Application of TOF-SIMS and LEIS for the Characterization of Ultra-thin Films

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TOF-SIMS Technique

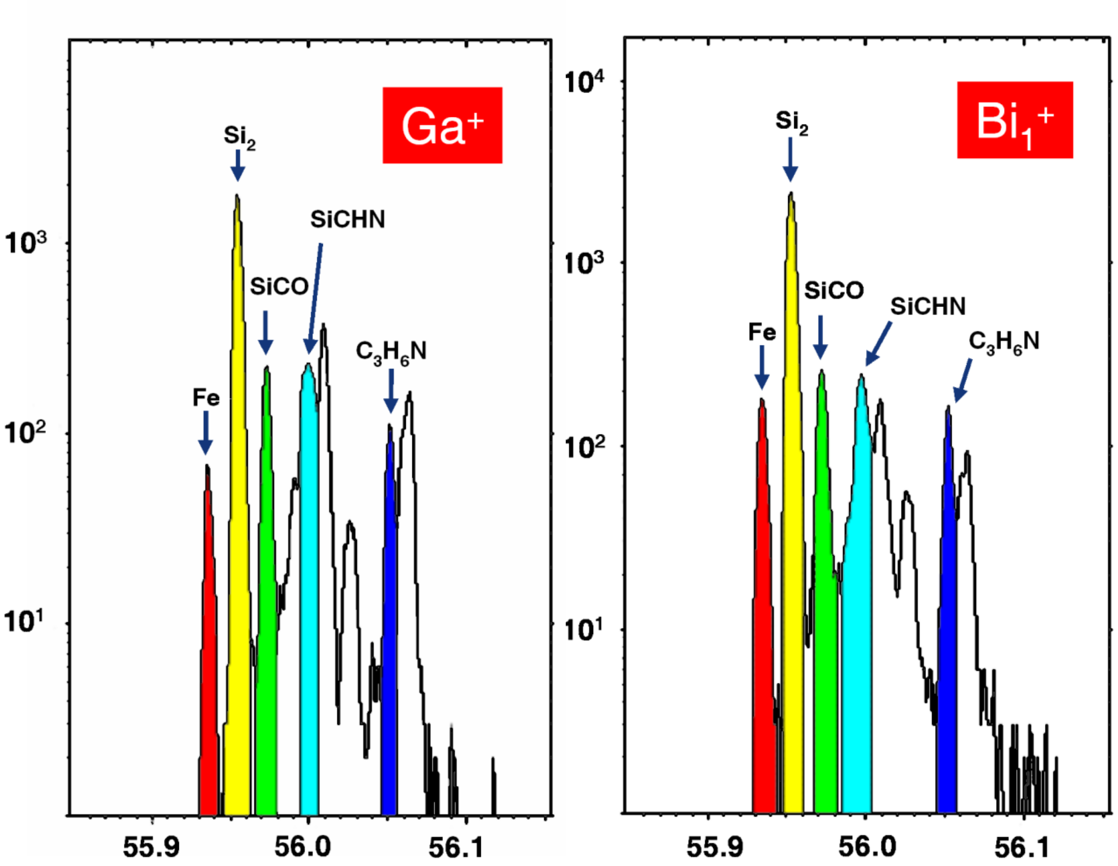
Characteristics

- **General**
  - Detection of elements and molecules
    → detailed chemical information
  - Parallel detection of all masses
- **Thin film analysis**
  - O_2 and Cs sputter depth profiling
    in dual beam mode
  - Depth resolution < 1 nm
  - Detection limit 1E16 atoms/cm^3
- **Problems in ultra-thin film analysis**
  - Quantification (complex systems)
  - Need for reactive species implantation
    (transient effects in sputter yield and ionisation over first several nm)
  - Information depth 1 – 3 monolayers

Detection limits at surface

High mass resolution and sensitivity

- Detection of all elements
- High mass resolution: ΔM/M > 12,000
- High sensitivity
  - < 1 ppm of 1 ML
  - 5E7 to 1E9 atoms/cm^2

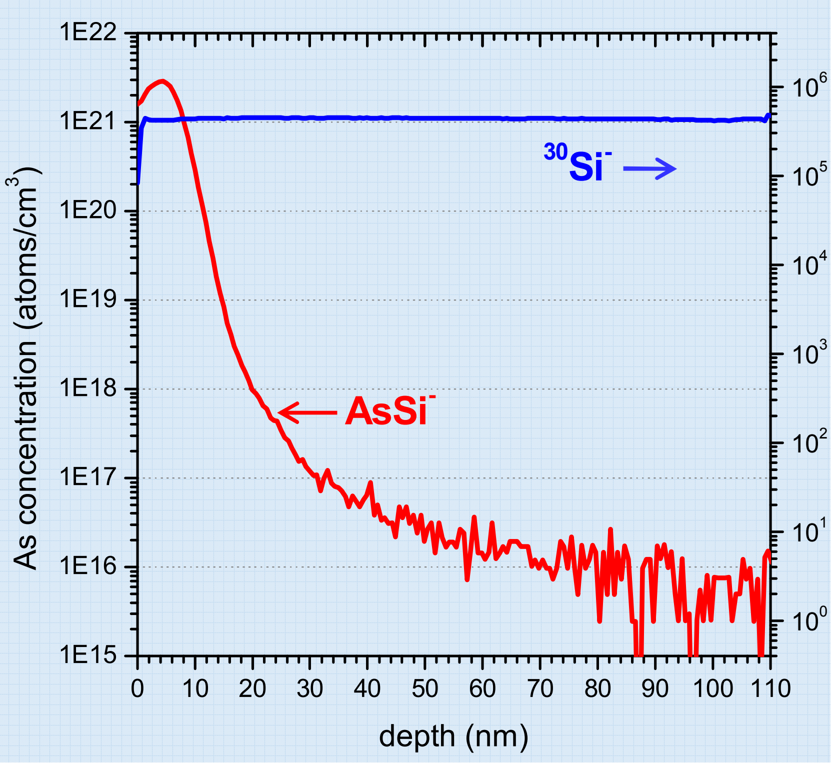


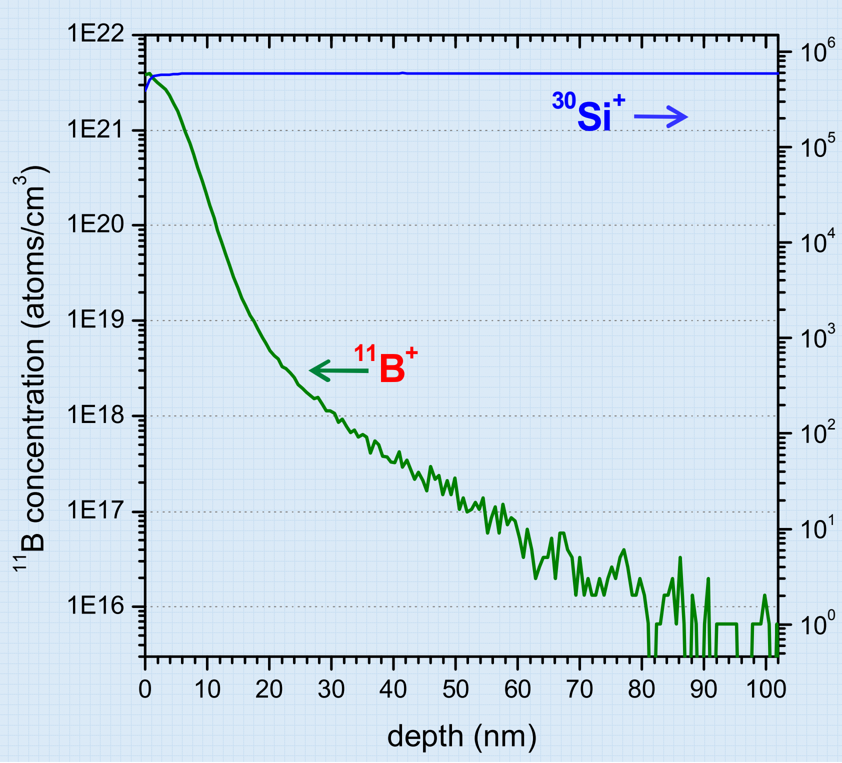
Shallow implants

Routine analysis with TOF-SIMS

- high dynamic range (> 1E5)
- good detection limits
- high speed analysis
- reliable quantification
- < 0.5 % RSD reproducibility
- high throughput, unattended operation

Very high dose → dilute limit?





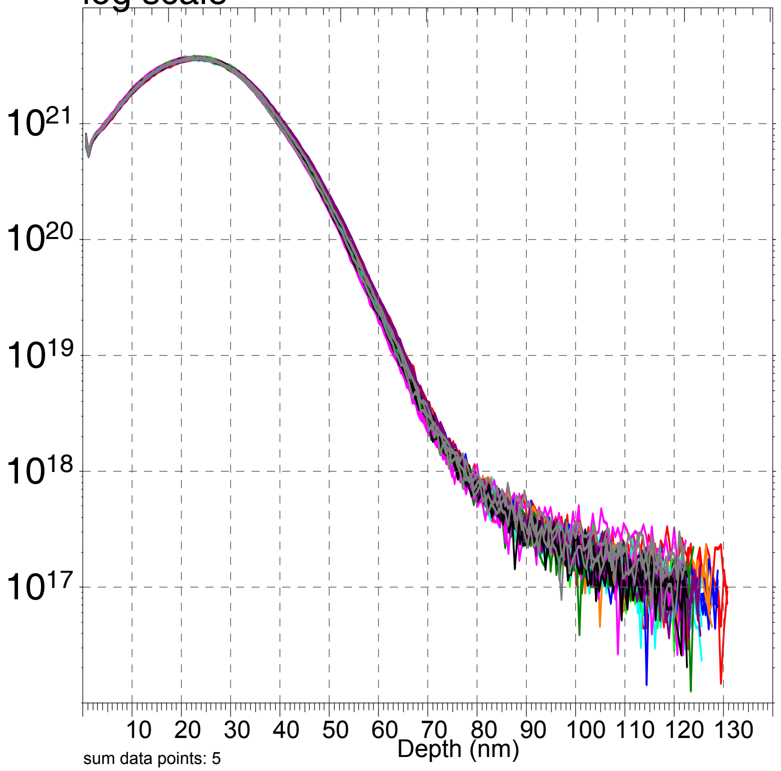
Shallow implants

Reproducibility

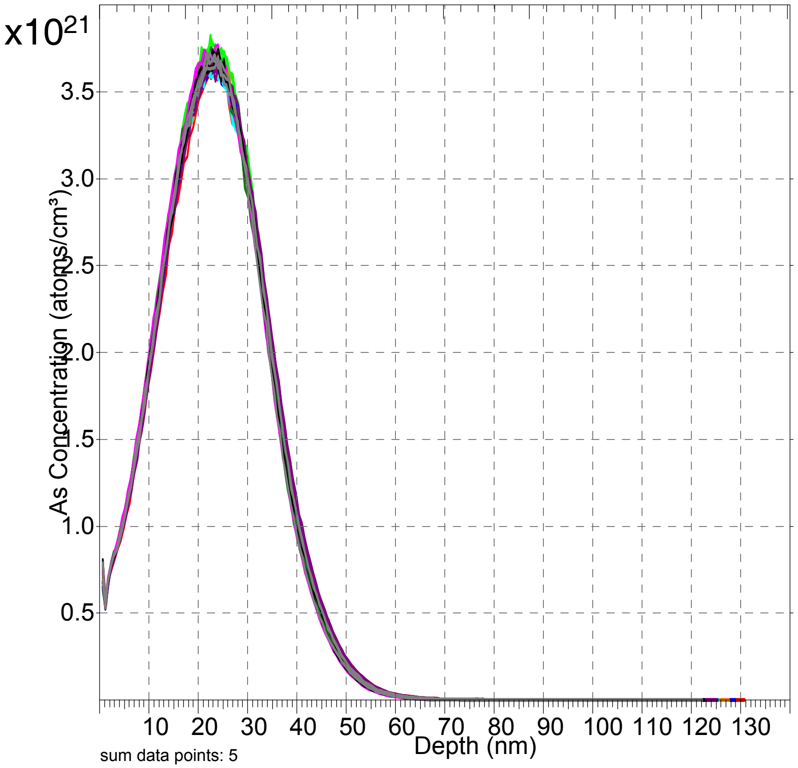
Example:

- 33 profiles of 1E16 at/cm² As implanted in Si
- one automated run

log scale



linear scale



Shallow implants

Reproducibility

Example:

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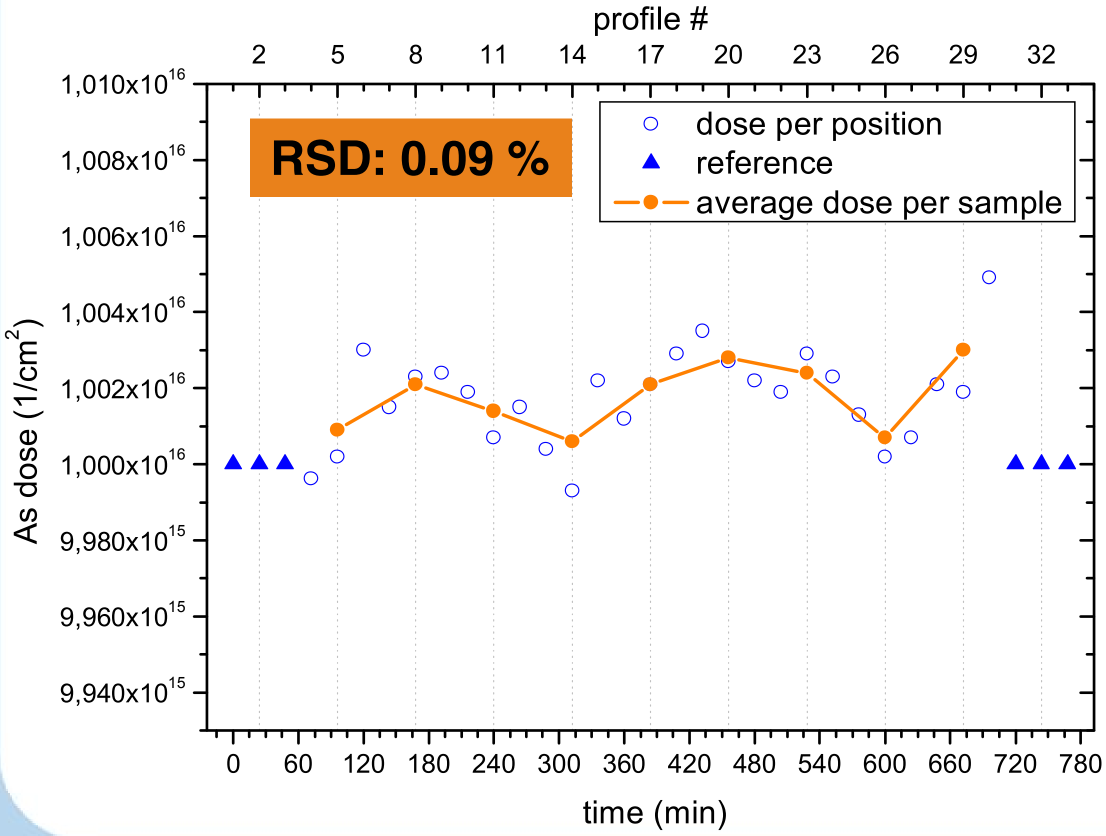
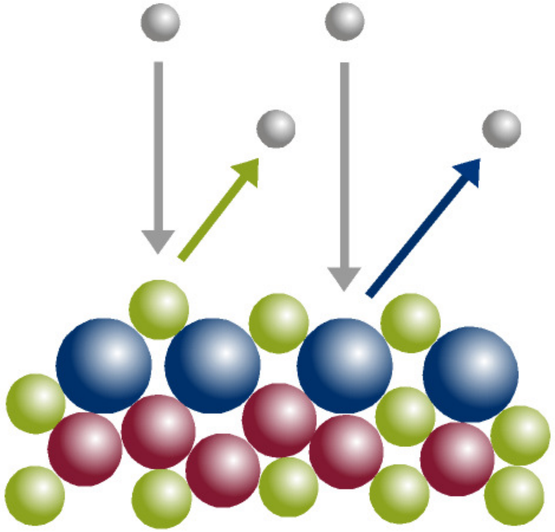


	detection limit (at/cm³)	reproducibility (RSD)	sputter rate @ 500 eV
B	6E15	< 0.5 %	3.3 nm/min
P	2E16	< 0.5 %	4.1 nm/min
As	1E16	< 0.5 %	4.1 nm/min

LEIS Technique

Features of Low Energy Ion Scattering (LEIS)

$^{3}He^{+}$, $^{4}He^{+}$, Ne^{+}, Ar^{+}, Kr^{+}

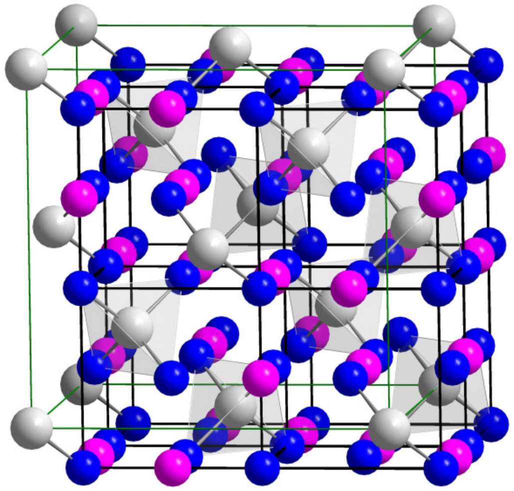


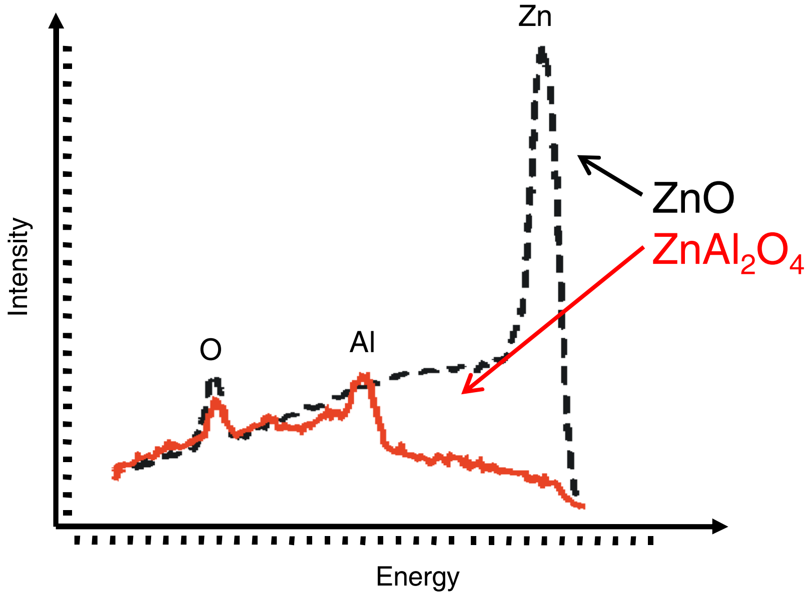
- Energy of projectiles: 1...8 keV
- Energy of scattered particles yields mass of target atom
- Intensity of scattered ions directly proportional to surface coverage
- Ultra-high surface sensitivity – top atomic layer analysis
- Detection limits:
  - Li - O ≥ 1 % of 1 ML
  - F - Cl 1 % - 0.05 % of 1 ML
  - K - U 500 ppm - 10 ppm of 1 ML

LEIS Technique

Ultimate surface sensitivity

- In spinels of type AB_2O_4 the ions of A are in tetrahedral sites below the surface
- LEIS spectra of ZnO and $ZnAl_2O_4$ (spinel)



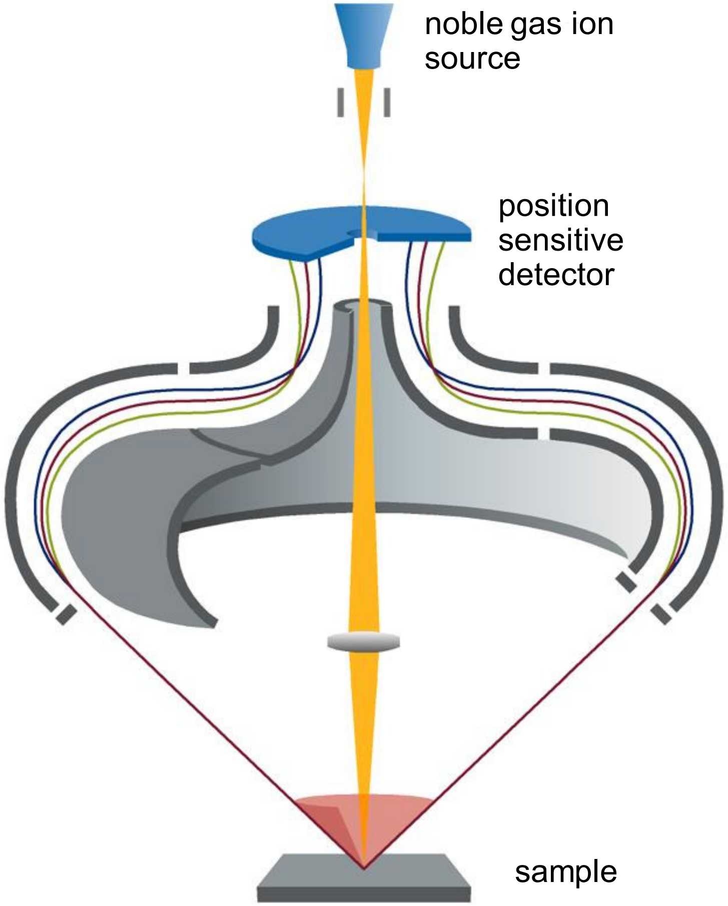


→ Zn not detected at the surface, but directly below!

LEIS Technique

Design of LEIS Instrument

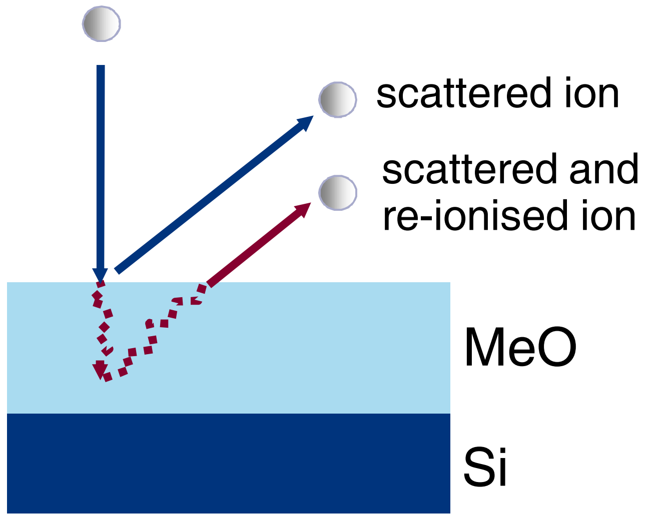
- Dedicated high sensitivity LEIS analyzer
  - scattering angle 145 ±1 degrees
  - integration over all azimuths
  - parallel energy detection
- Limitations in conventional LEIS / ISS instruments
  - low sensitivity (destructive technique)
  - mass resolution not sufficient

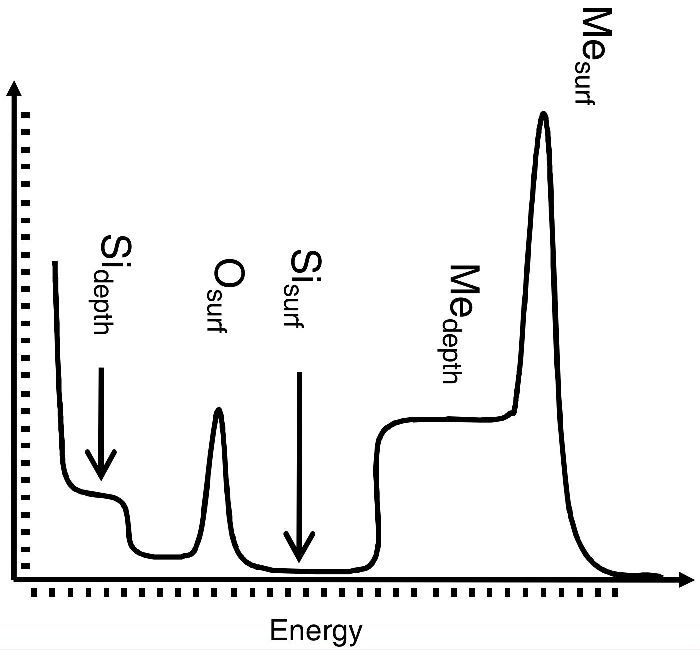


LEIS Technique

Sputter depth profiling in dual beam mode

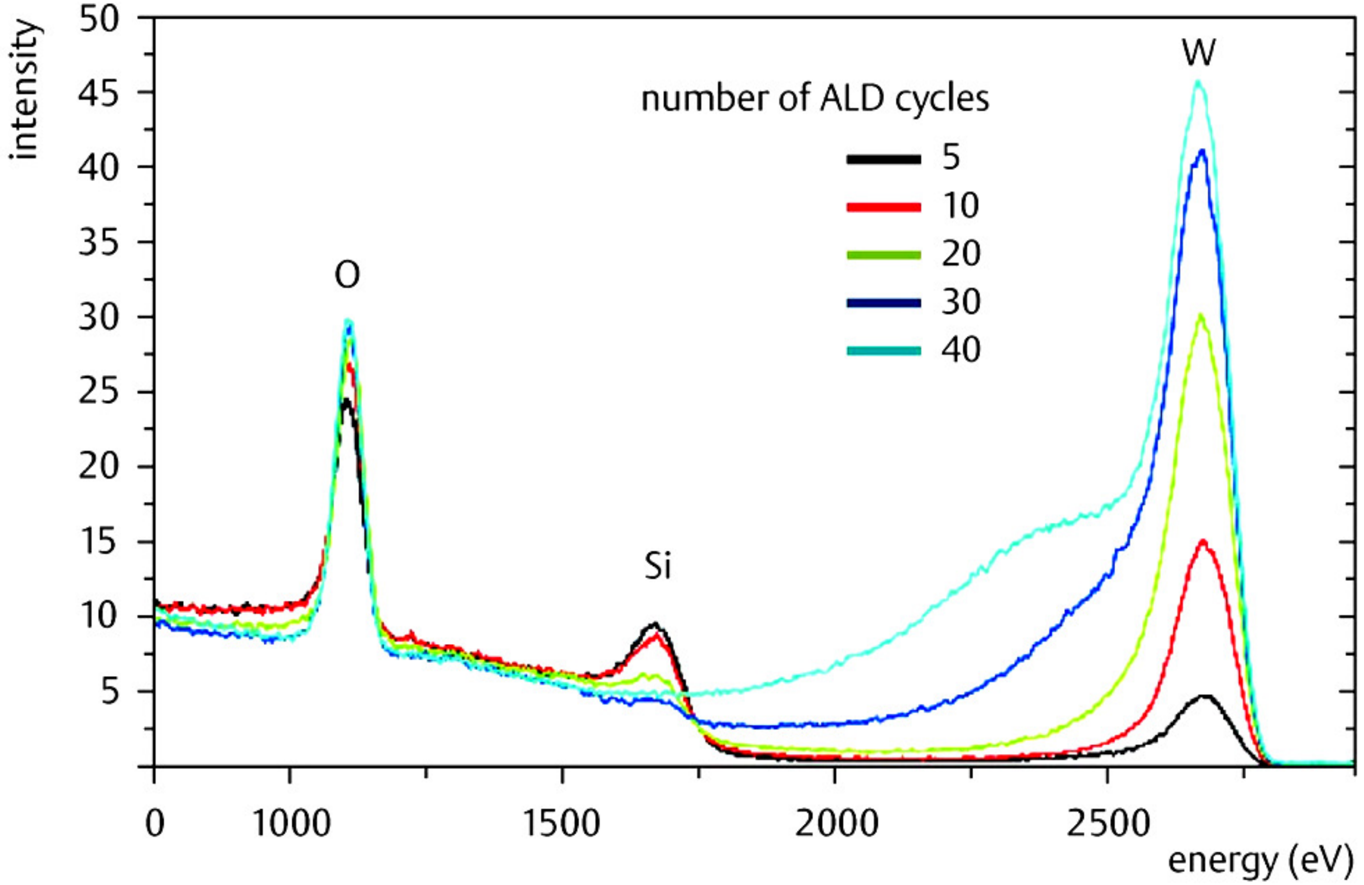
- Sputter depth profiling in dual beam mode
  - LEIS analysis while sputtering with low energy noble gas ions (Ar, Xe)
- Static depth profiling
  - scattering energy is specific for sample atom
  - additional energy loss on the way through the sample
    → in-depth distribution visible in spectrum
    under appropriate surface conditions (similar to MEIS and RBS)





Spectroscopy and Static Depth Profiling

WN_xC_y Diffusion Barrier for Cu on Silicon

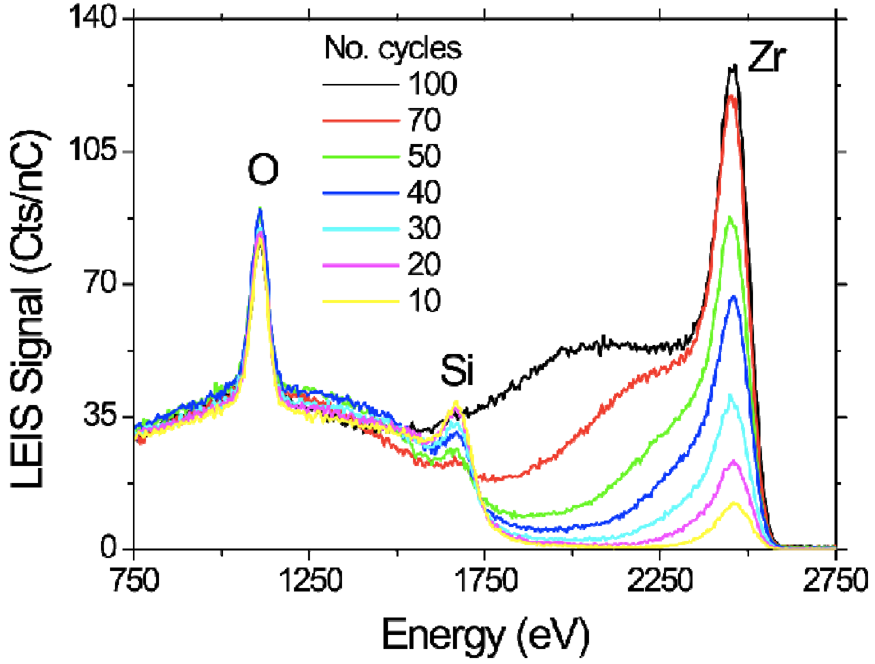


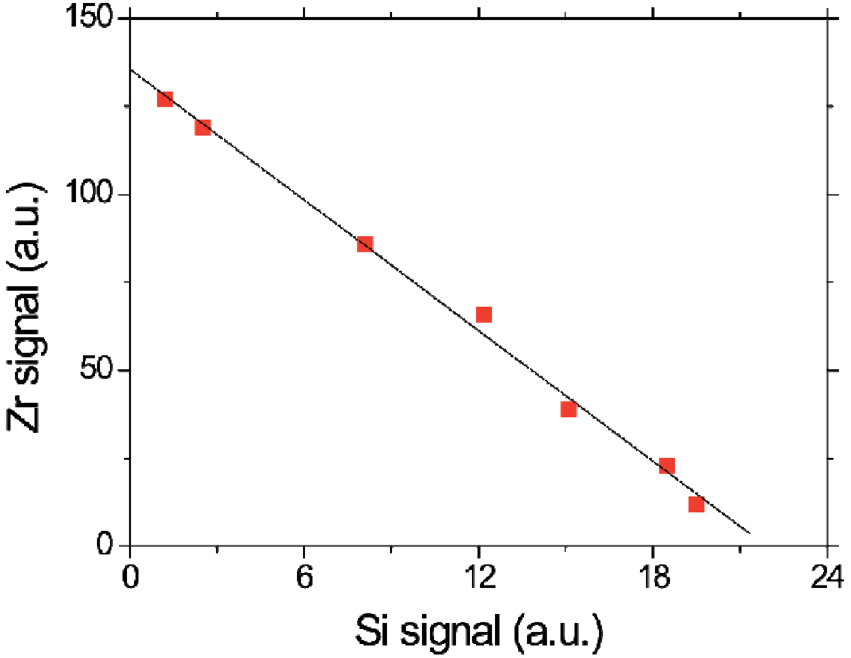
LEIS spectra taken after an increasing number of ALD cycles of WN_xC_y on silicon

Spectroscopy and Static Depth Profiling

ZrO_2 Atomic Layer Deposition on Silicon

- no matrix effect
- easy calibration / quantification for a two component system

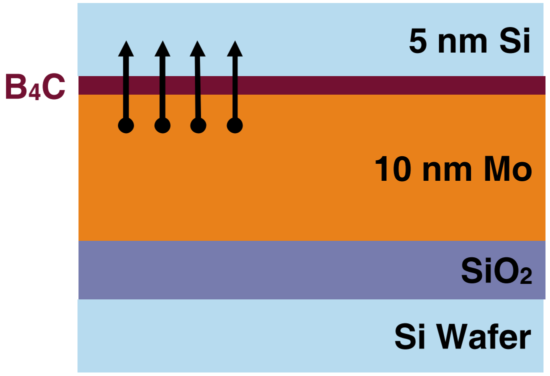


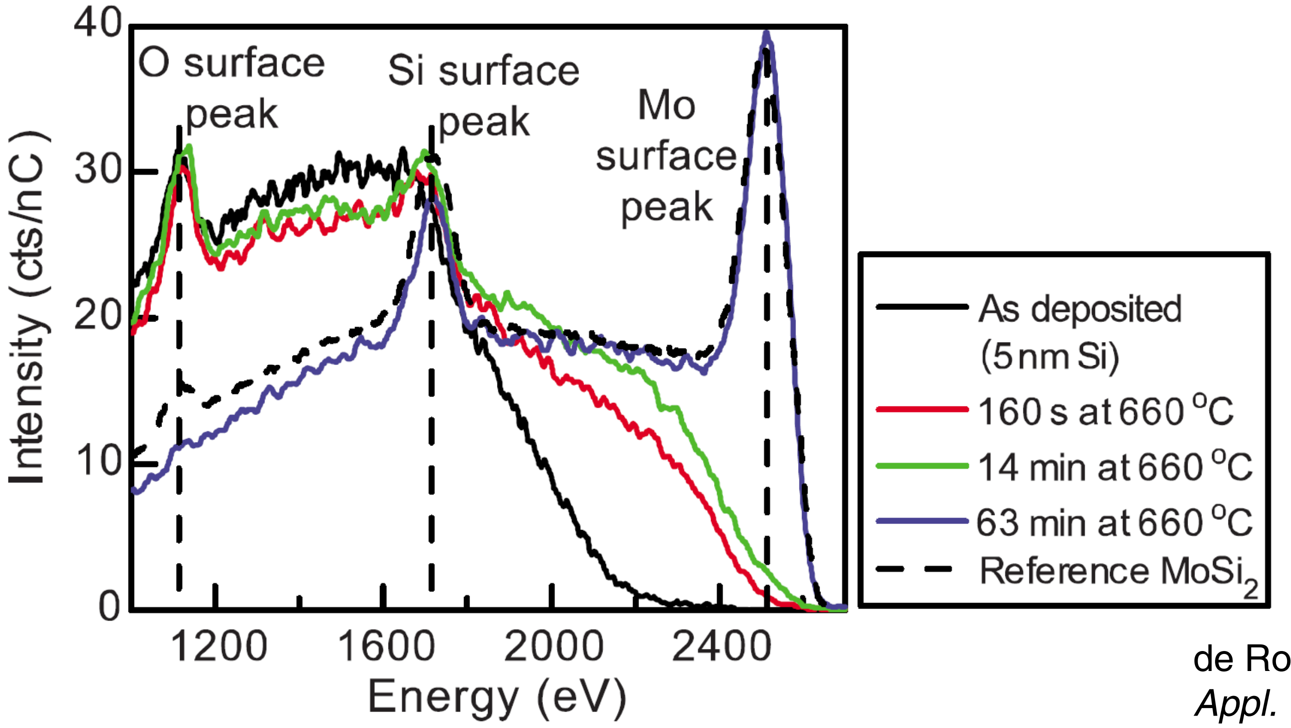


Spectroscopy and Static Depth Profiling

Diffusion Study in Mo/Si layers

- 10 nm Mo/1.6 nm B_4C/5 nm Si
- Annealing @ 660°C
- Formation of $MoSi_2$ by extensive diffusion



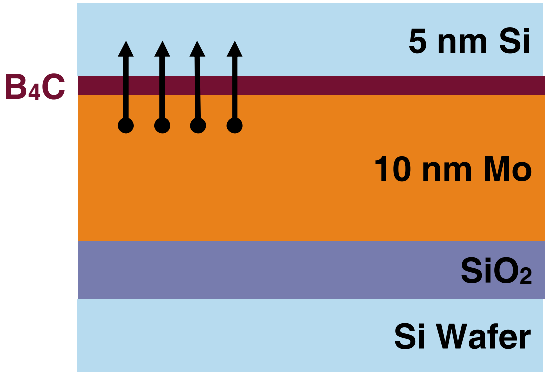


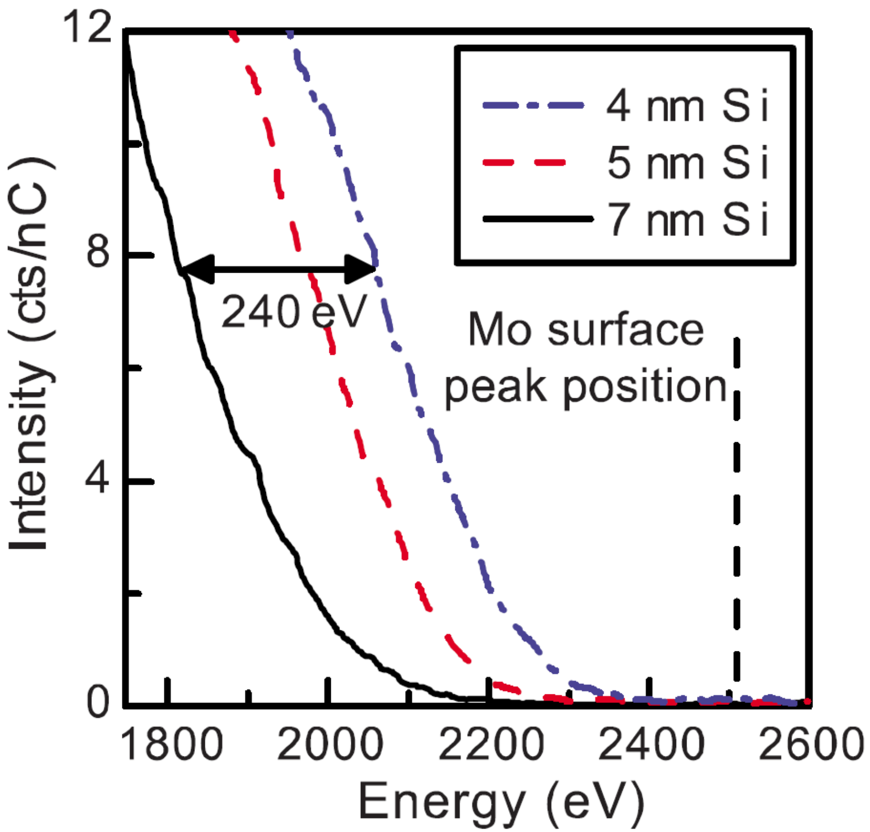
de Rooij-Lohmann *et. al.*,
Appl. Phys. Letters ***94*** *063107 (2009)*

Spectroscopy and Static Depth Profiling

Diffusion Study in Mo/Si layers

- 10 nm Mo/1.6 nm B_4C/5 nm Si
- Depth scale from variation of Si layer thickness





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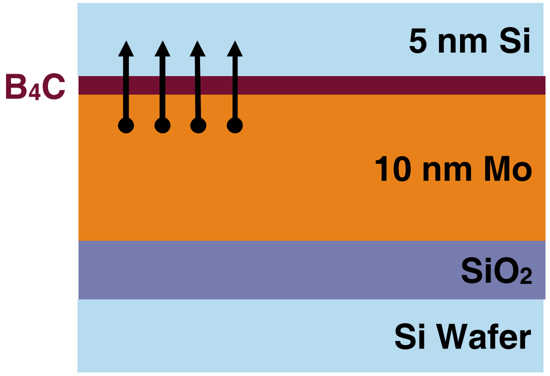
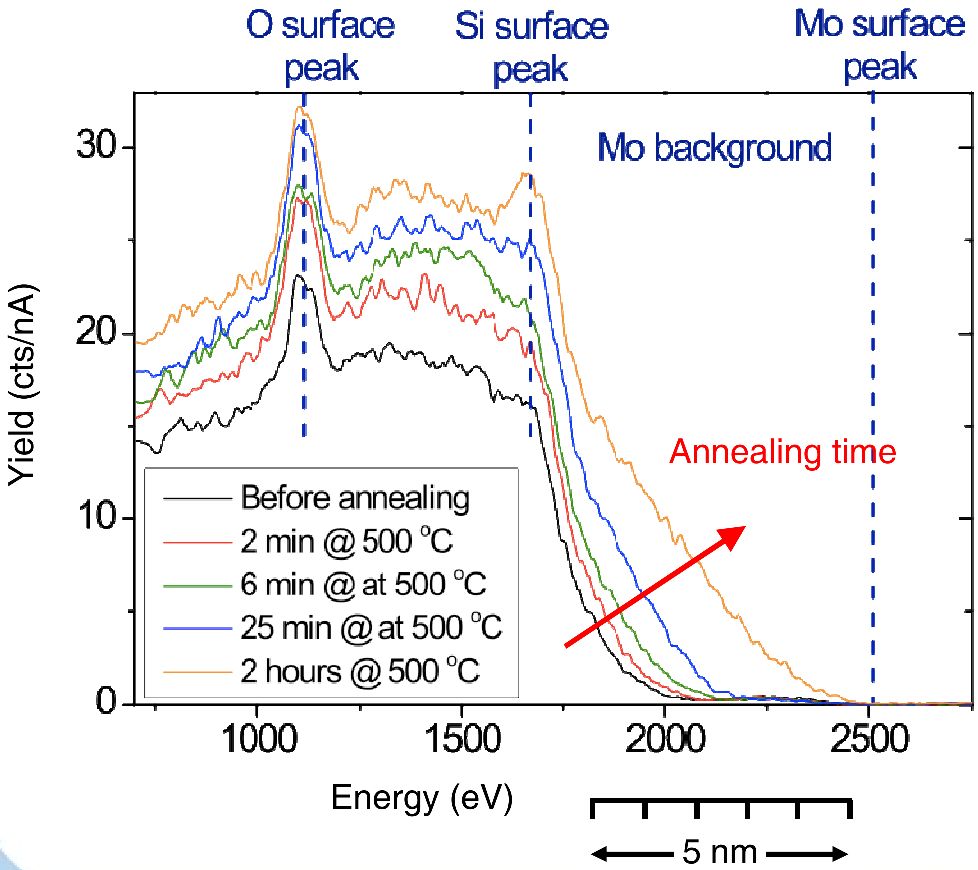
Spectroscopy and Static Depth Profiling

Diffusion Study in Mo/Si layers

- 10 nm Mo/1.6 nm B_4C/5 nm Si, annealing @ 500 °C
- Diffusion coefficient **without** B_4C: **$(8\pm2)\cdot10^{-20}$ m²/s**
  with 1.6 nm B_4C: **$(4\pm1)\cdot10^{-21}$ m²/s**





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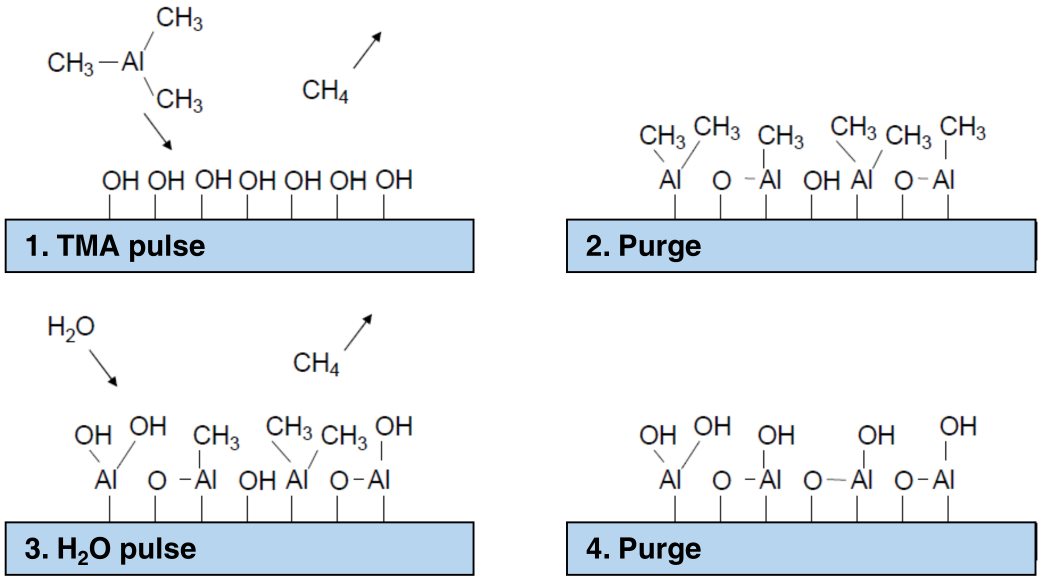
ALD Studies

Principle of Atomic Layer Deposition

Atomic Layer Deposition used for

- diffusion barriers
- high-k dielectrics (gate stack, DRAM capacitors)
- new applications are being developed (not only semiconductor!)

Example:
Al_2O_3 growth
using TMAl and H_2O



Questions:

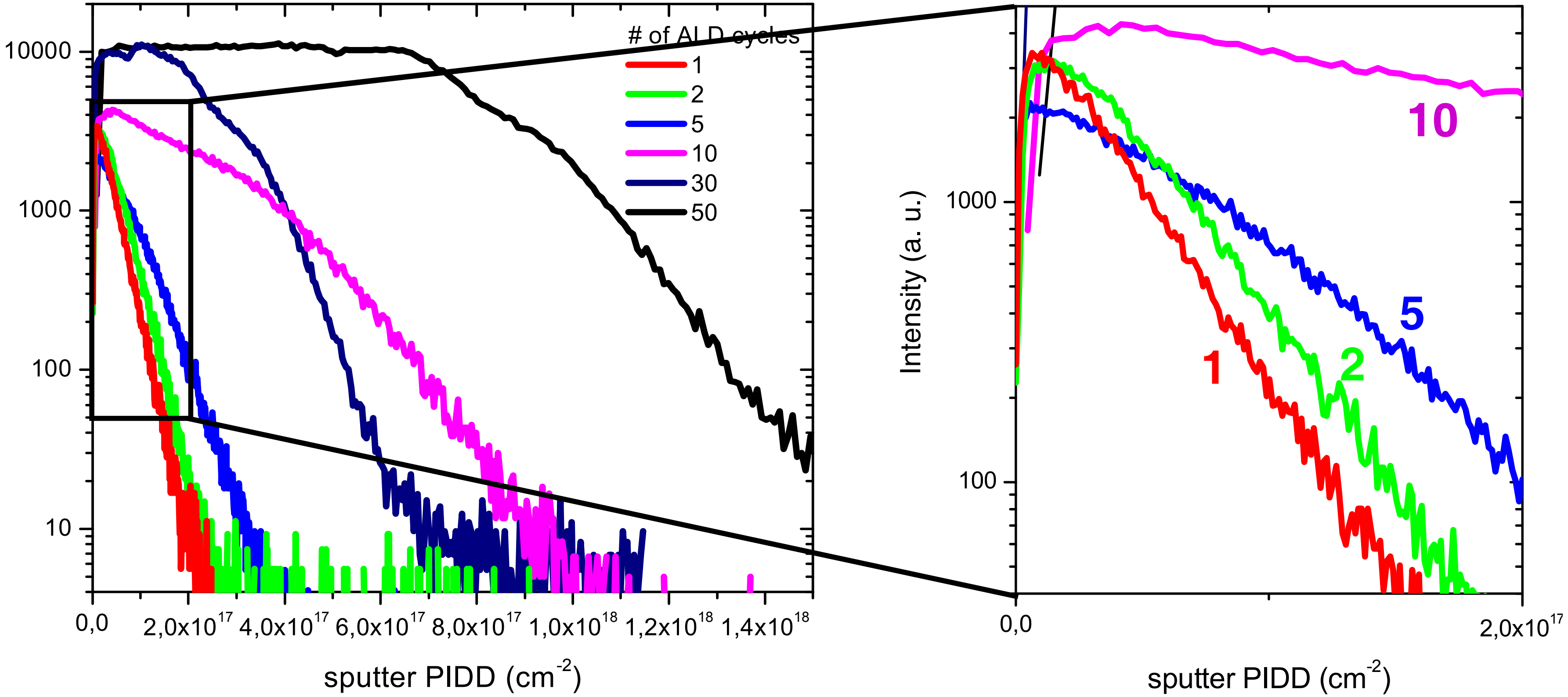
- nucleation phase
- growth per cycle
- homogeneity, conformity of films, pinholes

ALD Studies

TOF-SIMS Analysis of Ta (SiN) Film on Si

TOF-SIMS dual beam profiling:

Bi analysis and 500 eV O2 sputtering at 45°

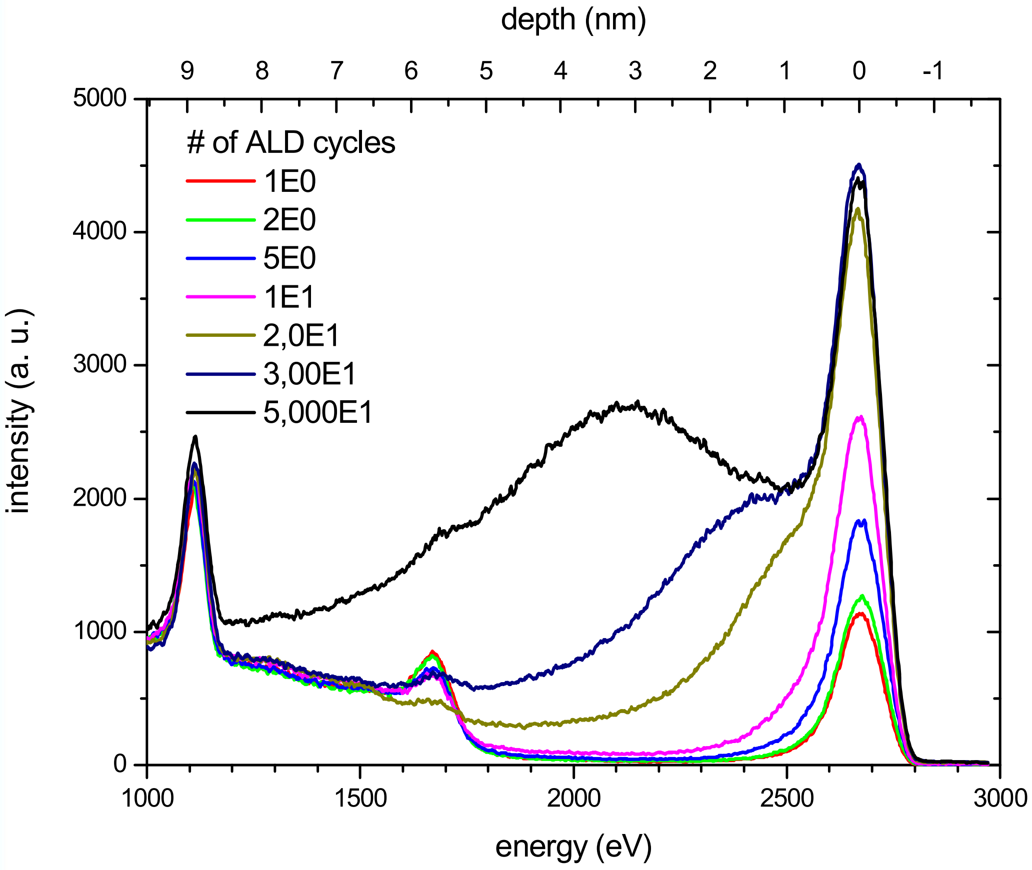


ALD Studies

LEIS Analysis of Ta (SiN) Film on Si

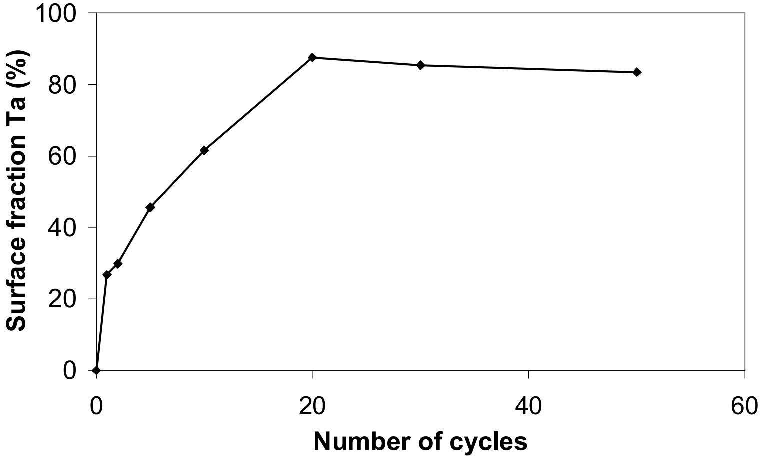
LEIS static analysis

He, 3 keV, 0°



Simplified quantification:

Assume Ta and Si to be the only species at surface (Ta + Si = 100%)



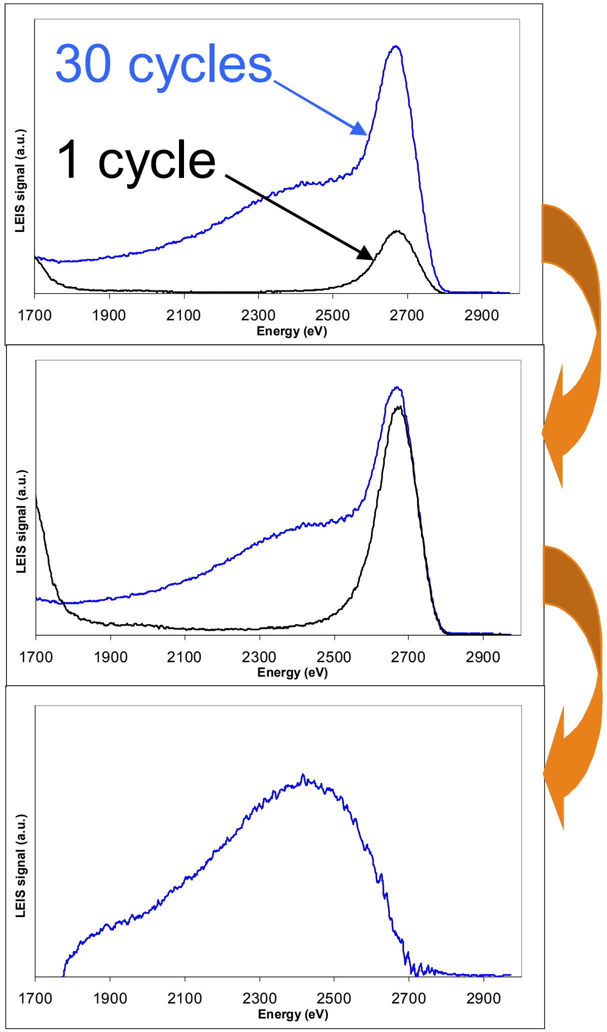
ALD Studies

LEIS Analysis of Ta (SiN) Film on Si

Separation of surface composition and depth information

↓

subtraction of sub-monolayer surface peak after appropriate scaling



Scale 1 cycle spectrum to fit high energy side

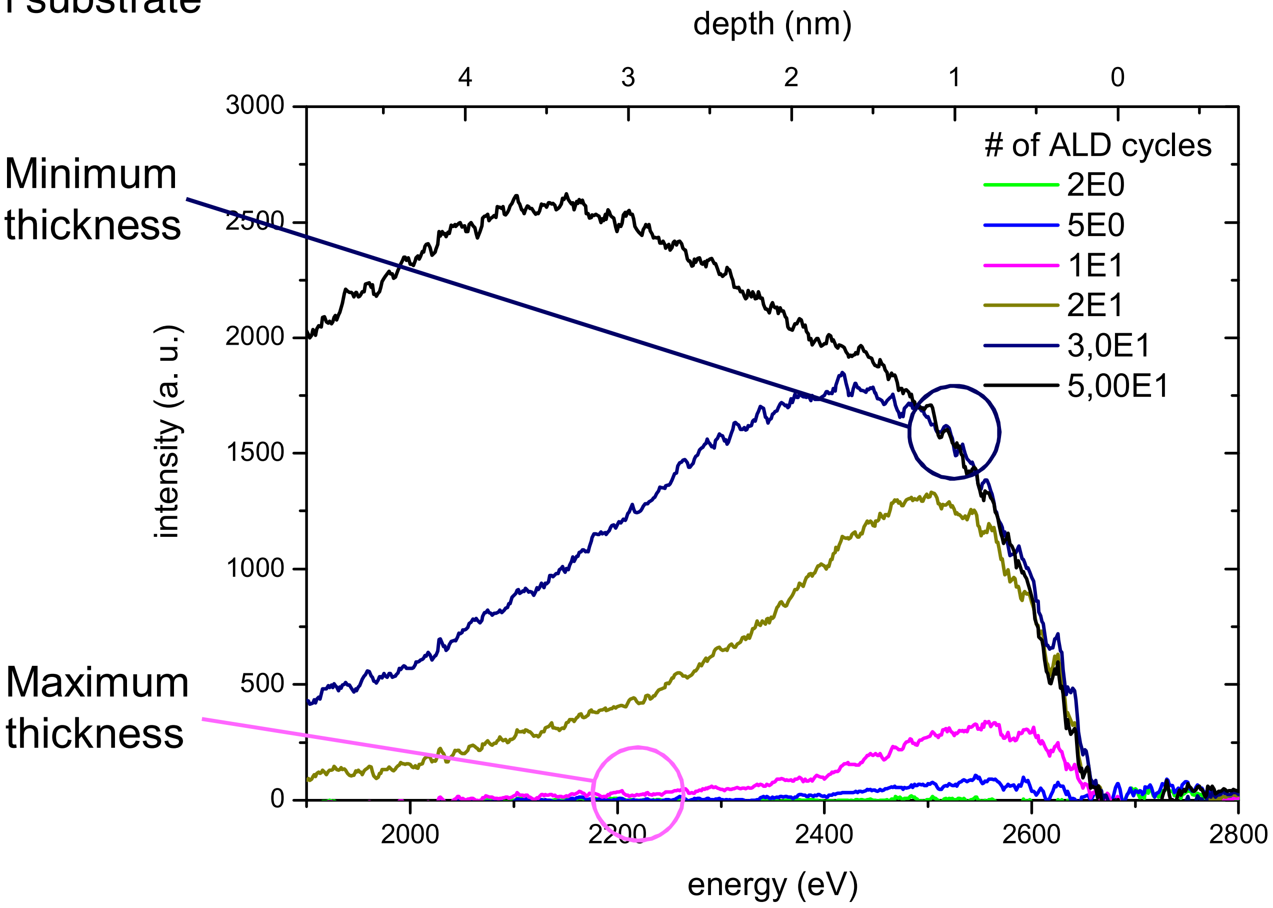
Subtract 1 cycle spectrum

ALD Studies

LEIS Analysis of Ta (SiN) Film on Si

In-depth signal shows

- nucleation behaviour
- layer closure
- possible intermixing with substrate

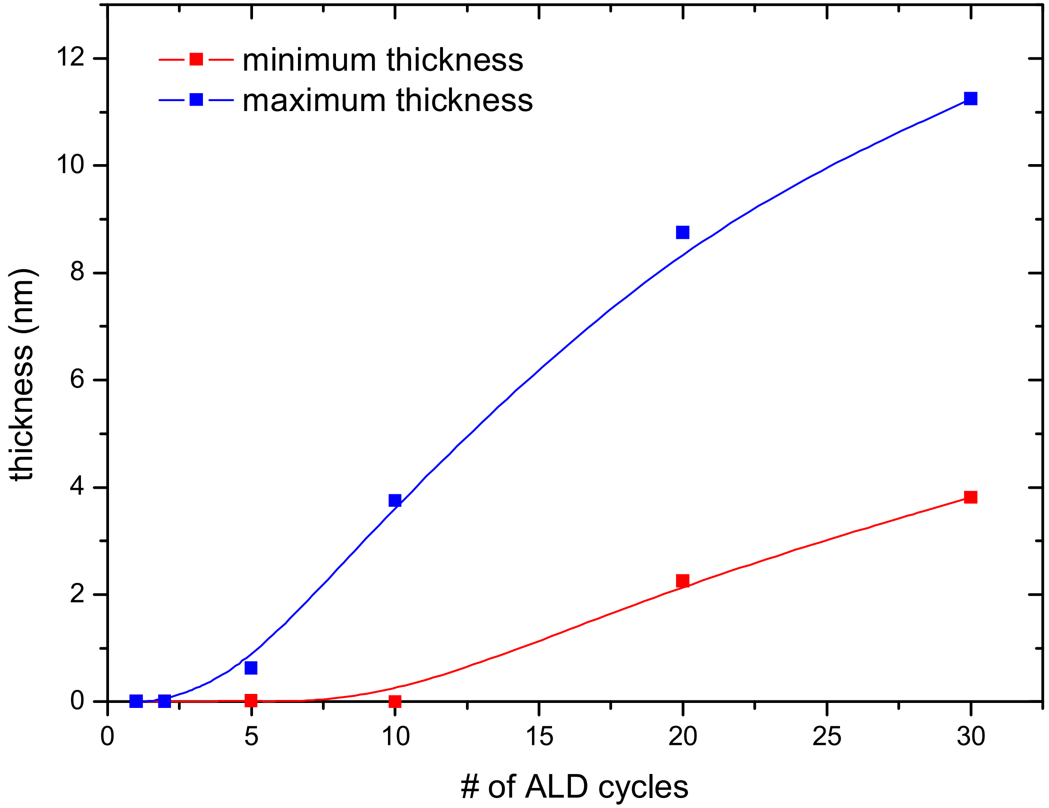


ALD Studies

LEIS Analysis of Ta (SiN) Film on Si

In-depth signal shows

- nucleation behaviour
- layer closure
- possible intermixing with substrate
- initial change in growth rate

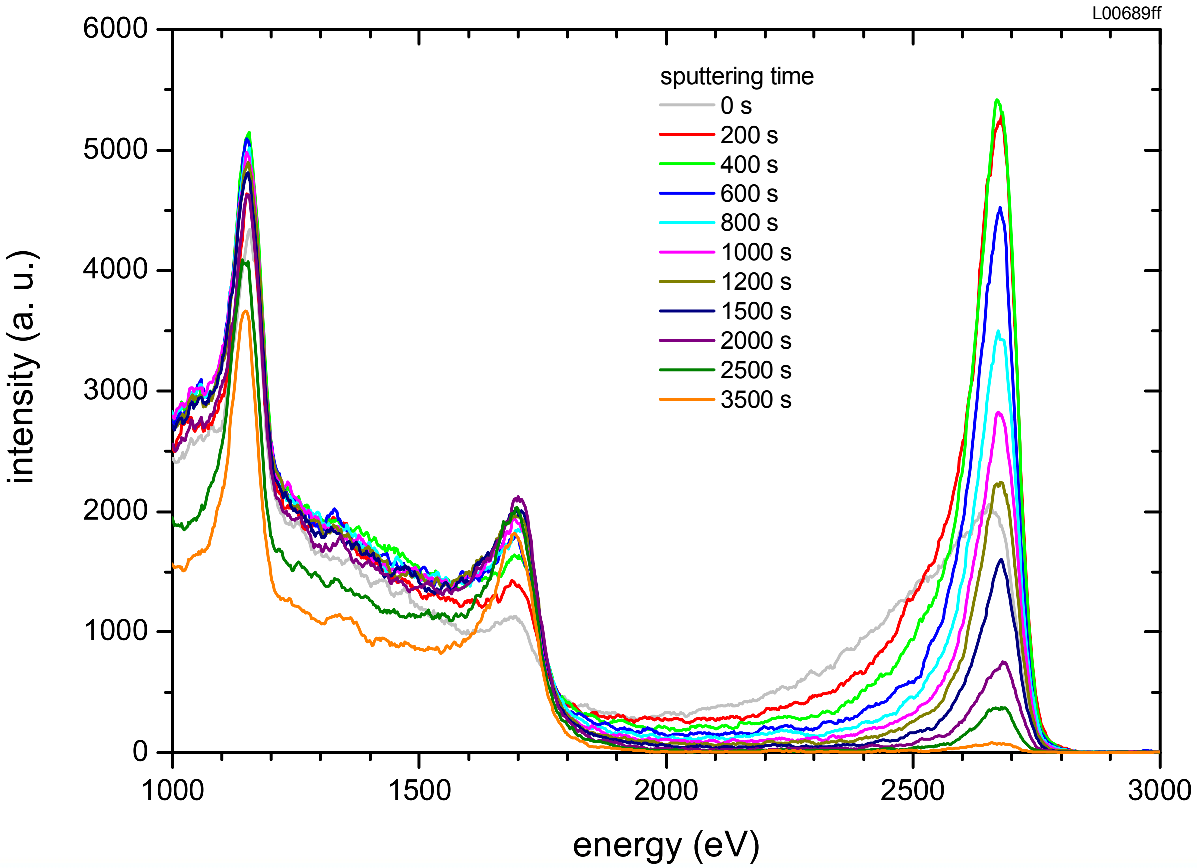


ALD Studies

LEIS Analysis of Ta (SiN) Film on Si

LEIS depth profiling in static mode combined with sputtering

- Sample with 10 cycle
- Analysis with 3 keV He scattering after each 500 eV Ar sputter cycle



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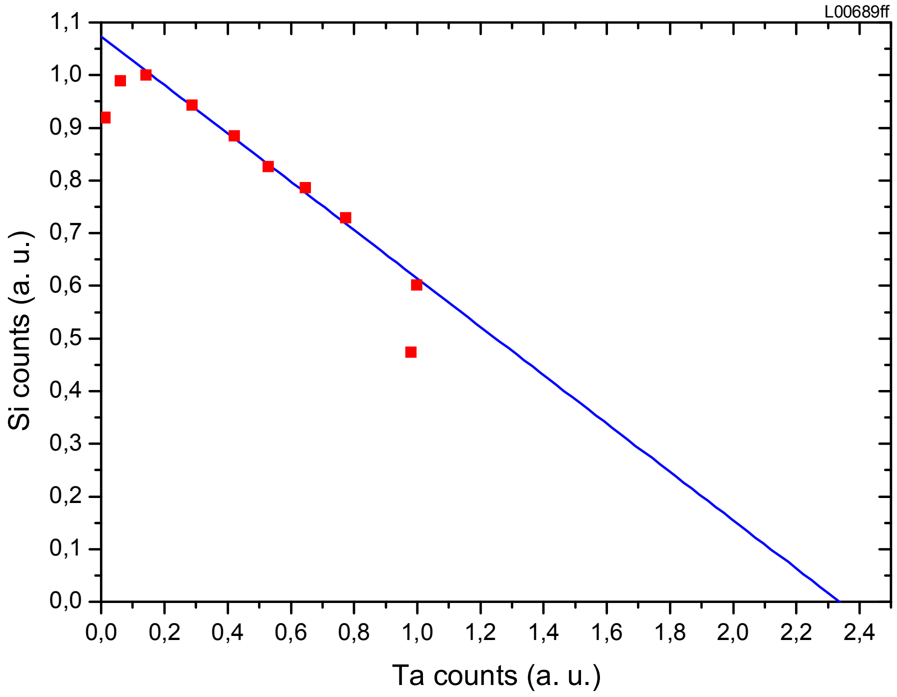


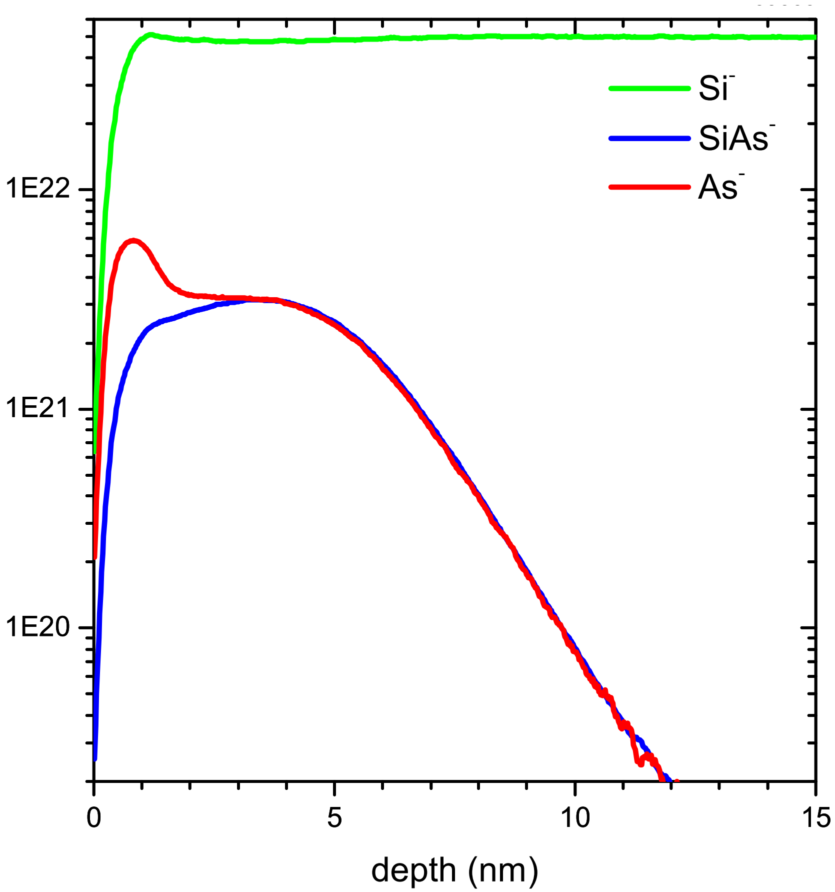
Ultra-Shallow Implants

As Implant Profiling by TOF-SIMS

Implant technology trend

- significant reduction of implant energy
- peak concentrations close to the surface
- concentrations above dilute limit

→ quantification near the surface becomes very important



sample provided by IHP Frankfurt (Oder), Germany

Ultra-Shallow Implants

As Implant Profiling by TOF-SIMS

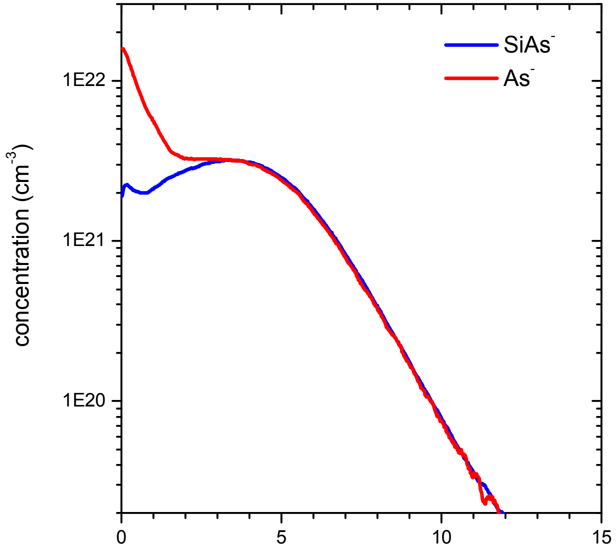
Example: As implant 2 keV, 1E15 atoms/cm²

- analysis: 15 keV Bi
- sputtering: 500 eV Cs, 45°

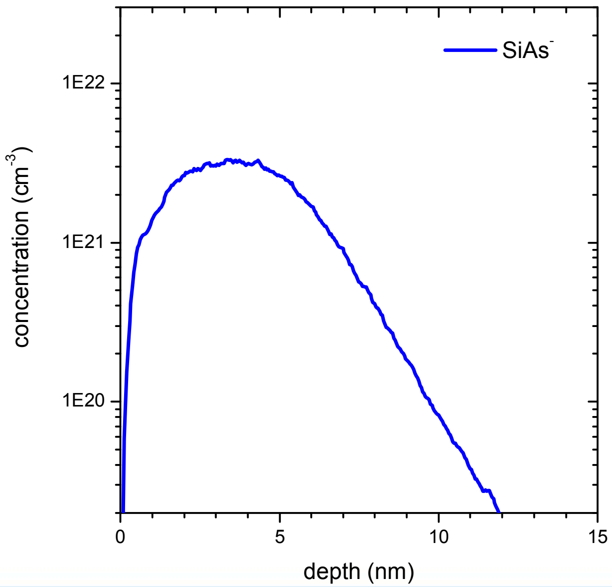
Quantification

Point-to-point normalization

As$^-$ to Si$^-$
AsSi$^-$ to Si$^-$



AsSi$^-$ to Si$_2^-$

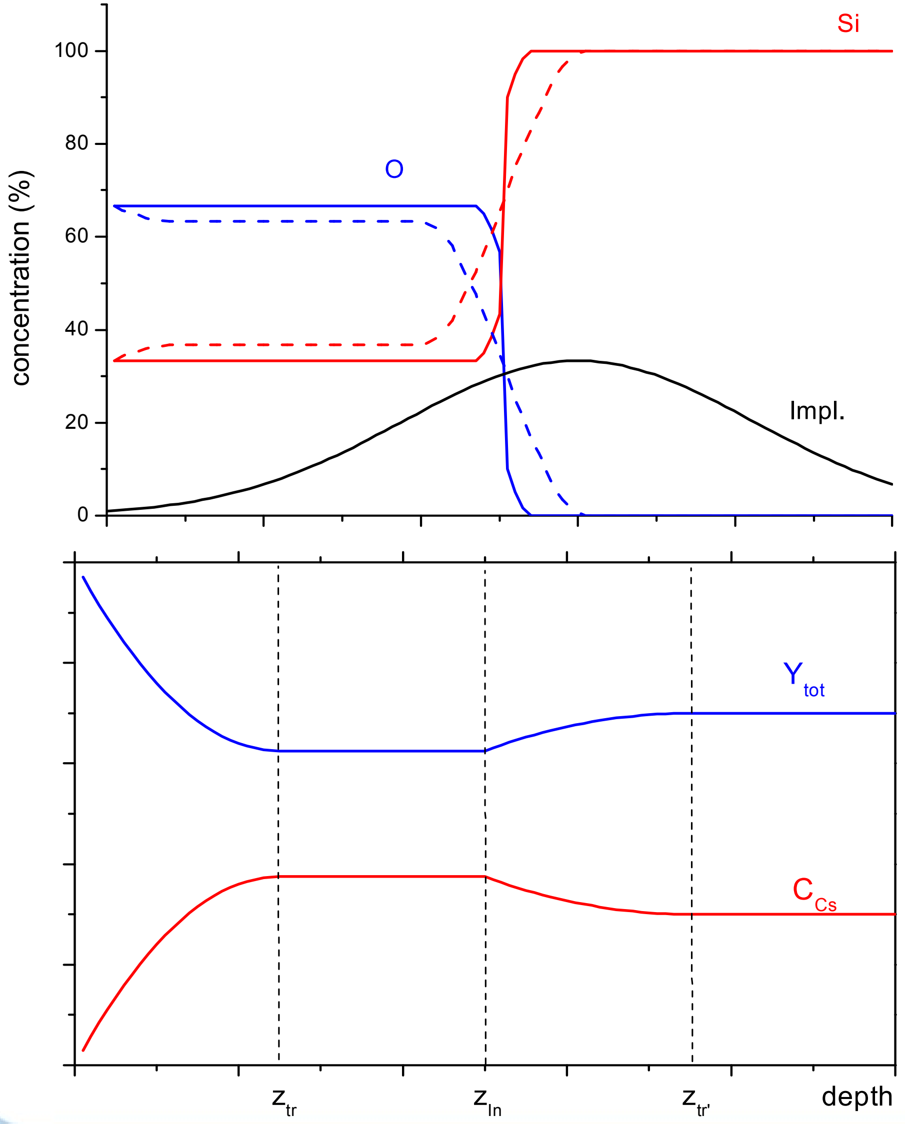


Variety of protocols has been tested by the SIMS community, but:

- depth scale on the first 3 - 5 nm is inaccurate (surface shift > 1 nm)
- concentration near the surface is inaccurate (poor agreement with simulations)
- implant dose for very shallow implants is inaccurate

Ultra-Shallow Implants

As Implant Profiling by TOF-SIMS



Schematic

Ultra-shallow implant with thin oxide

Problems in SIMS quantification

- matrix transition at SiO_2/Si interface (influence of O concentration)
- strong changes of ion yields by Cs (surface transient, interface)
- changes of sputter rate in transient and at interface (surface shift)
- change of concentration of Si (reference for p-to-p normalization)

Transient width $z_{tr} \approx 2$ x projected range

Ultra-Shallow Implants

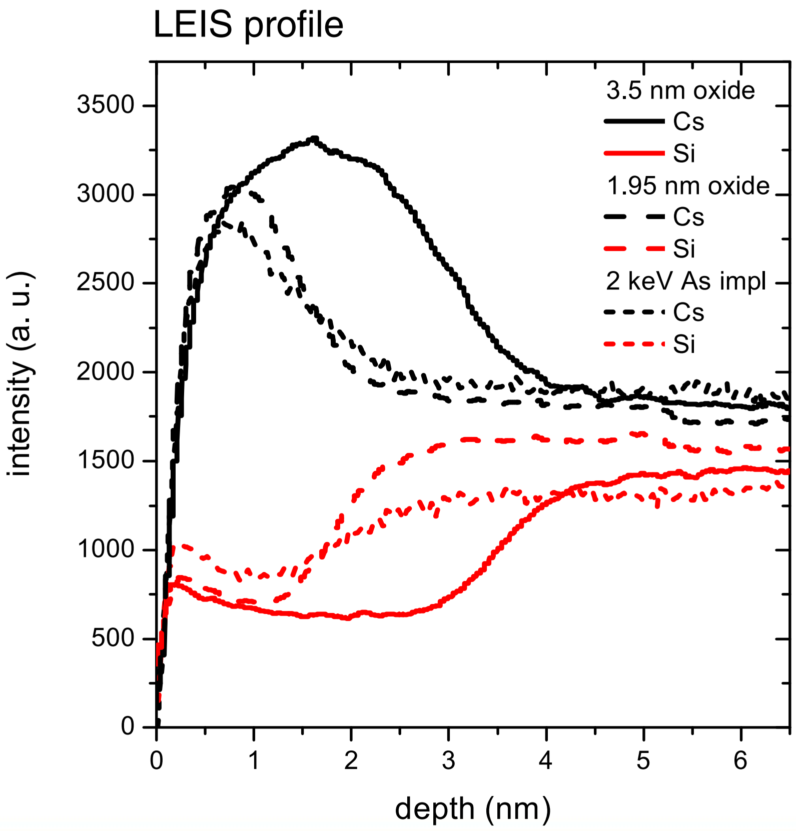
Fundamental Studies by LEIS - Cs sputter depth profiling

LEIS depth profiling in dual beam mode

- analysis: 3 keV He
- sputtering: 500 eV Cs, 60°

Cs sputtering of thin oxides

- strong variation of Cs concentration in the oxide layer (implantation of Cs)
- significant reduction of the Cs concentration at the interface
- interface width significantly different for As implant sample



Ultra-Shallow Implants

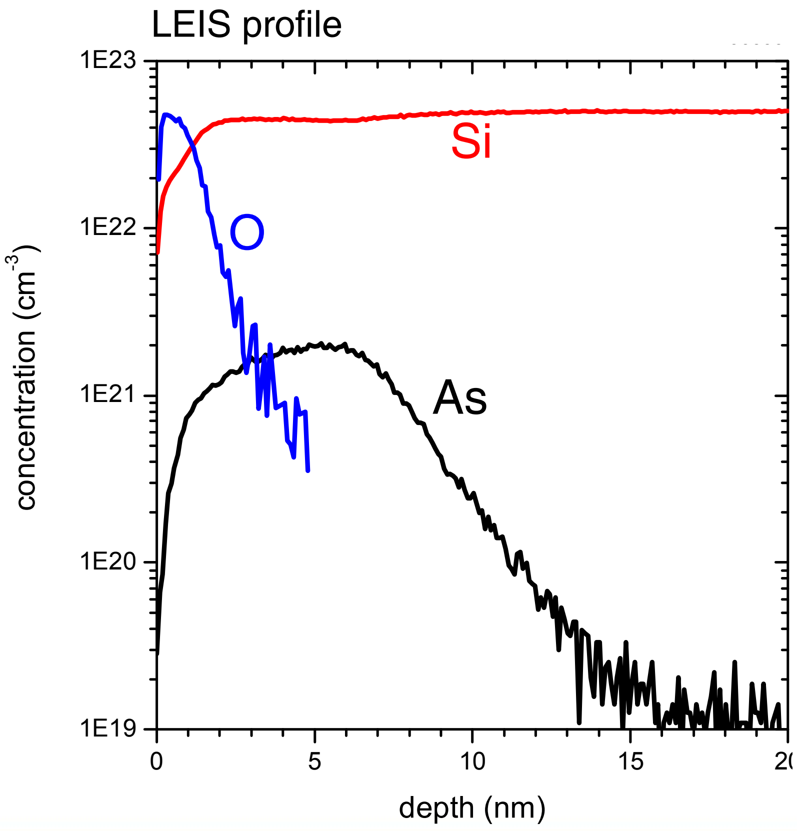
As Implant Profiling by LEIS - sputter depth profiling

LEIS depth profiling in dual beam mode

- analysis: 3 keV He
- sputtering: 1 keV Ar, 60°
- sample: **2 keV As implant, 1E15 /cm^2**

Results:

- oxide thickness approx. 1.9 nm
- As concentration at the surface is very low → confirmed by LEIS spectra
- simplified quantification: As + Si = 100 %



Ultra-Shallow Implants

As Implant Profiling by LEIS - sputter depth profiling

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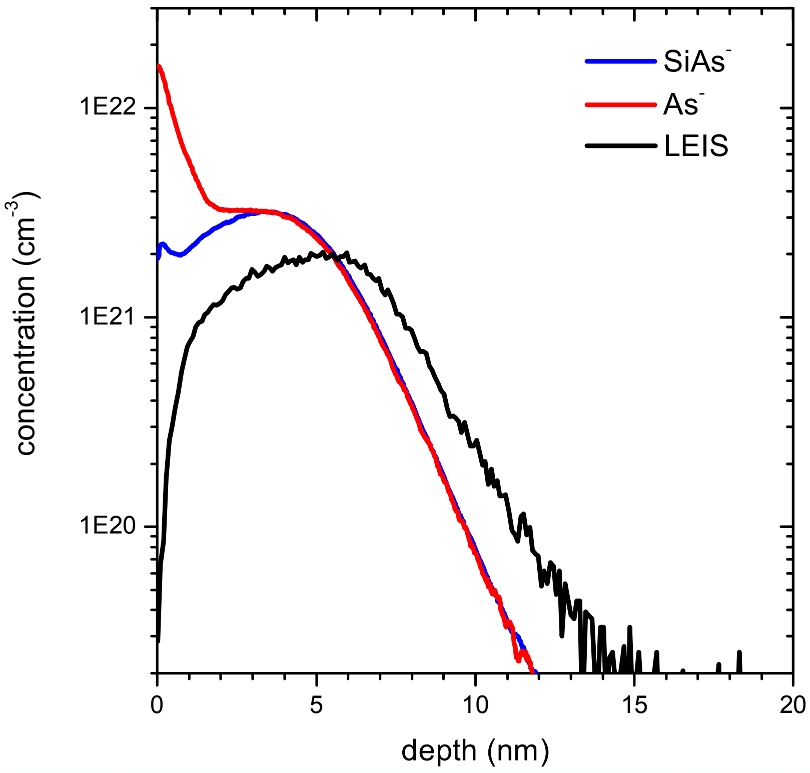
Results:

- oxide thickness approx. 1.9 nm
- As concentration at the surface is very low
  → confirmed by LEIS spectra
- simplified quantification:
  As + Si = 100 %
- implant maximum approx. 1.3 nm deeper
  compared to SIMS

Overlay of LEIS and SIMS profile



Conclusion

Complementarity of TOF-SIMS and LEIS

	LEIS	TOF-SIMS
Information Depth	1 monolayer	1 – 3 monolayers (even larger for organics)
Detection Limit	10 – 1,000 ppm	0.1 – 100 ppm
Mass Resolution	< 100	10,000
Type of Information	elemental	elemental, molecular
Quantification	simple (including major constituents)	difficult (matrix effects, trace constituents only)
Depth Profiling	static, noble gas sputtering	by sputtering with reactive ions

- TOF-SIMS and LEIS are **complementary** techniques
- **Combination** of the two techniques is very powerful for the analysis of ultra-thin layers (< 5 nm)

Thank you very much for your attention!