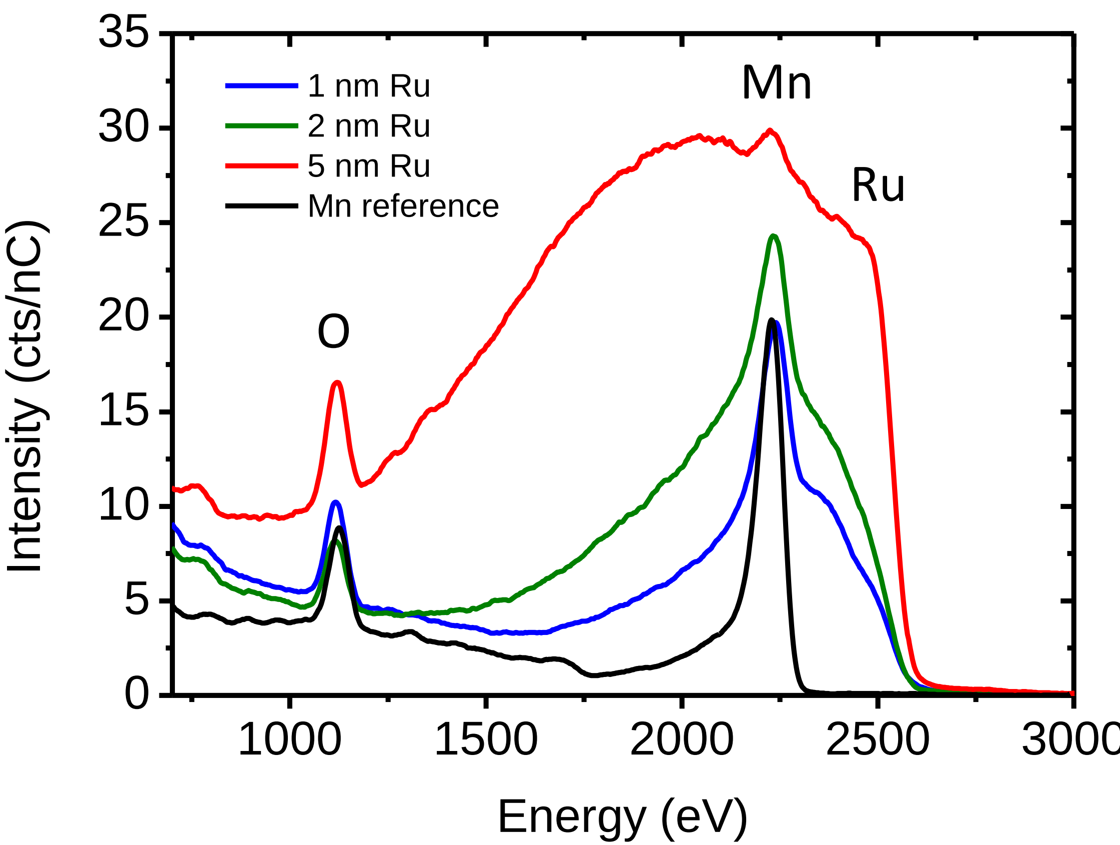


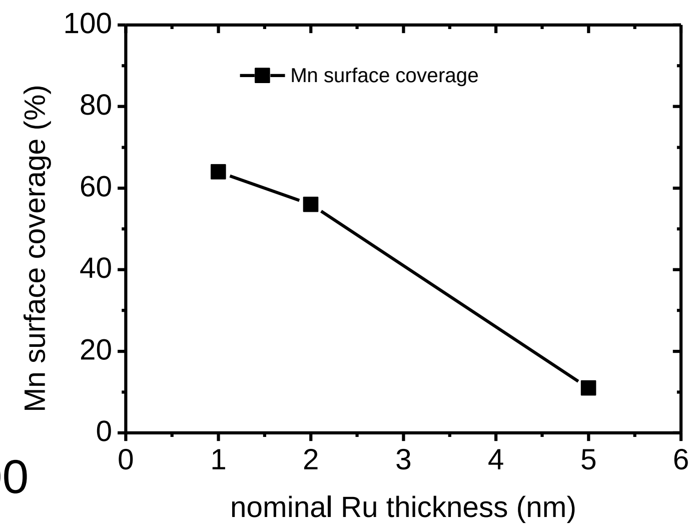
Sputter area: 2 x 2 mm^2
Analysis area: 1.5 x 1.5 mm^2

Ru film with Mn diffusion barrier

- 1/2/5 nm Ru on 1.5 nm Mn on Si
- Ru surface peak shielded after atomic H treatment
- Mn visible despite a layer of Ru covering it, even at 5 nm Ru – why?

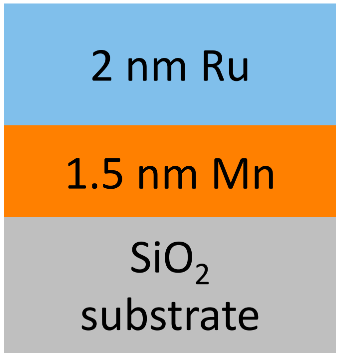


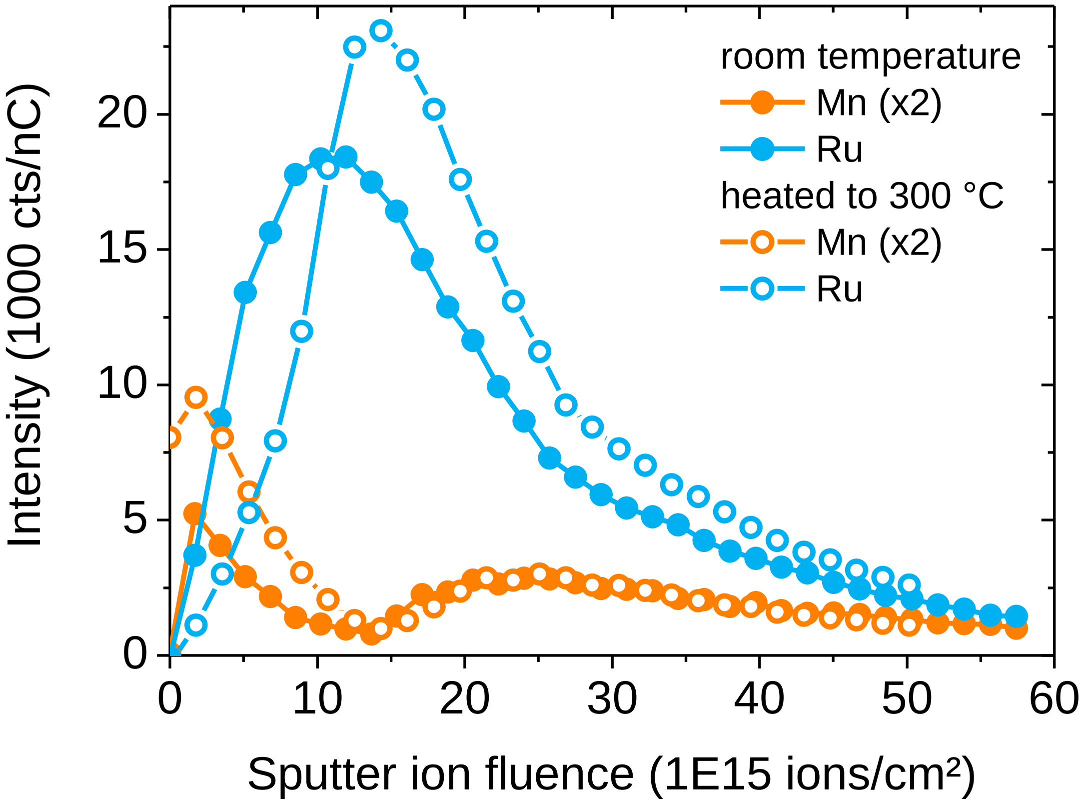




Ru film with Mn diffusion barrier

- 500 eV Ar sputter profile before and after heating to 300 °C
- Mn is enriched at the surface and below the Ru
- Enrichment increased by heating → diffusion through Ru film





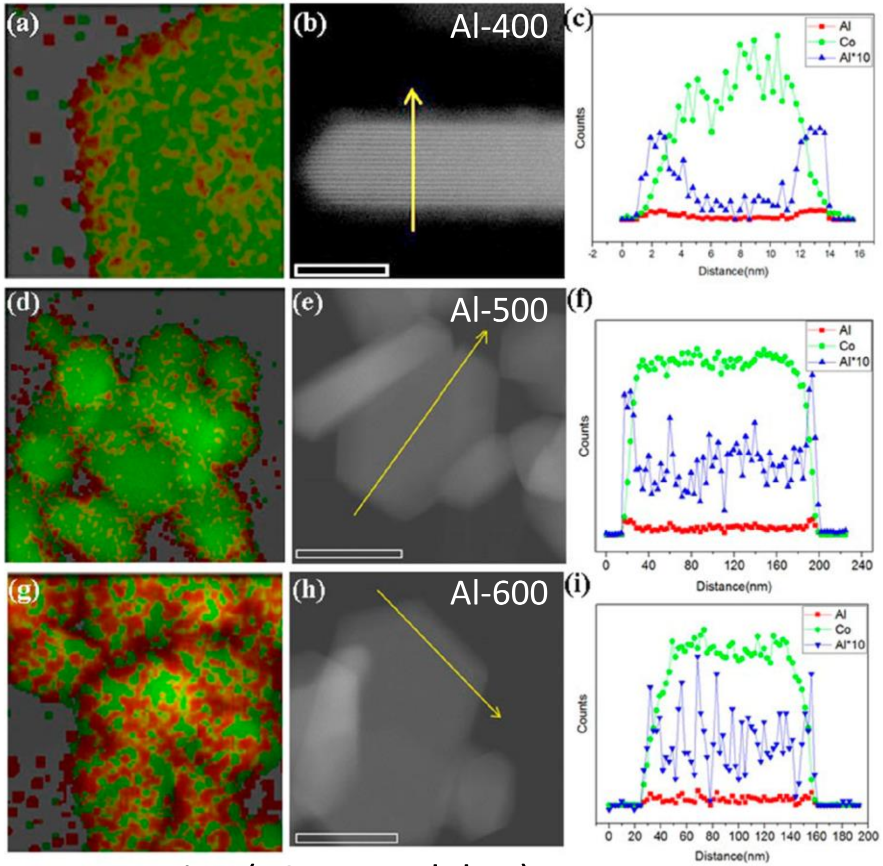
Energy materials

Electrode/electrolyte interface stabilization

UNIVERSITY OF ILLINOIS URBANA-CHAMPAIGN

- Li transparent passivation coating on electrode surfaces
- Wet chemical Al_2O_3 on $LiCoO_2$ nano-platelets
- Calcination at 400°C, 500°C, 600°C for 3 h (Al-400, Al-500, Al-600)

- EDX mapping shows coating, diffusion of Al present into core
- Quantification of surface coverage impossible
- XRD also sees diffusion with T

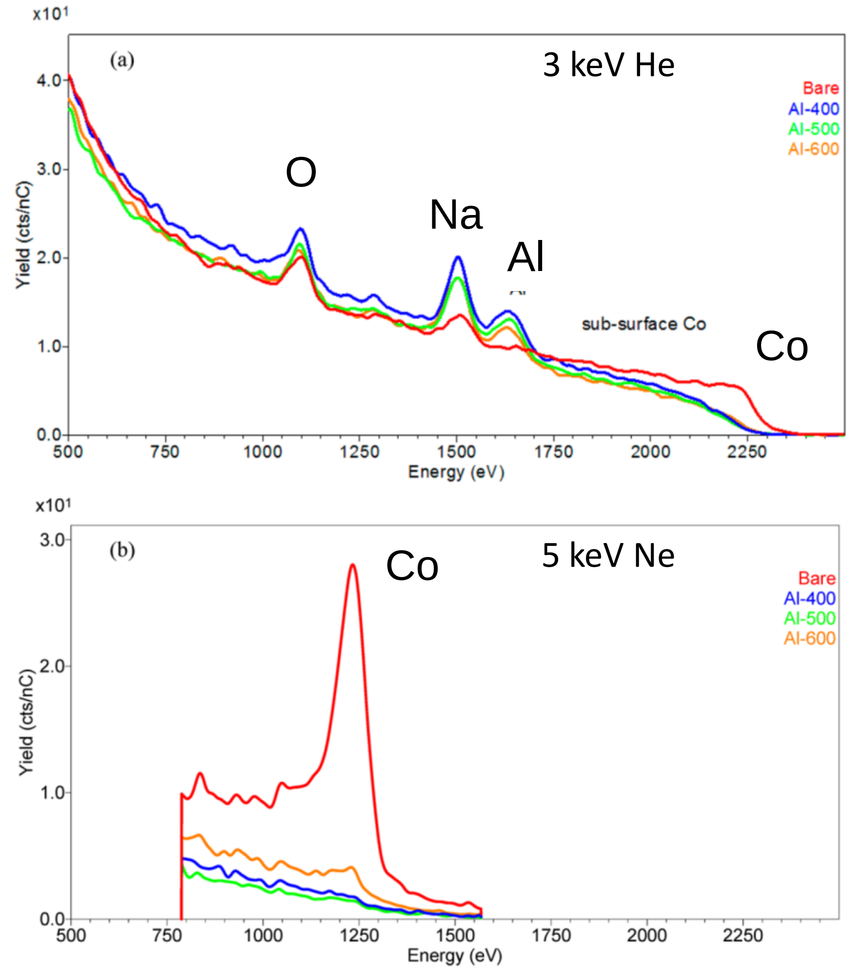


EDX mapping (10 nm scalebar)

Hu et al., *Chem. Mater.* 2017, 29, 5896−5905, DOI: 10.1021/acs.chemmater.7b01269

Electrode/electrolyte interface stabilization

- LEIS detects Al and residual Co at the surface (incomplete coating/diffusion)
- Sub-surface Co hardly changing
- Several 10 % Na detected (wet chemistry)



sample	Co signal (cts/nC)	Co surface coverage (%)
Bare	2208	100
Al-400	41	2
Al-500	41	2
Al-600	199	9

Hu et al., *Chem. Mater.* 2017, 29, 5896−5905, DOI: 10.1021/acs.chemmater.7b01269

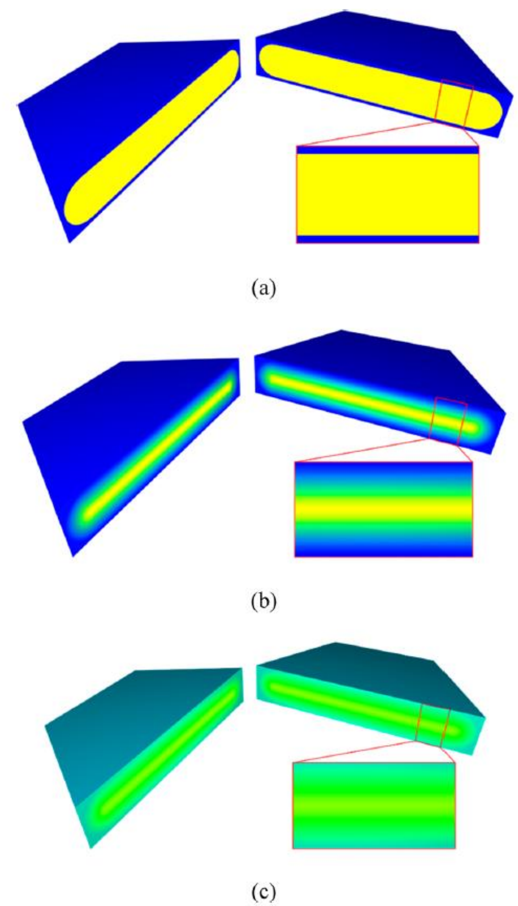
Electrode/electrolyte interface stabilization

- Calcination stimulates diffusion processes
- No complete intermixing (otherwise Co surface coverage would be much higher in LEIS)
  → Al ox preferred at surface, also seen in LEIS on $CoAl_2O_4$

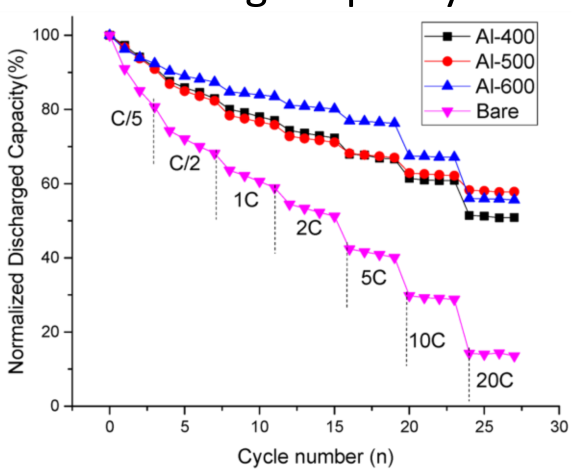
After coating

Low T

High T



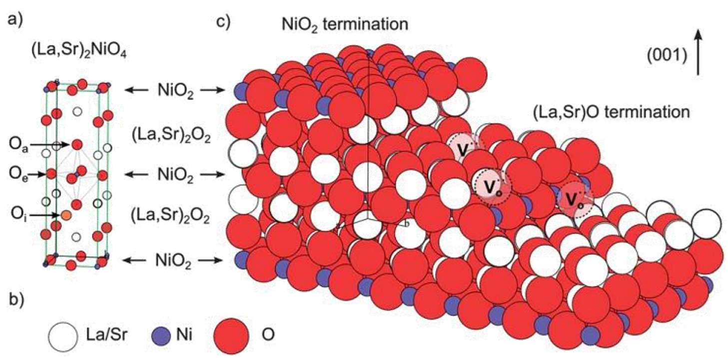
- At similar coulombic efficiency, normalised discharge capacity best for Al-600



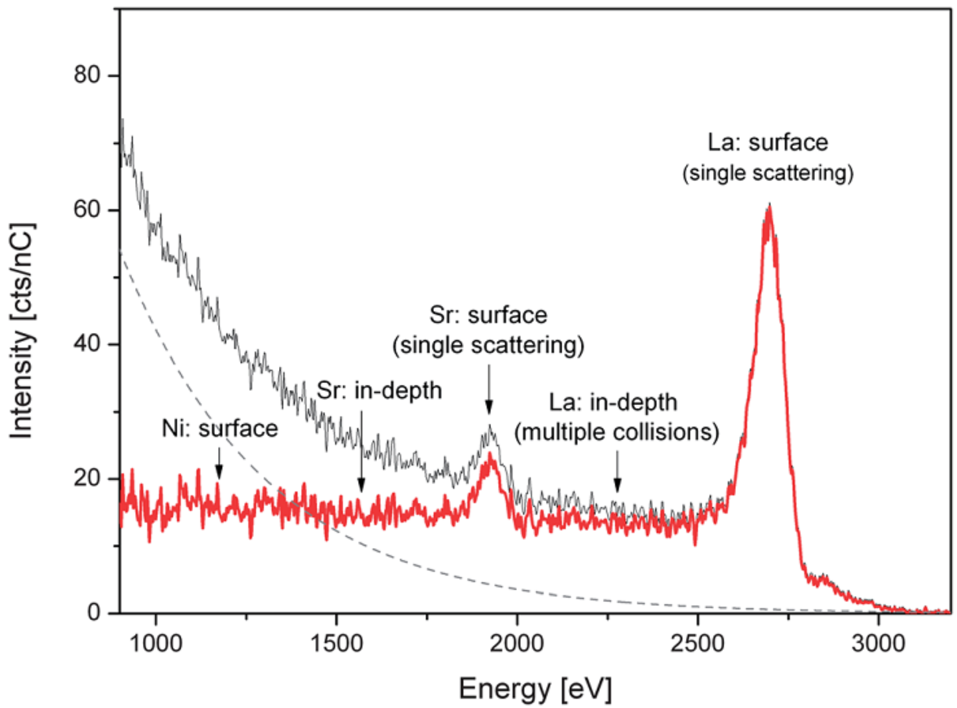
Hu et al., *Chem. Mater.* 2017, 29, 5896−5905, DOI: 10.1021/acs.chemmater.7b01269

Absence of Ni on outer layer of Sr doped La_2NiO_4 single crystals

- (La, Sr)$_2$NiO$_4$ is a candidate for SOFC cathodes – ionic O conductor
- Authors use LEIS, CTR and angle resolved XPS to analyzer low index faces of as-is and heat treated crystals (450° C, 72 h in air)
- LEIS data shows surface termination



Possible terminations of (La, Sr)$_2$NiO$_4$



M. Burriel et al., *Energy Environ. Sci.* **7**, 311 (2014)

Absence of Ni on outer layer of Sr doped La_2NiO_4 single crystals

- Angle resolved XPS and CTR less surface sensitive
- Agreement with LEIS findings: no Ni in (110) and (001) w/ and w/o annealing

AR-XPS: (La+Sr)/Ni ratio vs. depth

Depth (nm)	As cleaved single crystal	Heat treated single crystal
0.6	5.3 ± 1.2	6.7 ± 1.9
1.8	8.5 ± 1.6	5.5 ± 1.1
3.5	6.5 ± 1.0	5.2 ± 0.9
4.8	3.9 ± 0.5	4.3 ± 0.7
5.9	3.4 ± 0.4	4.6 ± 0.6
6.6	3.1 ± 0.4	4.7 ± 0.5
7.0	2.3 ± 0.2	4.5 ± 0.4
Bulk (theoretical)	2.0	2.0

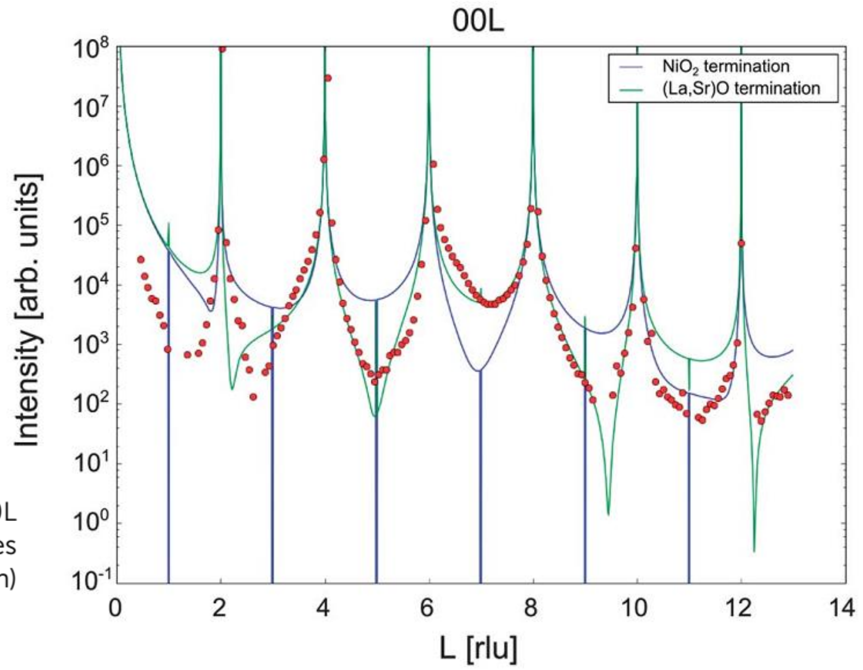
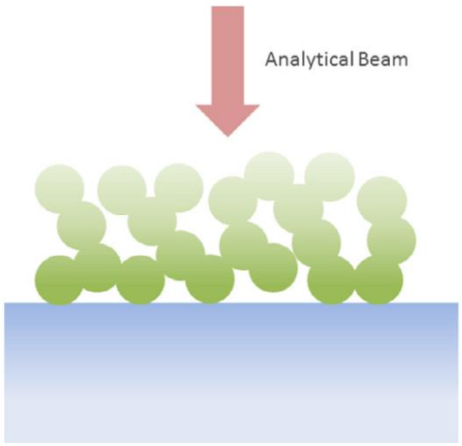


Fig. 2 Crystal truncation rod scattering as measured along the 00L direction in air at 450 °C. Red dots indicate the raw data and solid lines the model CTR patterns for NiO_2 (blue) or (La,Sr)O (green) terminations.

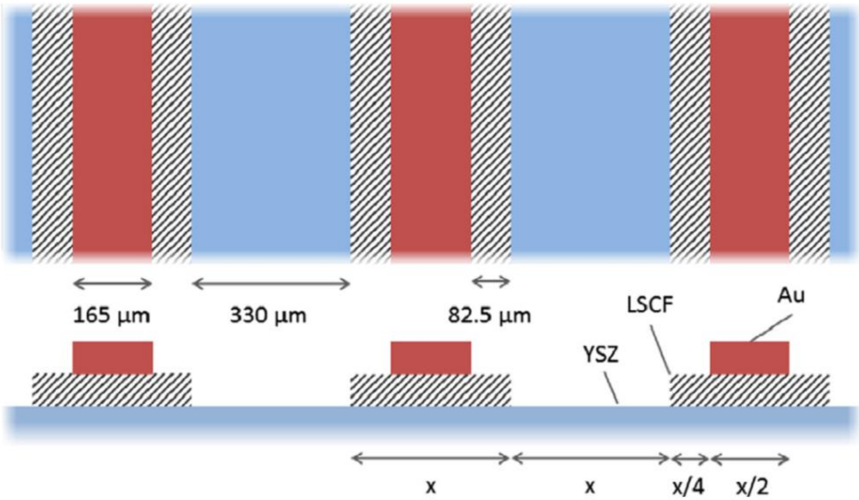
M. Burriel et al., *Energy Environ. Sci.* **7**, 311 (2014)

Laterally resolved analysis of fuel cell electrodes

- Fuel cell performance limited by oxygen exchange between solid electrolyte and gas phase
- Kinetics determined by transport properties and surface chemistry
- Interface usually not accessible to surface analysis → model structure



traditional porous electrode

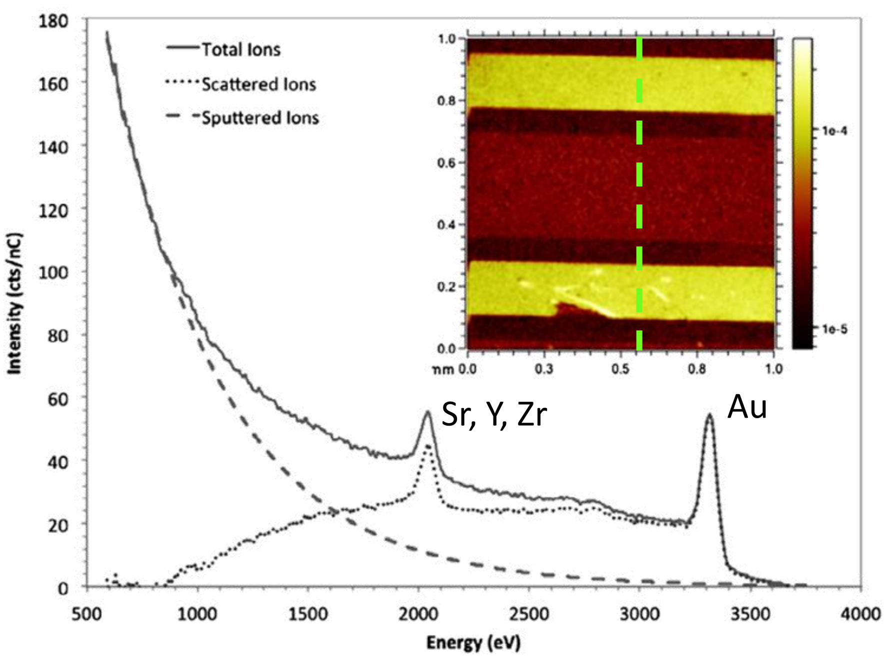


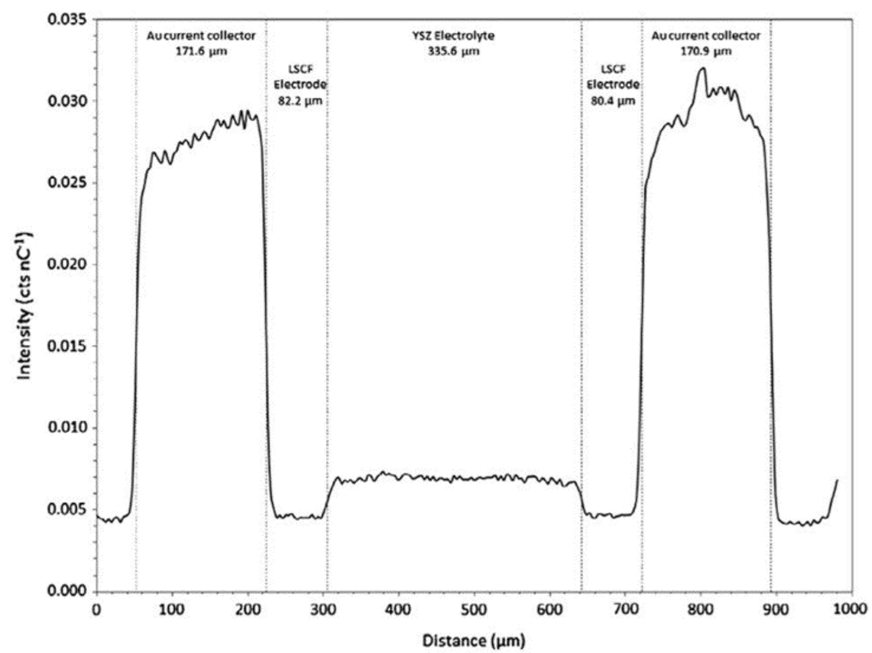
micropatterned LSCF electrodes on YSZ electrolyte

J. Druce et al., *Nucl. Instr. Meth. B*, **332** (2014) 261-265

Laterally resolved analysis of fuel cell electrodes

- Laterally resolved analysis is possible (here: 5 keV Ne scattering)
- Image resolution ≈5 µm

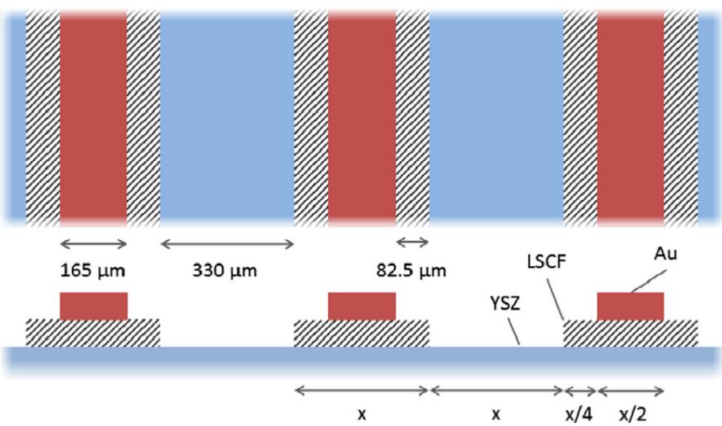


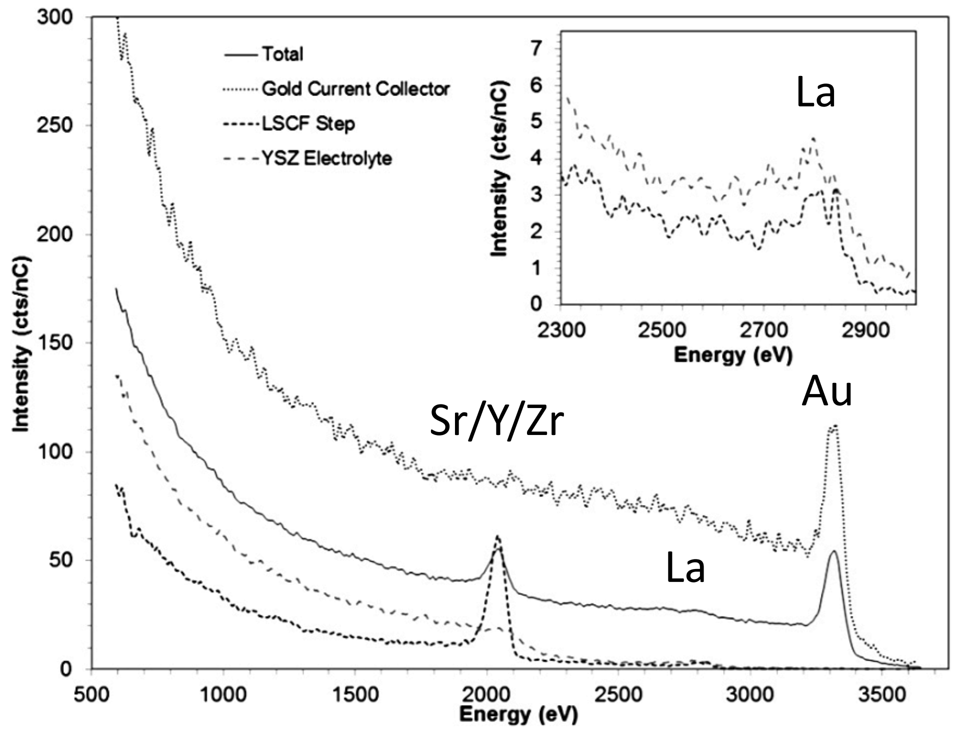


J. Druce et al., *Nucl. Instr. Meth. B*, **332** (2014) 261-265

Laterally resolved analysis of fuel cell electrodes

- LSCF step and electrolyte show no Au signal
- LSCF mainly terminated by Sr
- Electrolyte shows some La: Diffusion? Patterning? Electrochemical testing?
- Electrolyte shows no Y or Zr
  → monolayer contamination by Na, Si, Ca segregated from bulk





J. Druce et al., *Nucl. Instr. Meth. B*, **332** (2014) 261-265

Summary

- Low energy ion scattering (LEIS) is the most surface sensitive technique available - top atomic layer characterisation
- Static depth profiling provides detailed information up to 10 nm
- LEIS provides straight-forward and matrix effect free quantification
- The superior sensitivity of the Qtac100 double toroidal energy analyser allows real static LEIS analysis even with heavier projectiles at higher energies.
- The time-of-flight mass filtering significantly improves detection limits
- Ideal in combination with other analytical techniques such as TOF-SIMS or XPS


IONTOF
qtac100