3. Surface Analysis

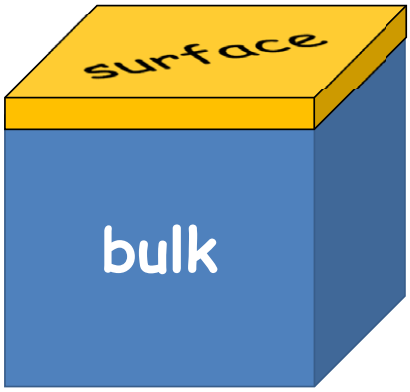
- *Introduction*

- *Methods: XPS, AES, RBS*
- *TOF-SIMS*

Why surface Analysis…?

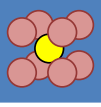
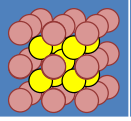
Bulk:
structural function
Electrical/thermal conduction
Volume increases properties

Surface:
Interface solid-gas: surface chemistry
(solid-oxide fuel cells, catalysers, corrosion)
Surface mechanics (solid-solid), tribology
Functionality: optics, biomaterials, bio-chemistry



1 monolayer = density: 10^{15} atoms /cm^2

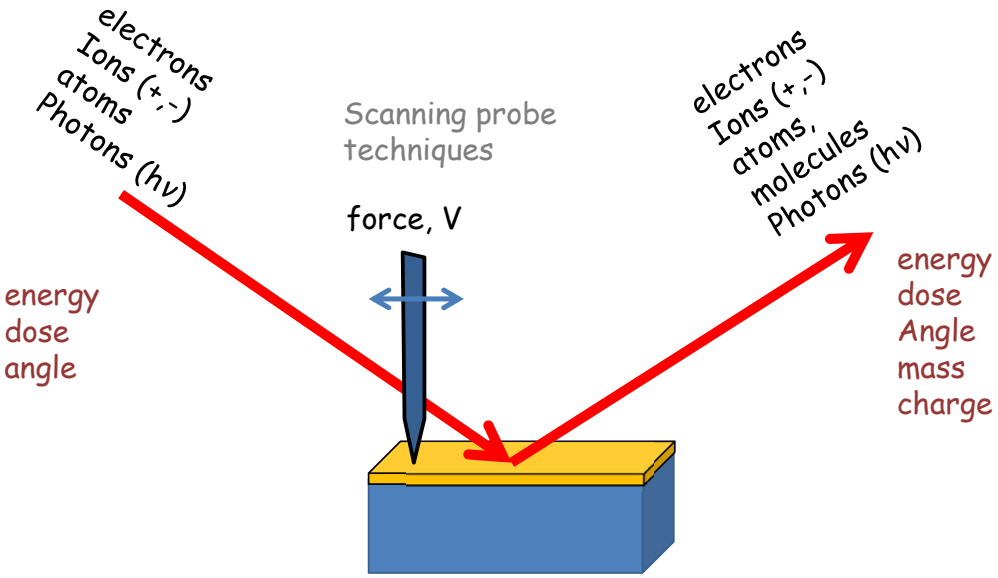
nanotechnology

size	0.5nm 	1nm 	1.5nm	1um
# volume atoms	1	5	27	2.7×10^{10}
# of surface atoms	8	26	56	5.4×10^{7}
surface fraction	8	5.2	2.07	0.002

The smaller the particle the more dominant becomes the surface

How analyse a surface...?

methods of surface analysis



methods matrix

Primary particle	Secondary particle			
	hv	electron	ion	atom
hv	ELL, ESR, FTIR, NMR, Raman, XRD, SNOM	XPS UPS, XPD	LAMMA MALDI	
e	EDX	AUGER, EELS, LEED, RHEED, SEM		
i +/-	PIXE, GDOES		GDMS SIMS ISS, RBS	
a				FAB He SC

acronyms

- ELL: Ellipsometry
- ESR: Electron Spin Resonance
- FTIR: Fourier Transform Infrared Spectroscopy
- NMR: Nuclear Magnetic Resonance
- Raman Spectroscopy
- XRD: X-ray Diffraction
- XPS: X-ray Photoelectron Spectroscopy
- UPS: Ultraviolet Spectroscopy
- XPD: X-ray Photoelectron Diffraction
- LAMMA: Laser Microprobe Mass Analysis
- MALDI Matrix Assisted Laser Desorption Ionization
- EL: Electron Microprobe
- AES: Auger Electron Spectroscopy
- EELS: Electron Energy Loss Spectroscopy
- LEED: Low Energy Electron Diffraction
- RHEED: Reflection High Energy Electron Diffraction
- SEM: Scanning Electron Microscopy
- PIXE: Proton Induced X-ray Emission
- GDOES: Glow discharge Optical Emission Spectroscopy
- GDMS: Glow Discharge Mass spectroscopy
- SIMS: Secondary Ion Mass Spectroscopy
- ISS Ion Scattering Spectroscopy
- RBS: Rutherford Back Scattering
- FAB: Fast Atom Bombardment
- He Sc: Helium Scattering

Surface analysis: under vacuum !

- Surface has to remain in the same state during the measurement
  - temperature
  - stability
  - contamination (formation of monolayer 10^{19} site/m^2)

- Exception:
  Photons (optical microscopy)
  Force measurements: AFM
  Liquid-solid interfaces

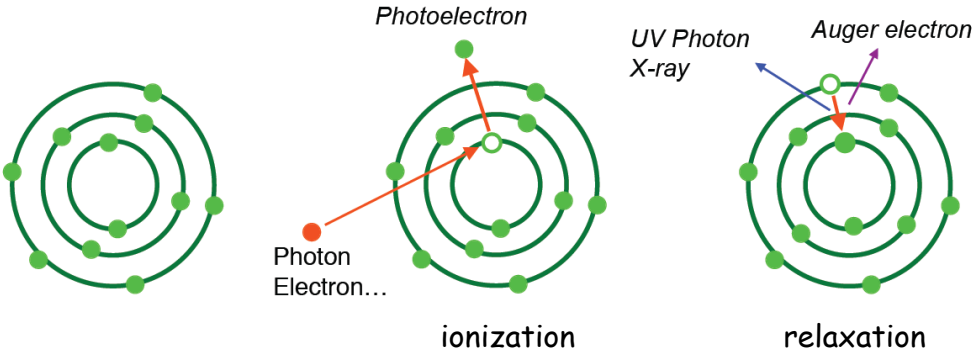
- Excitation/detection with particles
  10^{-4} mbar or better

- To avoid contaminants:
  10^{-10} mbar

Common problems and solutions
outgassing, leaks, hydrocarbons
Heating at 150°C, cold traps
UHV systems..!

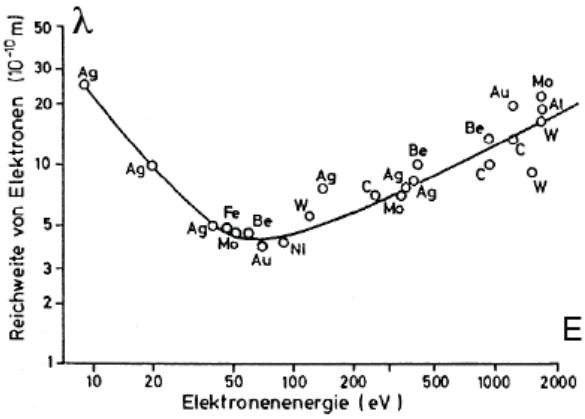
photon and electron probes
elemental and electronic analysis

- Electron transition between atomic energy levels
  - Core electrons: binding energy depends on the element
  - Excitation/ionisation by a probe particle (photon, electron, ion, ...)
    - Photoelectron
    - After relaxation: X-ray, Auger electron, ...
    - Energy of interaction product is characteristic of the element

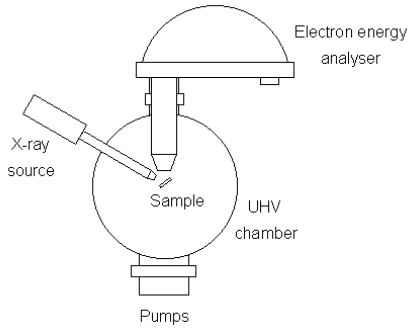


photon and electron probes
elemental and electronic analysis

Range of low energy electrons



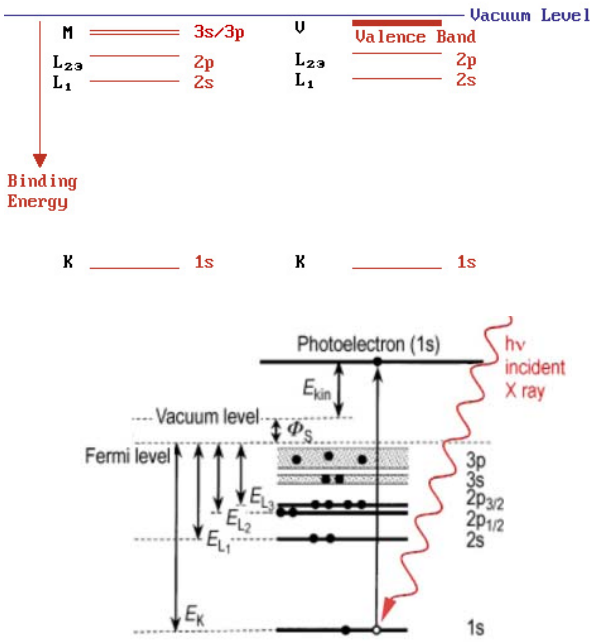
Electron energy analyser principle



X-ray Photoelectron Spectroscopy XPS

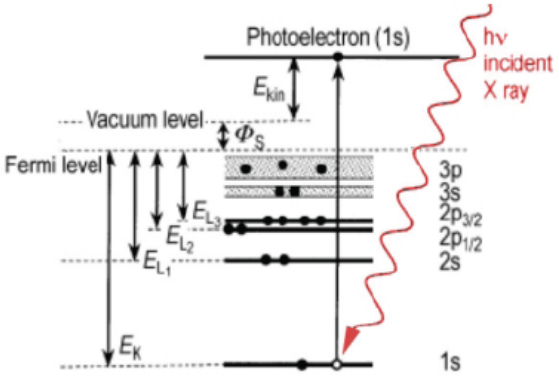
Principle

- Excitation of core or valence electrons
- Energy-dispersive analysis of emitted photoelectrons
- Core levels
  - Binding energy: 200 eV - a few keV
  - Excitation: X-rays (or UV)
  - Set of lines characteristic for each element
- Valence levels
  - Binding energy: a few eV
  - Excitation: UV light
  - Reflects the electronic properties of the surface



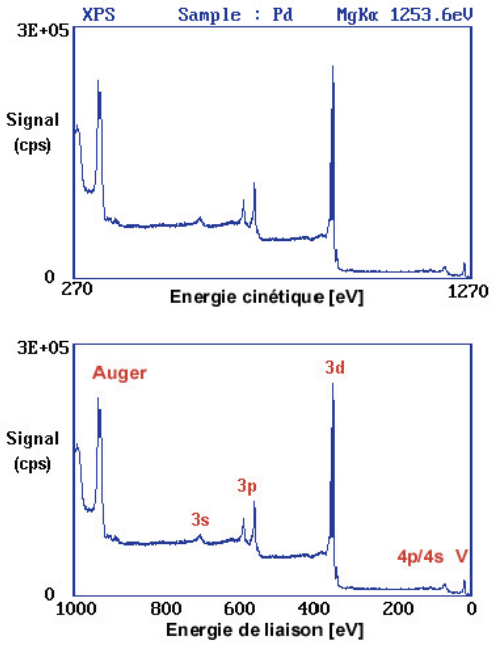
Photoelectron spectrum

- Analysis as a function of electron energy
  - Kinetic energy E_{kin} allows to determine the binding energy E_B
    - $E_{kin} = h\nu - E_B - \phi_s$
    - ϕ_s: work function
      - In practice, spectrum calibrated with a well-known energy peak (C, O, ...)



Photoelectron spectroscopy

- Kinetic energy E_{kin} depends on binding energy E_B
  - Atom + hν → Atom$^+$ + e$^-$
  - E(A) + hν = E(A$^+$) + E_{kin}(e$^-$)
  - E_{kin}(e$^-$) = hν - [E(A$^+$) - E(A)]
    - E_{kin}(e$^-$): kinetic energy of photoelectron
    - [E(A$^+$) - E(A)]: binding energy of electron
  - One-electron process ("photon in - electron out")



Photoelectron spectroscopy
chemical shift

- Shift of peak energy provoked by chemical environment and oxidation state
  - Typ. 0.5-10 eV
- Allows to determine
  - Oxidation state of metallic elements
  - Nature of chemical bond - e.g. for
    - C (C-H, C-O, C-F, ...)
    - O (O^{2-}, OH, ...)
    - Si (metallic, SiO_2, silicones)

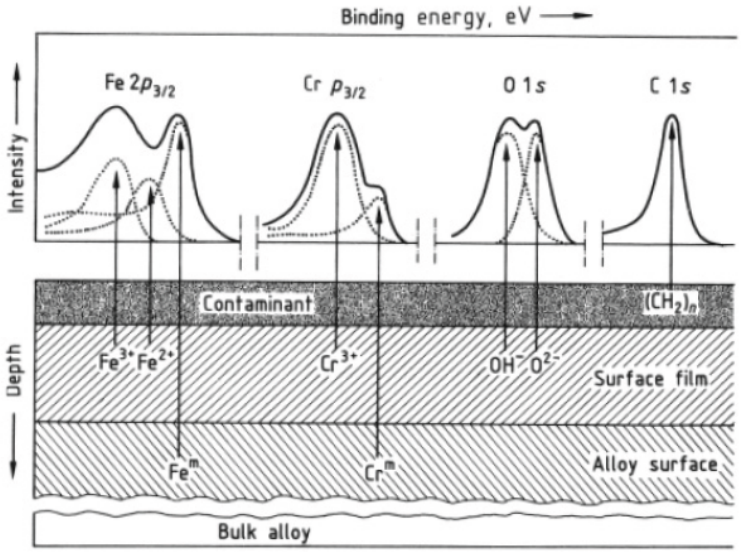
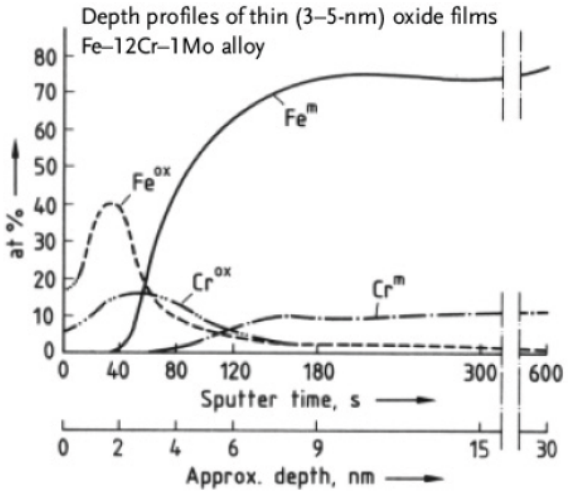


Fig. 2.13. Schematic diagram of the type of information obtainable from XPS spectra from an Fe–Cr alloy with oxide film underneath a contaminant film [2.57].

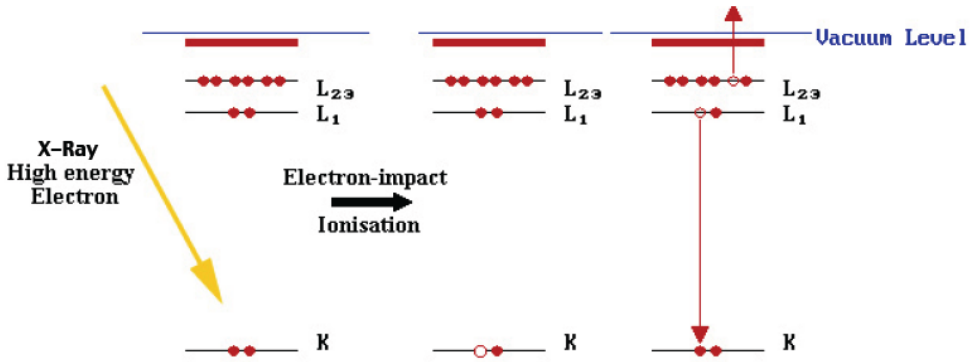
Photoelectron spectroscopy
depth profile

- XPS sensitive to surface (~5nm)
- Depth profile measurement by sputtering the sample
  - Cycles of ion beam etching (Ar+) followed by measurement
- Max. depth: ~1 µm
  - Degradation of sample due to ion bombardment
  - Atomic displacement
  - Surface roughness
  - Variable etching rates

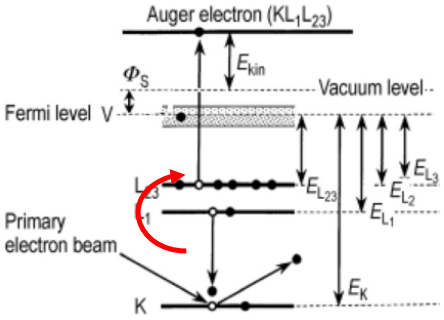


Waves: electrons
AES: Auger electron spectroscopy

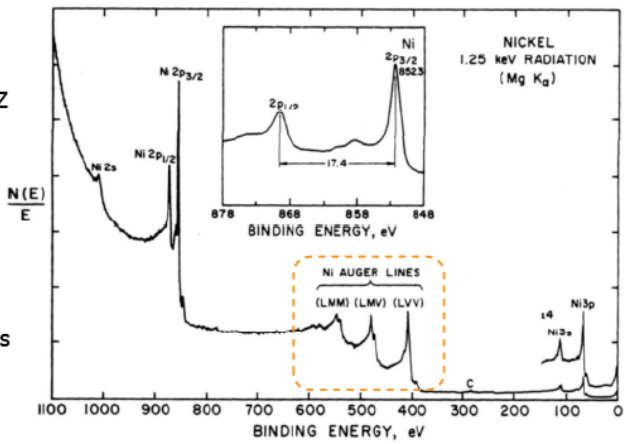
- Excitation of core electrons with electrons or X-rays
- Relaxation of an electron
  - X-ray emission
  - Auger emission: energy transfer to a second electron
- Kinetic energy determined by
  - Position of "initial" hole
  - Position of two "final" holes
  - Characteristic for each element
- Analysis of electron energy



Auger Emission

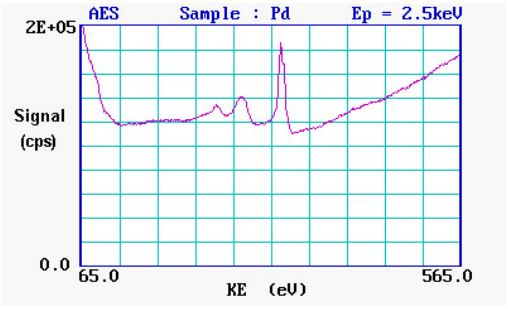


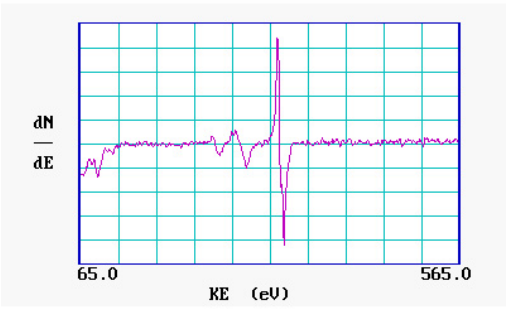
- Secondary process
  - Competition between X-ray fluorescence and Auger emission
    - Auger emission favoured of shallow core levels: light elements
  - Auger electron XYZ
    - Initial hole: X
    - Relaxation of electron Y
    - Energy transferred to another electron Z that is emitted by the solid: Auger emission
    - For example: (KL_1L_{23})
  - Energy $E_{kin}(XYZ)$
    - $E_{kin}(XYZ) = (E_X-E_Y)-E_Z-E_{inter}$
      - Independent of probe particle energy
      - E_{inter}: interaction energy between holes L_1 and L_{23}; relaxation energy, ... $E_{inter} << E_{kin}(XYZ)$ (typ. 1 eV)



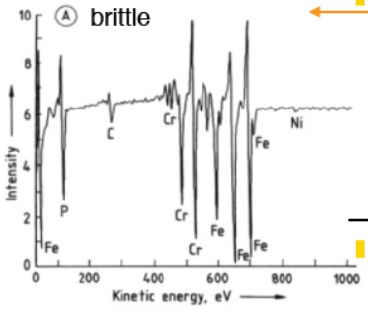
Auger spectrum

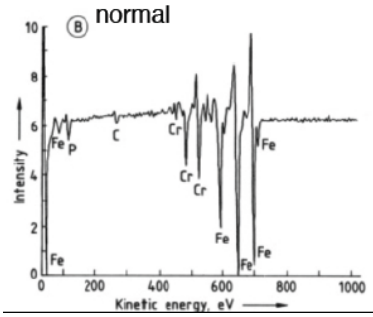
- Many transitions
  - Strong background signal (low energy secondary electrons)
    - Usually, 1st derivative of detected electron current for graphs/analysis
  - High surface sensitivity
    - Kinetic energy between 20...1000 eV (λ between 2...6 monolayers)
  - Mapping by rastering an electron beam
    - Resolution ≈ 50 nm
  - Depth concentration profiles by sputtering the surface
  - Faster acquisition than XPS
  - Quantitative analysis with composition standards
  - Chemical effects difficult to interpret



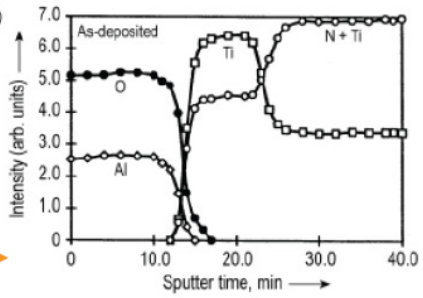


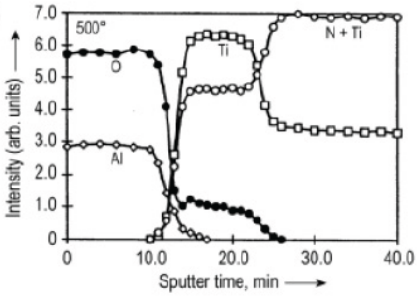
AES examples





- Chemical composition at the surface: FeCr steel in normal and brittle state
  - Higher P, Cr and Ni concentration in brittle steel
- Depth profile: thin layers of Al_2O_3-Ti-TiN on Si
  - After annealing: O diffuses in Ti layer, but not in TiN layer
    - Ti+N: superposition of N and Ti peaks
    - Layer thicknesses: 45nm of Ti, 55nm of Al_2O_3





XPS and AES

Infos	XPS	AES
Quantification	Yes	Yes light elements!
Chemical bond	Yes	Possible
Electronic structure	Yes	–
Mapping	Possible (50 nm?)	SEM (50 nm)
Depth profiles	Yes (Ar^+ sputtering)	Yes (Ar^+ sputtering)
Surface sensitivity	some nm	some nm
Detection limit	~‰	~%
Vacuum	UHV needed	UHV needed

Particles: Ions (alpha-particles)
Rutherford Backscattering Spectroscopy (RBS)

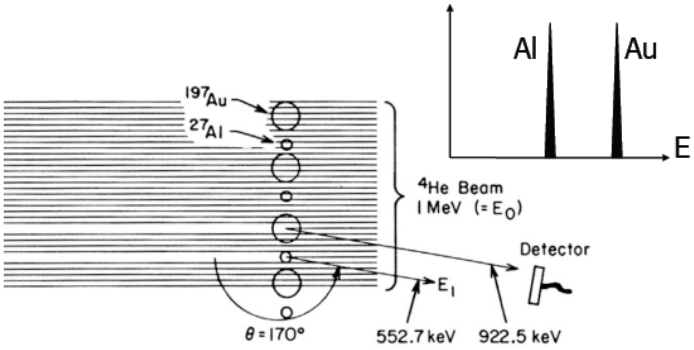
- Bombardment of surface with α particles
- Analysis of energy of backscattered particles
- Thin sample
  - "Elastic collisions" with atoms of mass m_2

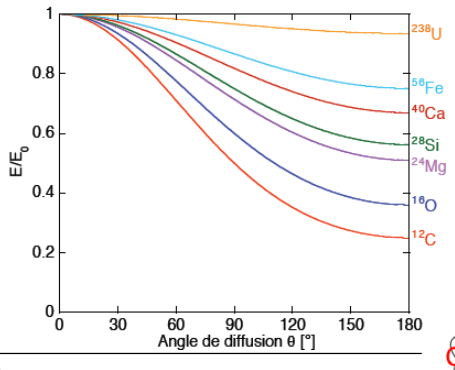
$$\frac{E_1}{E_0} = K = \left[\frac{(M_2^2 - M_1^2 \sin^2\theta)^{1/2} + M_1 \cos\theta}{M_2 + M_1}\right]^2$$

  - Backscattering geometry (θ=180°)

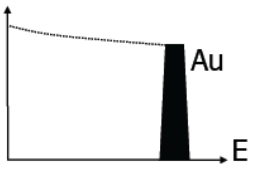
$$\frac{E_1}{E_0} = \left(\frac{M_2 - M_1}{M_2 + M_1}\right)^2$$

    - Maximum sensitivity to chemical composition
  - Peak at well-defined energy E_1

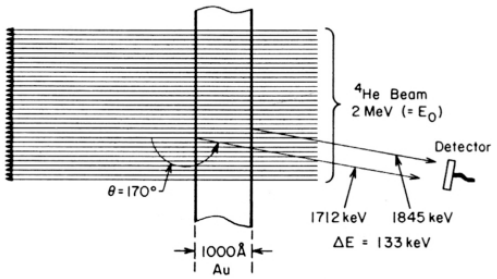




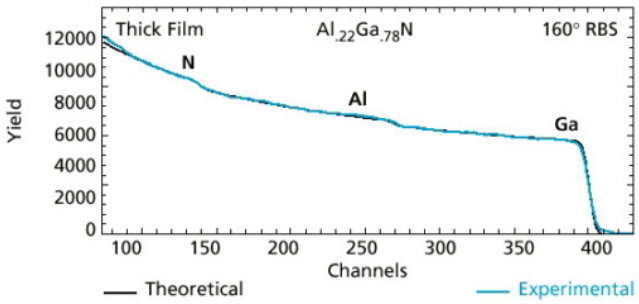
Particles: Ions
RBS



- Thick sample
  - Inelastic collision before elastic backscattering
  - Continuous spectrum with cut-off energy E_1
  - Several elements: superposition of spectra for each element

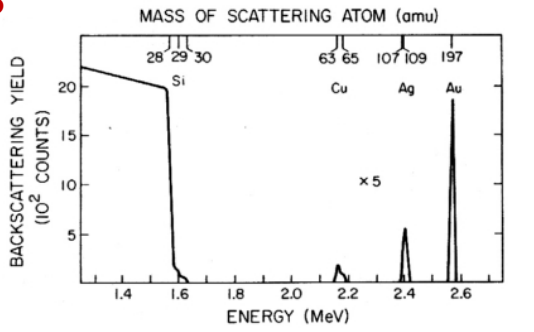


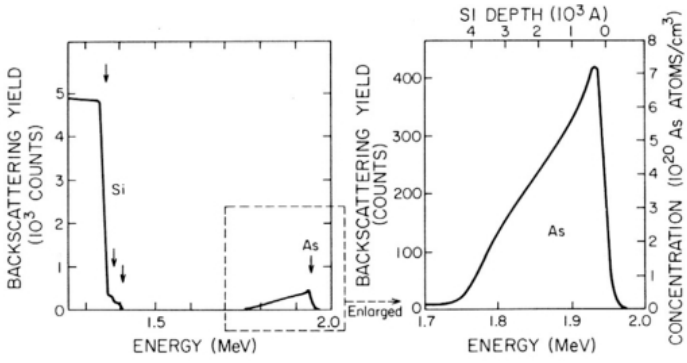
- Example
  - Thick film of AlGaN (e.g. blue-emission laser diodes)



Particles: Ions
RBS

- Example 1
  - Surface impurities on Si
  - Isotopes are resolved for light elements
  - Area of each peak proportional to concentration and scattering cross-section
- Example 2
  - Diffusion of As in Si
  - Depth resolution of 10 nm
  - Ideal cases…

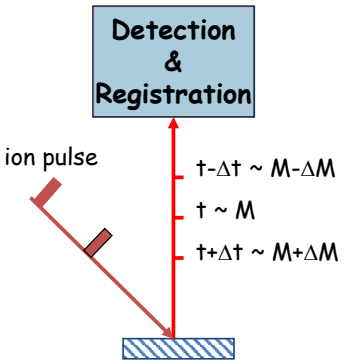




Particles: Ions
RBS

- Advantages
  - Fast, quantitative method, no need for standards
  - Depth profiling possible without ablation
  - Good resolution in mass for light elements
  - Good sensitivity to heavy elements
  - High sensitivity to crystallographic defects
- Drawbacks
  - Particle accelerator needed
  - Irradiation defects (10^{13} He atoms implanted per measurement)

Time-of-Flight
Secondary Ion Mass Spectrometry
ToF-SIMS

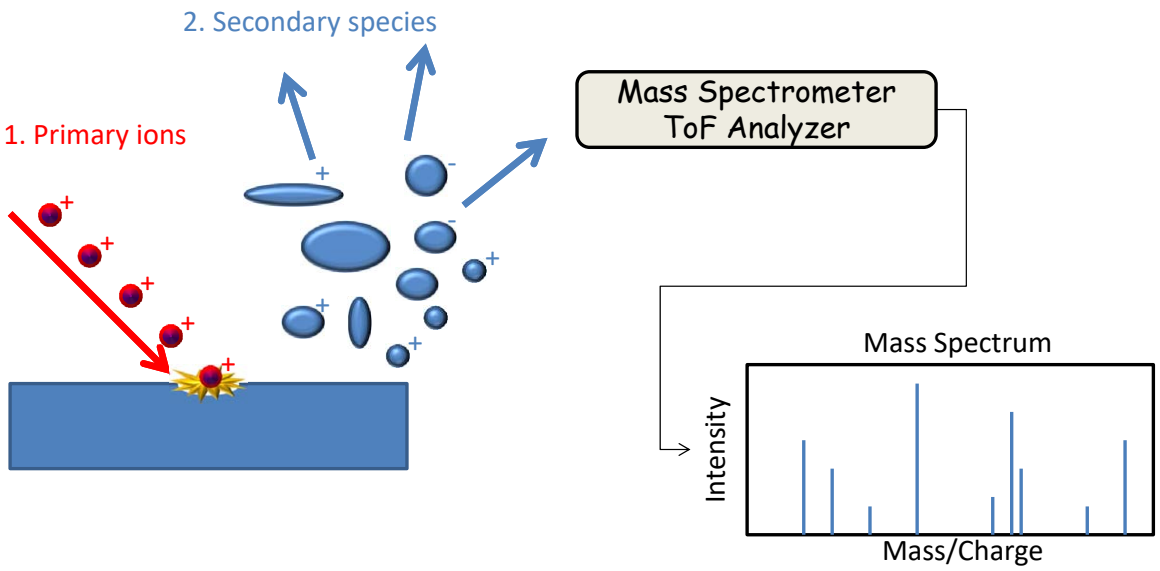


Analyse de Surface (V. Laporte)

Outline

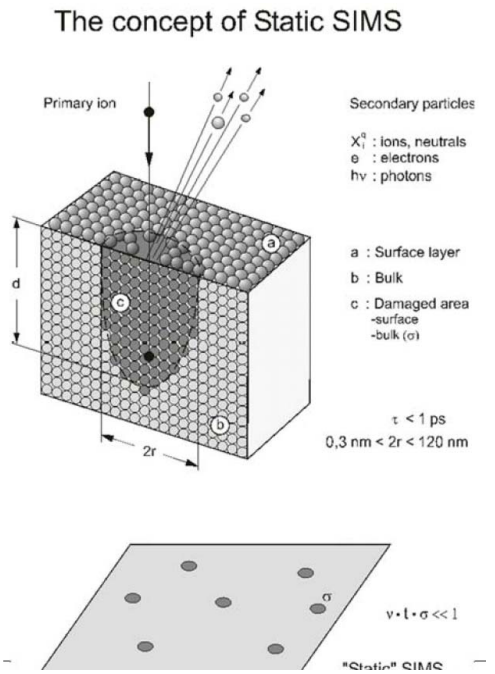
- ToF-SIMS basics
- ToF-SIMS for Surface Analysis
- ToF-SIMS for depth profiling

ToF-SIMS principle



Surface sensitive if the static limit is not exceeded

The « static » limit



In the static mode, less than 1% of the surface is struck by incoming primary ions i.e. the dose of primary ions is less than 10^{13} ions/cm^2.

Benninghoven, ToF-SIMS: Surface Analysis by Mass Spectrometry Surface Spectra - IMPublications 2001

A complex process!

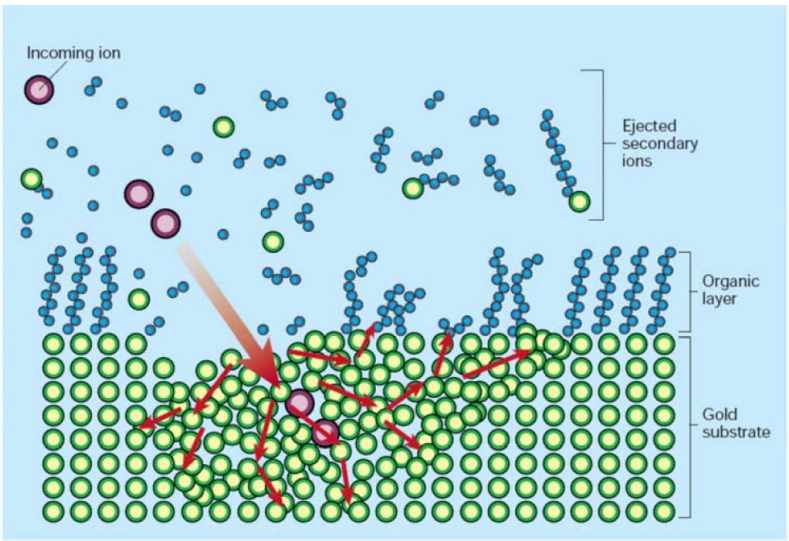
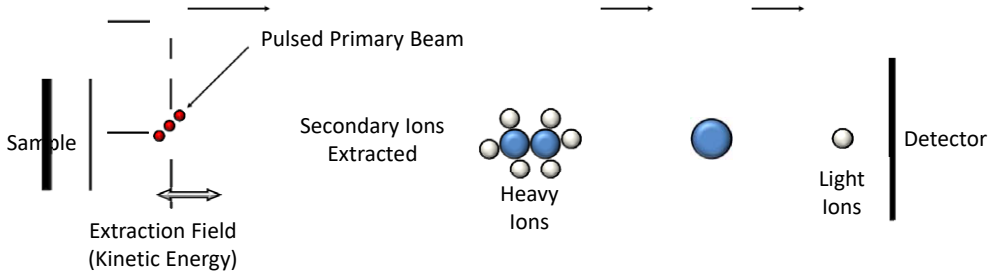


Figure 1 Surface analysis using secondary-ion mass spectrometry (SIMS). In this example, ions are fired into an organic self-assembled monolayer on a gold substrate. The energy deposited in the surface region from the incoming primary ions produces a collision cascade. This results in the ejection of a wide range of atomic and molecular fragments, of which about 1% are ions. Mass analysis of the ejected secondary ions is the key to exploring the structure of the surface.

Castner, Nature 2003

ToF Analyzer



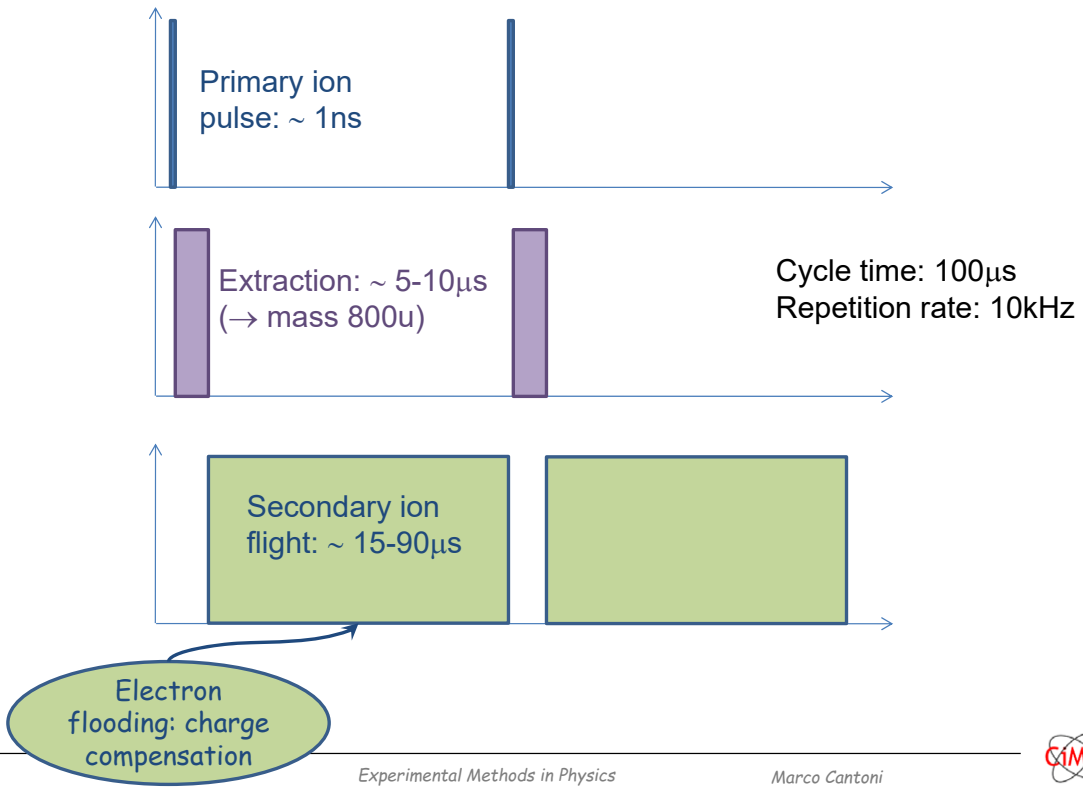
(1) Each **pulse** of primary ions creates a pulse of secondary ions.

(2) Secondaries of different masses within a single 'cycle' arrive at the detector at different times according to the relation:

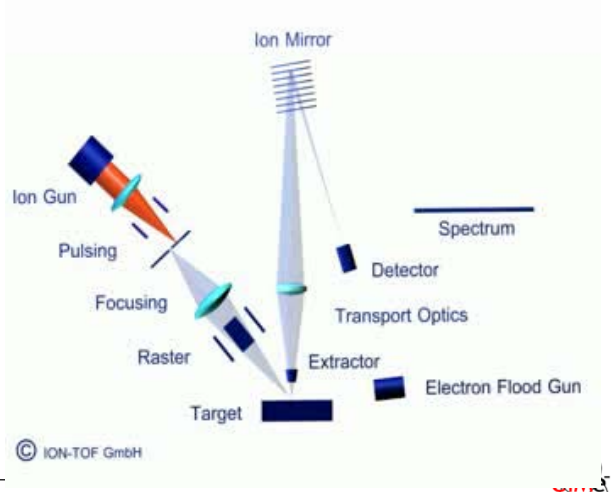
$$K.E. = mv^2/2 \rightarrow m \propto t^2$$

(3) Secondary ion with m/z = 1,000 has flight time ~100μs, therefore 'cycle time' = 100μs, so typical pulsing frequency = 10kHz.

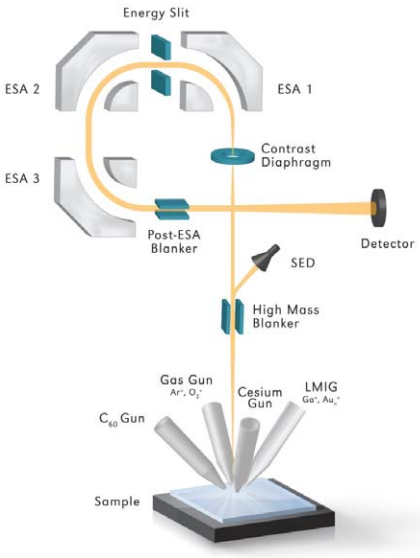
Cycle Time



ION-TOF Instrument



PHI instrument



PHYSICAL ELECTRONICS

Quantification

- The SIMS basic equation: $I_m = I_p Y_m \alpha^{\pm} \theta_m \eta$

Secondary ion current of species *m*

Primary particle flux (1-10pA)

Sputter yield

Ionisation probability

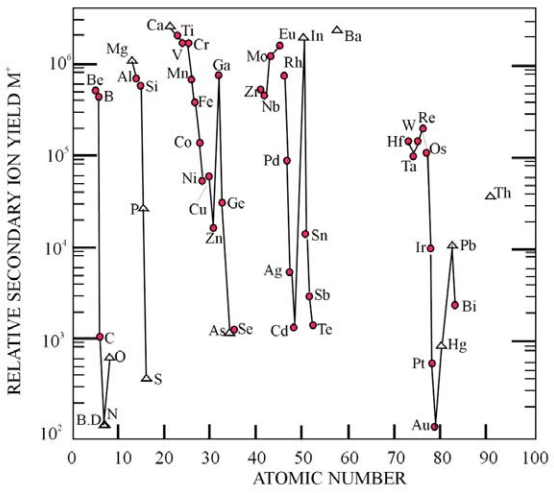
Fractional concentration of *m* in the surface layer

Transmission of the analysis system

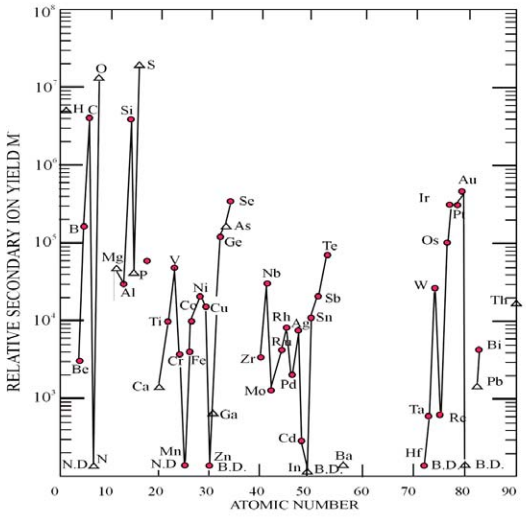
Secondary ion yield

Need for internal standards

Relative secondary ion yield



13.5keV oxygen ion gun
positive mode

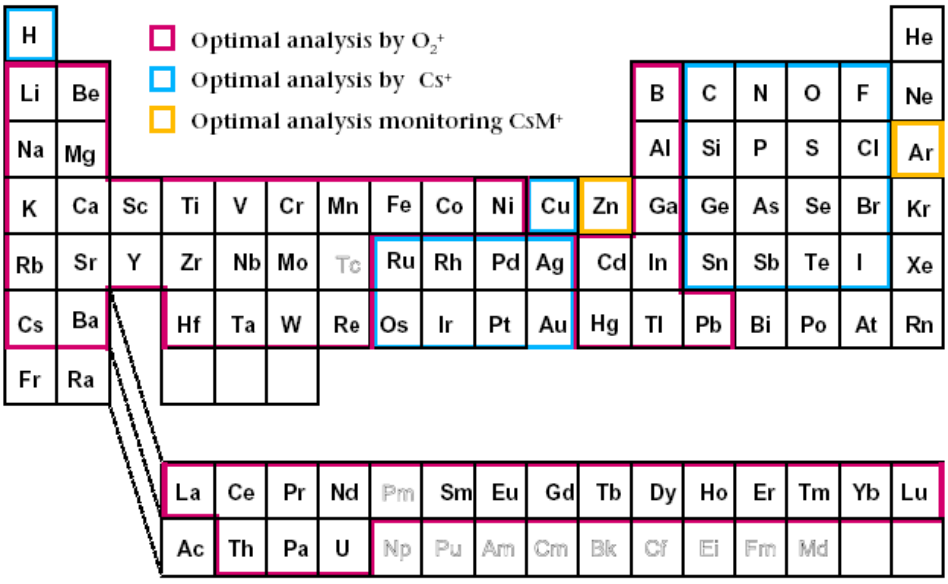


16.5keV caesium ion gun
negative mode

+MATRIX EFFECTS!

Storms, Anal. Chem. (1977)

General rules

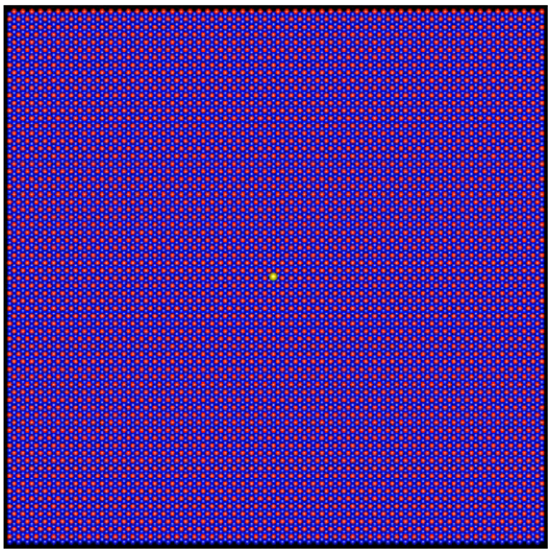


Recent Developments

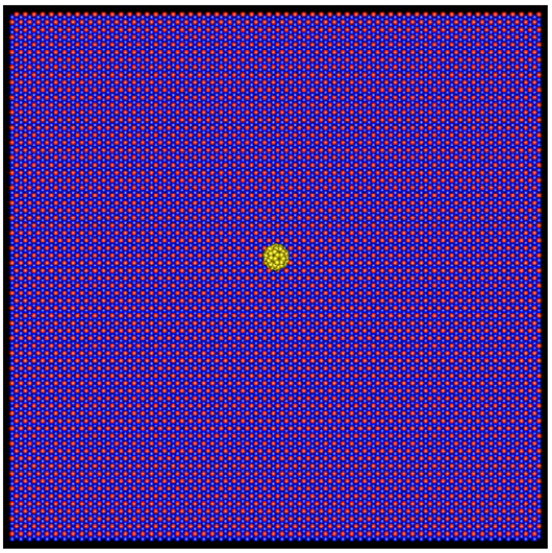
- Ion guns:
  - LMIG (Bi, Au)
    - Lateral resolution
    - Imaging
  - Cluster ion guns (C_{60}, Ar_{2500})
    - Ion yields
    - Damage in organics
- Data treatment
  - Chemometrics (PCA)

MD simulations

15keV Ga



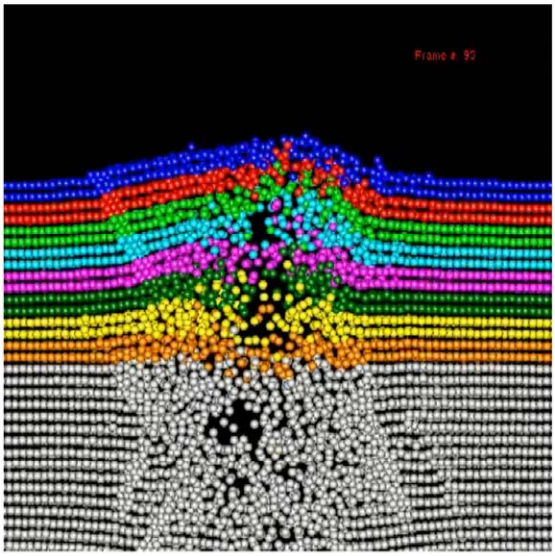
15keV C60



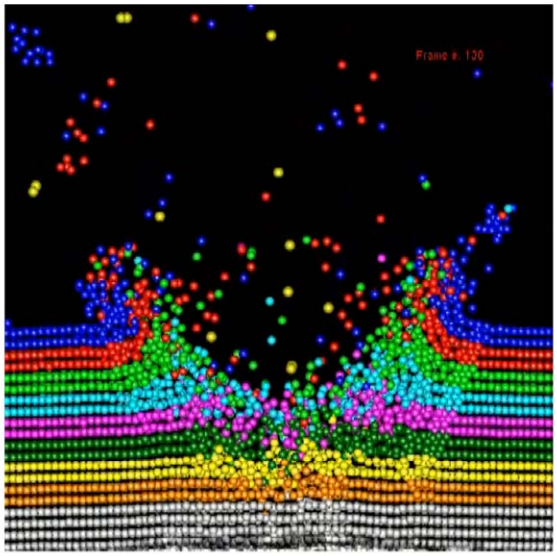
Courtesy of Pr. B. Garrison, Penn State University

MD simulations

15keV Ga



15keV C60



Courtesy of Pr. B. Garrison, Penn State University

ToF advantages

- Parallel mass detection
- High (unlimited) mass range
- High mass resolution > 10 000
- High mass accuracy (1-10 ppm)
- High transmission for high masses and at high mass resolution

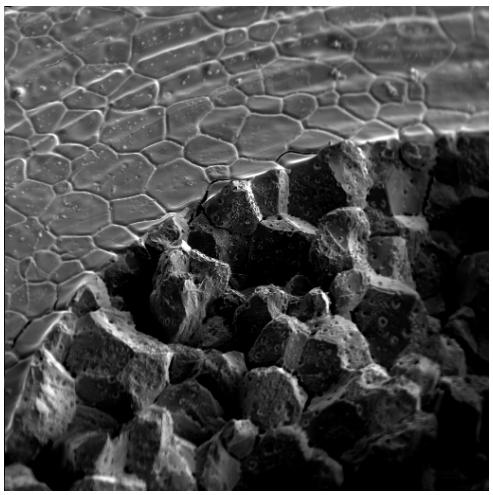
- All elements and isotopes
- Molecular species
- High sensitivity (ppm, 10^{16}at/cm^3)
- High lateral (100 nm) resolution

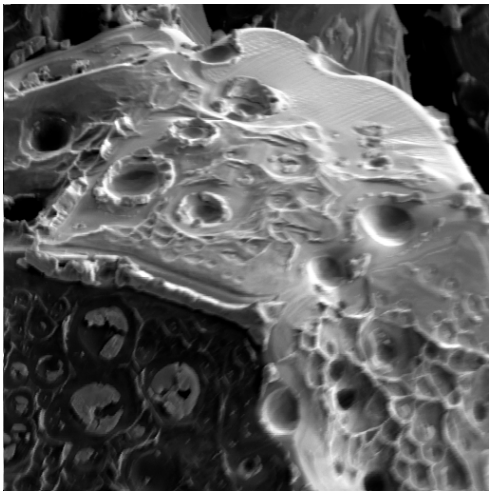
ToF-SIMS for Surface Analysis

- Historical surface science fields: corrosion, oxidation, adsorption, catalysis, biocompatibility, …
- New fields: optics, photonics, organics, surface functionalization…
- Examples:
  - Segregation in a metallic alloy
  - Cleaning of Surfaces (*Tascon* examples)
  - Tribology
  - Organic materials
    - Polymer thin film
    - Forensic science
    - Biology

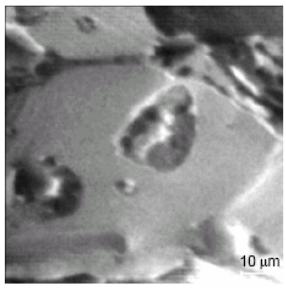
ToF-SIMS for surface analysis
Example #1: segregation in a Cu-PbBi alloy

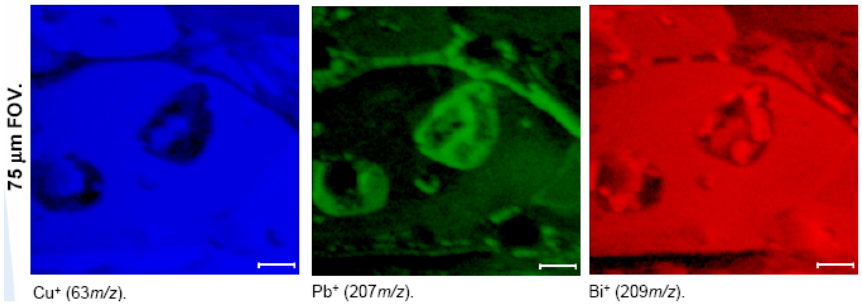
Cu-0.5Pb0.5Bi alloy, tensile fractured under UHV for Auger analyses
Polycrystalline fracture surface
Auger analyses → ~1ML of Bi



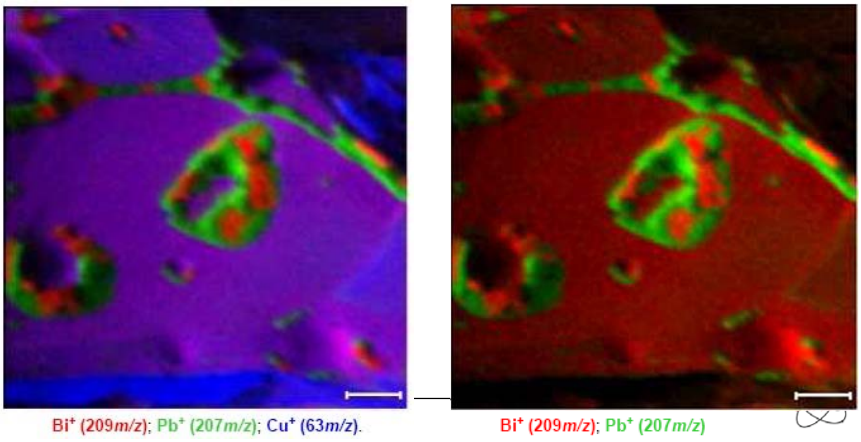


ToF-SIMS for surface analysis
Example #1: segregation in a Cu-PbBi alloy

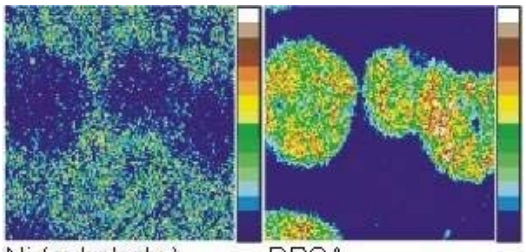




Analysis beam:
30keV Au^+
Positive mode



ToF-SIMS for surface analysis
Example #2: Cleaning of Surfaces

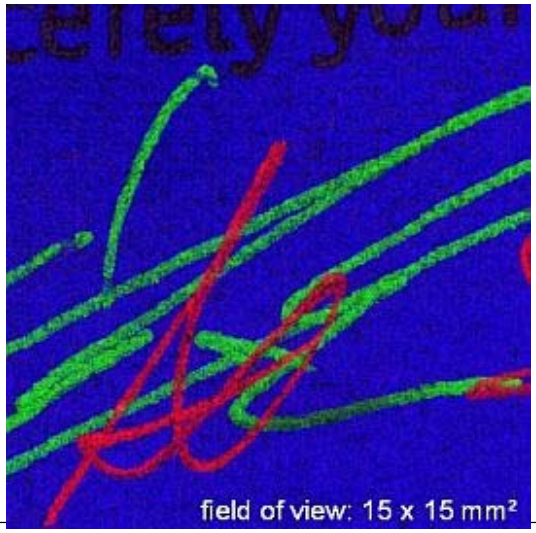


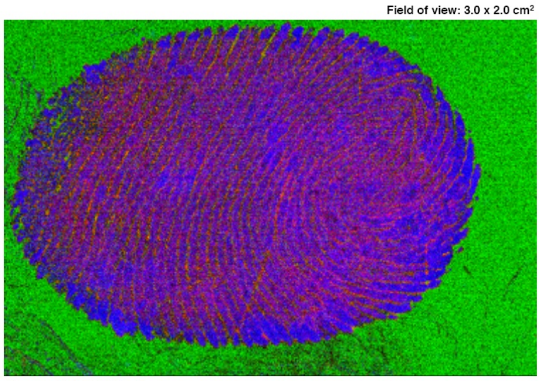
Ni (substrate) mc: 7 tc: 19463 DBSA mc: 40 tc: 136806

Despite a thorough degreasing step and a subsequent plasma cleaning treatment, adhesion problems occurred on a **nickel** surface.
ToF-SIMS analysis showed the presence of dodecylbenzenesulphonic acid (DBSA) on the surface of the cleaned metal.

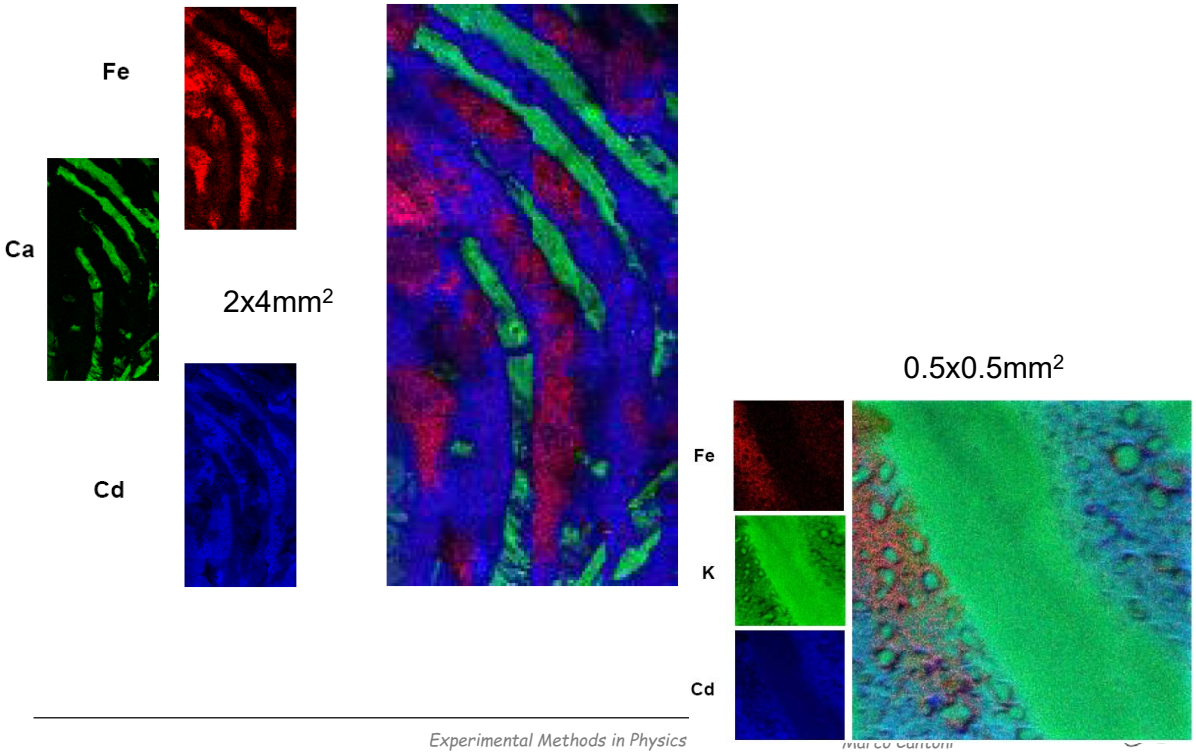
This chemical was identified as a component of the used **cleaning agent** and was not removed completely from the metal surface due to **insufficient rinsing**. A subsequent plasma cleaning step did not lead to a complete removal of the DBSA layer either, which led to adhesive failure in the next process step. Based on these analytical results, the final cleaning of the nickel plate could be improved and the failure rate due to adhesive failure could be reduced considerably.

ToF-SIMS for surface analysis of organics
Forensic Science



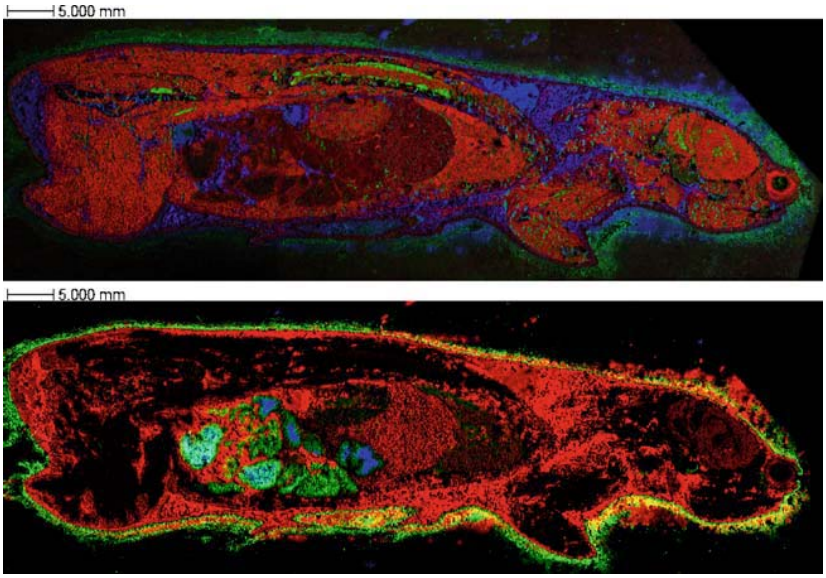


ToF-SIMS for surface analysis of organics
Forensic Science, Fingerprints



ToF-SIMS for surface analysis of organics
Biology: lipid imaging

Fig. 4 TOF–SIMS images (three-color overlays) of a whole mouse section. Field of view 28×84 mm^2, 768×256 pixels, pixel size 109 μm, Bi_3^+ primary ion fluence 6×10^8 ions cm^{-2}. **a** Positive secondary ions: *red* phosphatidylcholine fragment (*m/z* 224); *green* cholesterol (*m/z* 369 and 385); *blue* diacylglycerol (*m/z* 577). **b** Negative secondary ions: *red* sum of stearic (*m/z* 255) and oleic (*m/z* 281) fatty acid carboxylates; *green* cholesterol sulfate (*m/z* 465); *blue* taurocholic acid carboxylate (*m/z* 514)



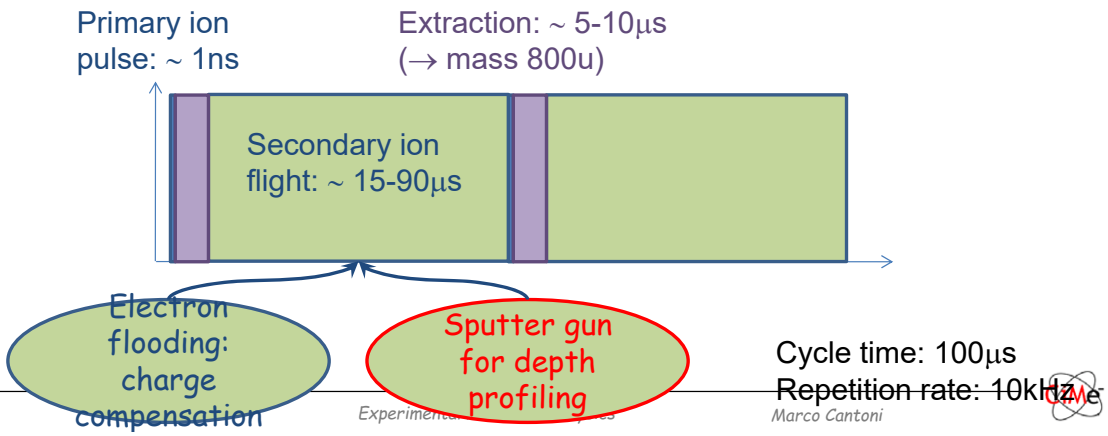
Brunelle, Anal. Bioanal. Chem. (2009)

ToF-SIMS for Surface Analysis Conclusions

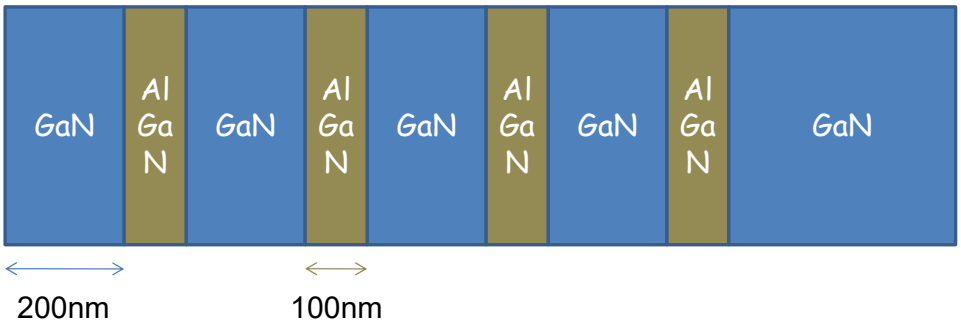
- Complementary with Auger and XPS analyses
  - Better lateral resolution than XPS for insulating samples
  - Better sensitivity than Auger and XPS
  - Larger imaging capabilities than Auger with mosaic reconstruction
  - Efficient for light elements
  - Less quantitative data
- Additional features for organic samples
  - Molecular information
  - More efficient neutralization

Dynamic mode

- Dynamic SIMS: sputter depth profiling with DC beam and a continuous collection of sputtered ions
- Dual-beam mode for ToF-SIMS depth profiling:



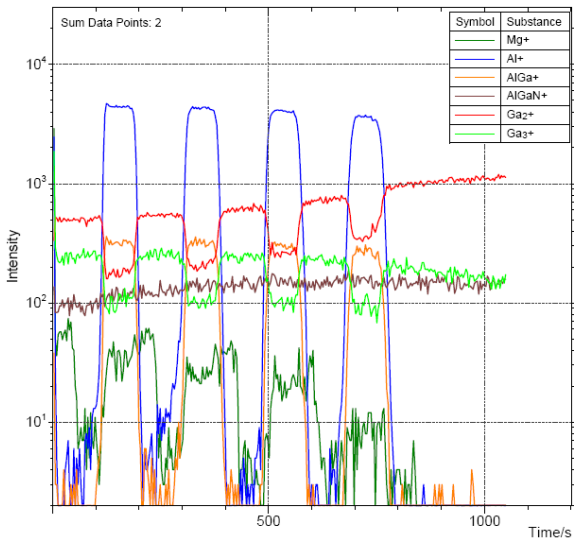
ToF-SIMS for Depth profiling
Example #1: GaN/AlGaN multilayer

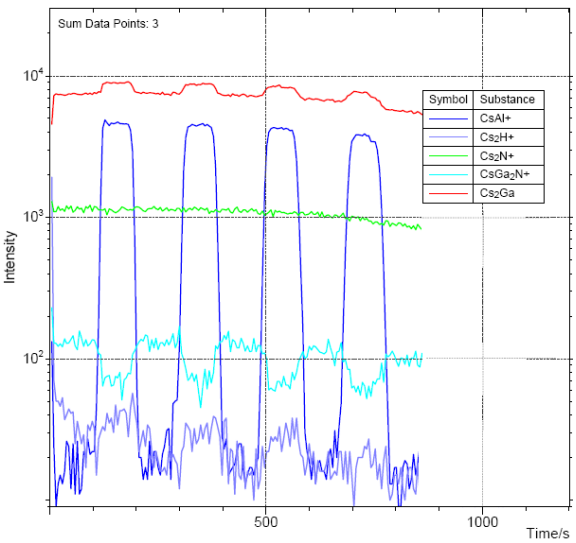


Mg doping in AlGaN layers

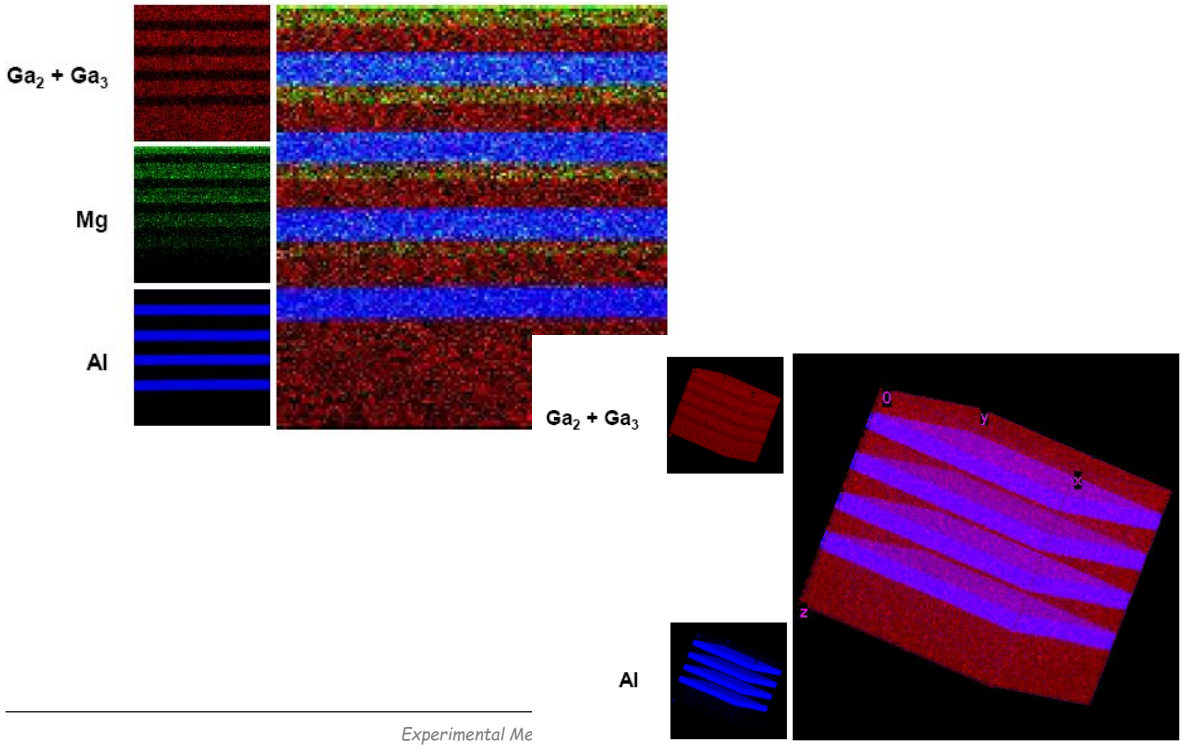
ToF-SIMS for Depth profiling
Example #1: GaN/AlGaN multilayer

300x300μm^2, 2keV **Cs^+**, 162nA
101x101μm^2, 25keV Bi_3^+, 0.8pA, positive mode

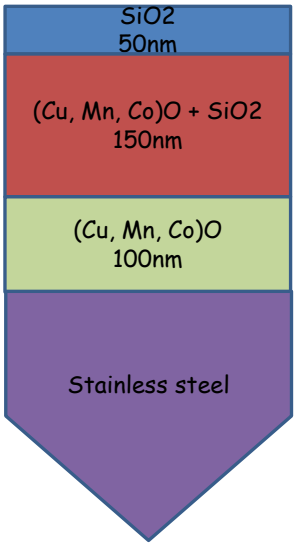


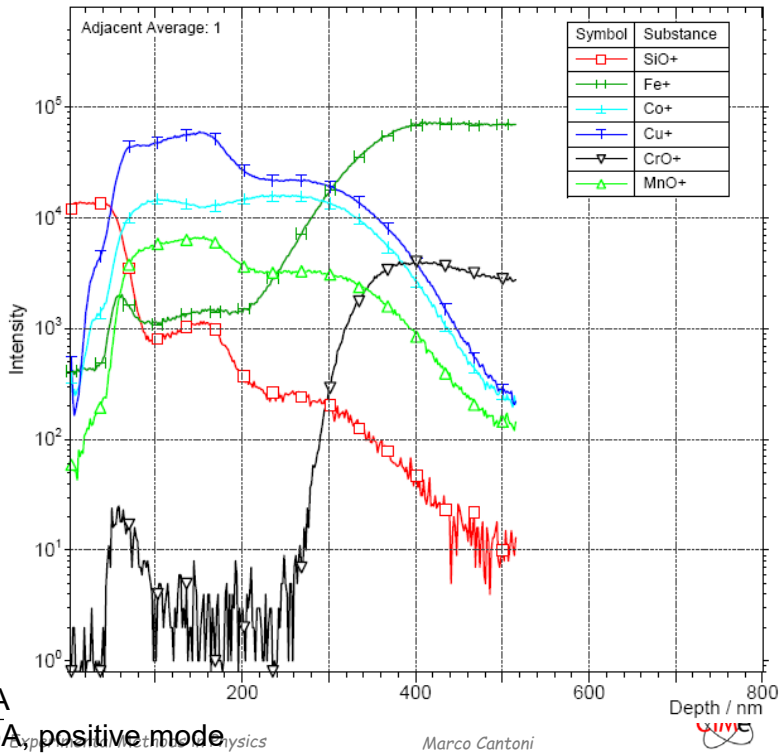


ToF-SIMS for Depth profiling
Example #1: GaN/AlGaN multilayer



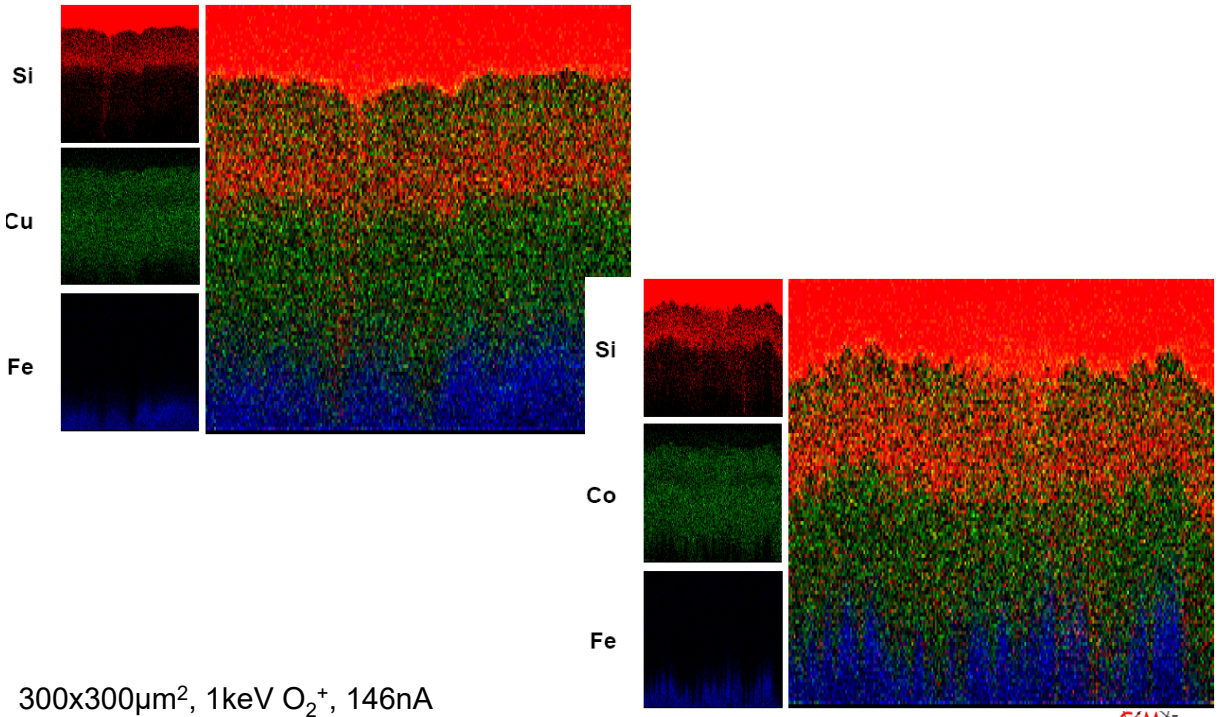
ToF-SIMS for Depth profiling
Example #2: multilayer on steel





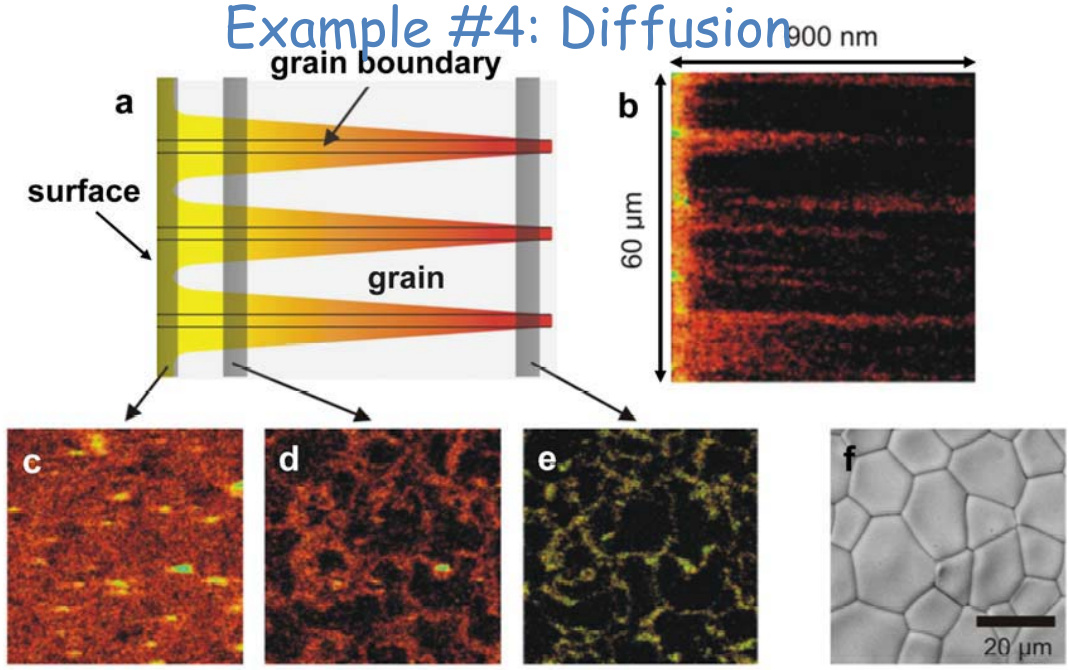
300x300µm², 1keV O_2^+, 146nA
102x102µm², 25keV Bi_1^+, 1.2pA, positive mode

ToF-SIMS for Depth profiling
Example #2: multilayer on steel



300x300μm^2, 1keV O_2^+, 146nA
75x75μm^2, 25keV Bi_1^+, 0.05pA, positive mode

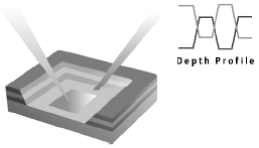
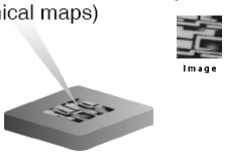
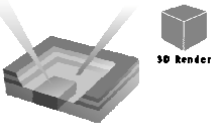
ToF-SIMS for depth profiling
Example #4: Diffusion



Fe diffusion into polycrystalline LSGM 1010 ($La_{0.1}Sr_{0.1}Ga_{0.1}Mg_{0.1}O_{2.9}$)

De Souza, Phys. Stat. Sol. (c), 2007

Conclusions

	no sample erosion (static SIMS)	sample erosion (dynamic SIMS)
no localization	**surface spectrometry** application of low primary ion dose densities ⇒ quasi non-destructive surface analysis 	**depth profiling** application of high primary ion dose densities ⇒ successive removal of top surface layers depth distribution of elements 
localization	**surface imaging** scanning of a focused ion beam over the surface ⇒ mass resolved secondary ion images (chemical maps) 	**3D micro analysis** combination of depth profiling and imaging acquisition of raw data with subsequent retrospective evaluation ⇒ 3D distribution of elements in a volume 

Complementary with XPS and Auger

Summary