Nanostrukturen-Analysemethoden

Secondary Ion Mass Spectrometry (SIMS)

Principles, Instrumentation, Applications

- **Principles**
- **Instrumentation**
- **Applications**
  - Depth profiling
  - 2D imaging
  - 3D imaging

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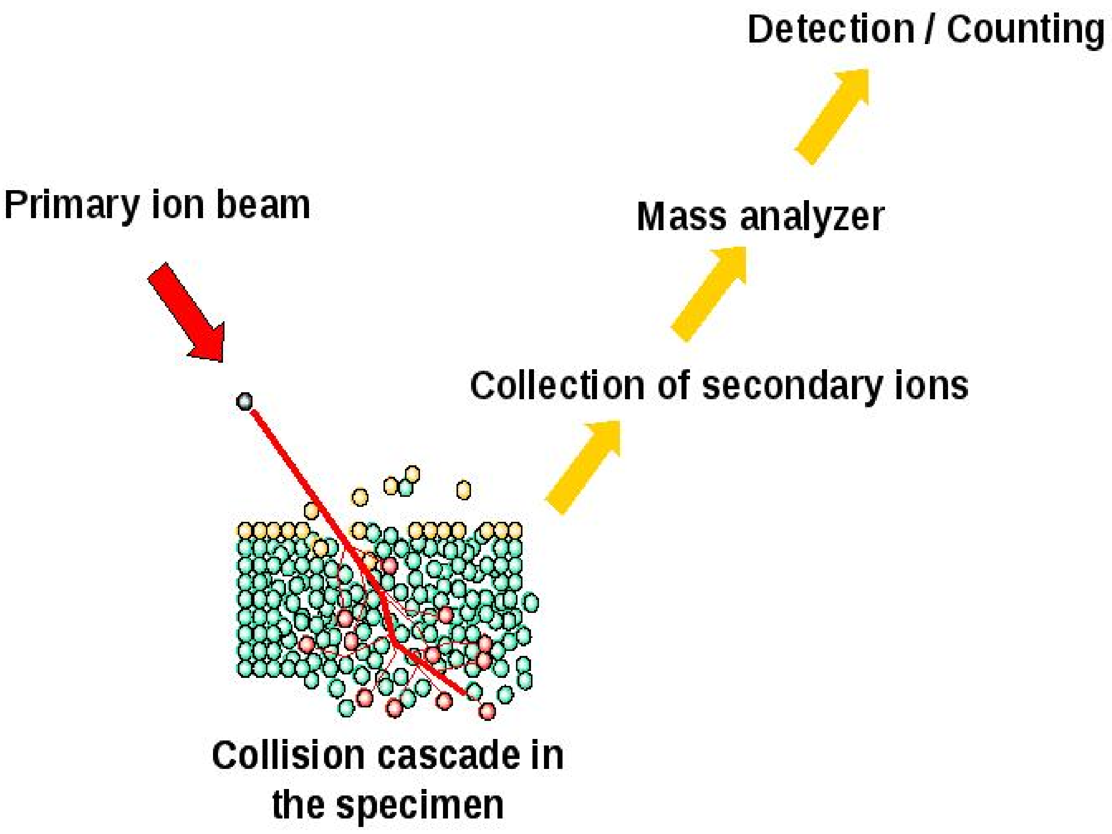
based on slides from ***T. Wirtz, CRP-Gabriel Lippmann, Luxembourg***

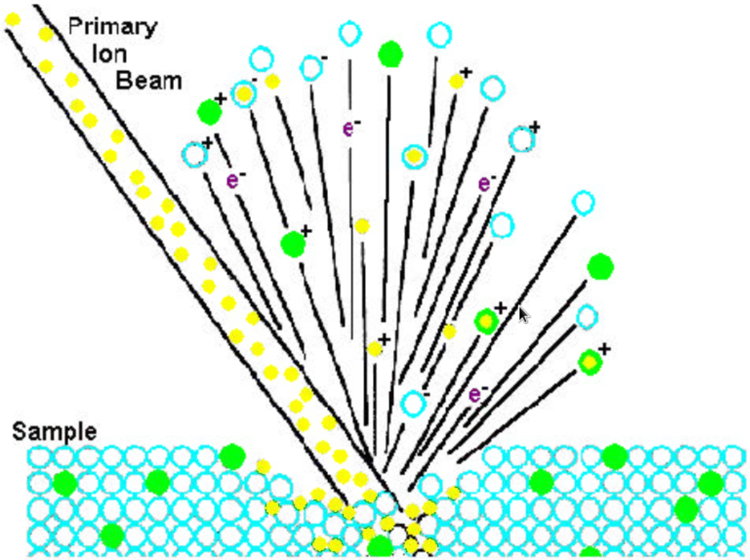
Principles



SIMS is a surface analysis technique used to characterize the **surface and sub-surface region** of materials. It effectively employs the **mass spectrometry of ionised particles** which are emitted when a surface, normally a solid, is bombarded by energetic primary particles. The **primary particles may be electrons, ions, neutrals or photons**.

Principles

Ion Beam Sputtering



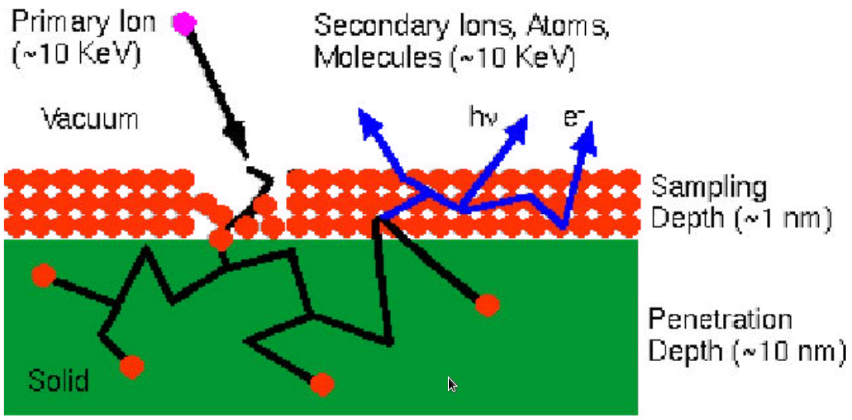
The bombarding primary ion beam produces **monatomic and polyatomic particles of sample material** and **resputtered primary ions**, along with **electrons and photons**. The secondary particles carry negative, positive, and neutral charges and they have **kinetic energies that range from zero to several hundred eV**.

Primary beam species useful in SIMS include Cs^+, O_2^+, O , Ar^+, and Ga^+ at energies between 1 and 30keV. Primary ions are implanted and mix with sample atoms to depths of 1 to 10nm. Sputter rates in typical SIMS experiments vary between 0.5 and 5nm/s. Sputter rates depend on primary beam intensity, sample material, and crystal orientation.

The sputter yield is the ratio of the number of atoms sputtered to the number of impinging primary ions. Typical SIMS sputter yields fall in a range from 5 and 15.

Principles

Sputtering Effects



Sputtering leads to **surface roughness in the sputter craters**. **Lattice imperfections**, either already present or introduced by surface mixing, can be germs for roughness that takes the form of ribbons, furrows, ridges, cones, and agglomerations of cones. Polycrystalline materials form rough crater bottoms because of differential **sputter rates that depend on crystal orientation**.

The **collision cascade model** has the best success at quantitatively explaining how the primary beam interacts with the sample atoms. In this model, a fast primary ion passes energy to target atoms in a series of binary collisions. Energetic target atoms (called **recoil atoms**) collide with more target atoms. Target atoms that recoil back through the sample surface constitute sputtered material. Atoms from the sample's outer monolayer can be driven in about 10 nm, thus **producing surface mixing**.

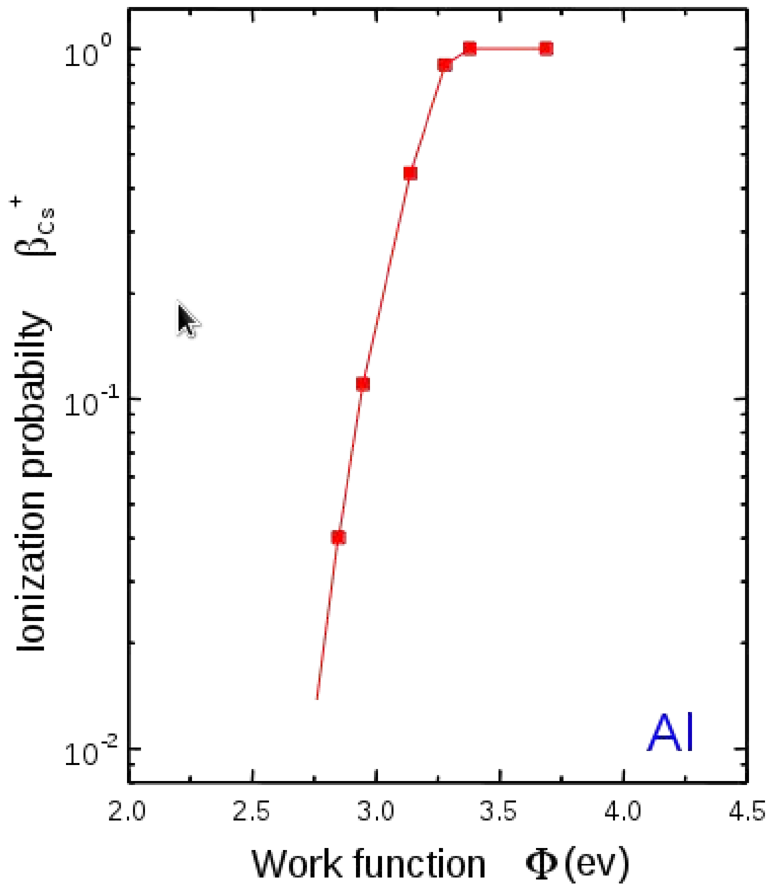
Principle

Secondary ion intensity: $$I(M^{+/-}) \approx I_p \times Y_M \times c_M \times \beta_M^{+/-} \times T$$

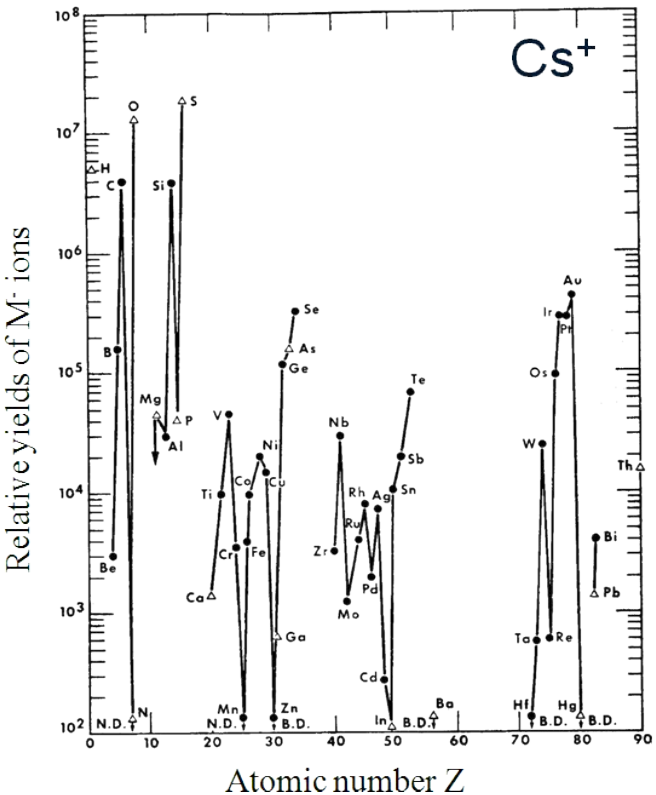
I_p: primary ion current
Y_M: partial sputtering yield of the element M
c_M: concentration of the element M
$\beta_M^{+/-}$: positive/negative ionisation probability of the emitted atom M
T: Instrumental transmission function

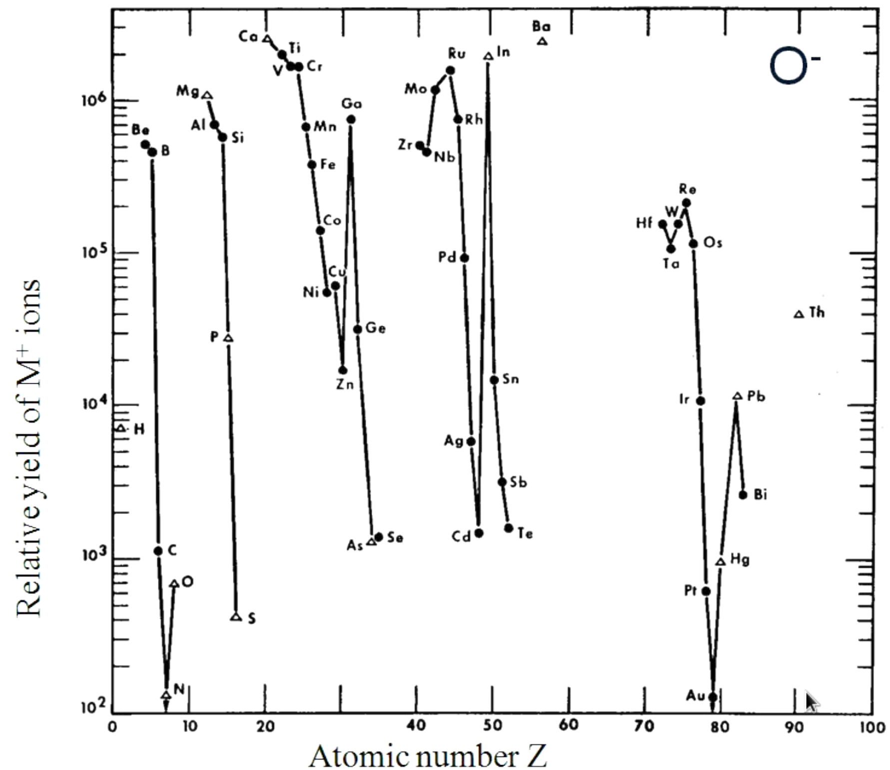
Different models for ion formation:
- electron tunneling model
- bond breaking model
- …

► difficult to predict $\beta_M^{+/-}$
(variation over several orders of magnitude)



Principles



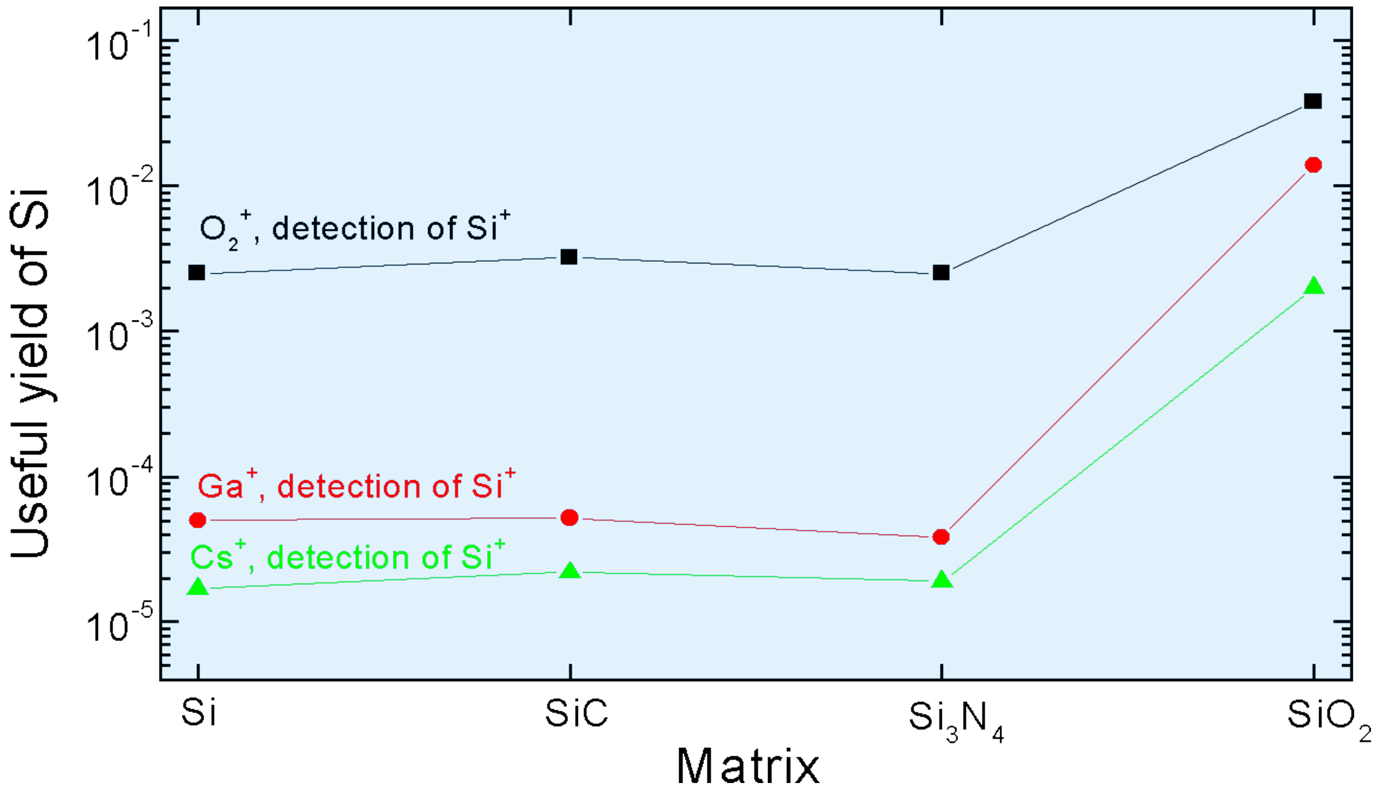


The emission of secondary ions is very sensitive to the chemical state of the sample surface:

- electro-positive primary ions (e.g. Cs^{+}) > increase of negative secondary ion emission
- electro-negative primary ions (e.g. O_2^{+} or O^{-}) > increase of positive secondary ion emission

Principles

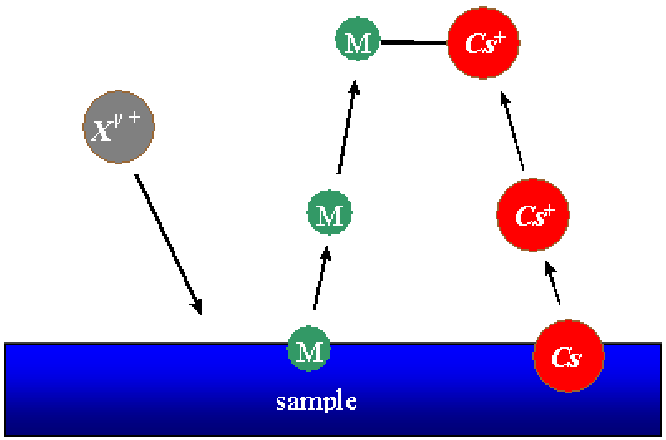
Matrix-effect



The ionization probability depends on the sample composition
Problems when interpreting and quantifying the results

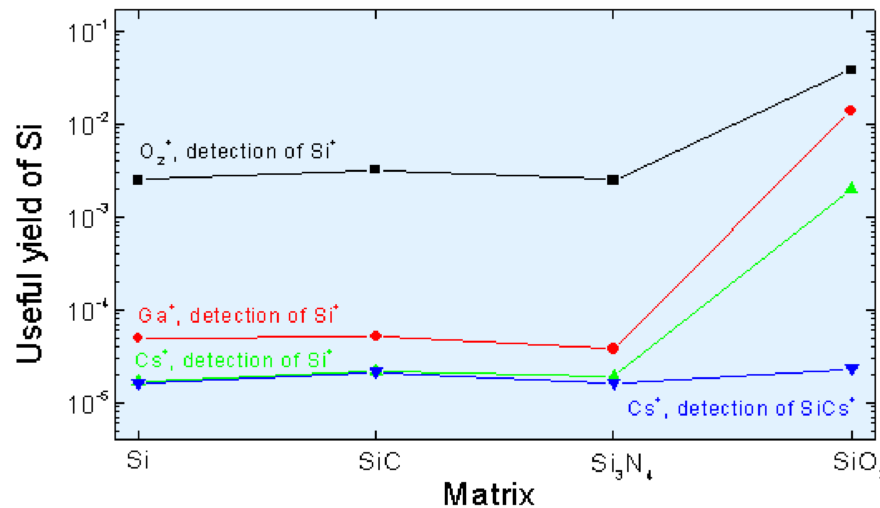
Principles

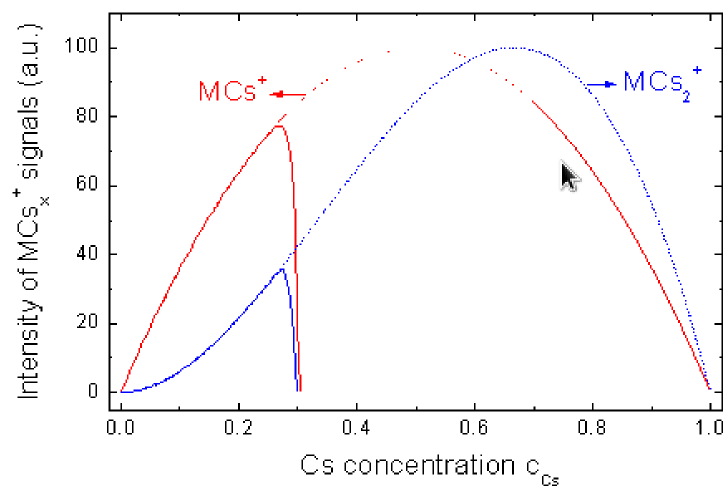
Quantification – MCs_x^+ technique



$$M^0 + Cs^+ \rightarrow MCs^+$$

$$\begin{cases} M^0 + Cs_2^+ \rightarrow MCs_2^+ \\ MCs^0 + Cs^+ \rightarrow MCs_2^+ \\ M^- + Cs^+ + Cs^+ \rightarrow MCs_2^+ \end{cases}$$





Instrumentation

Spectrometers

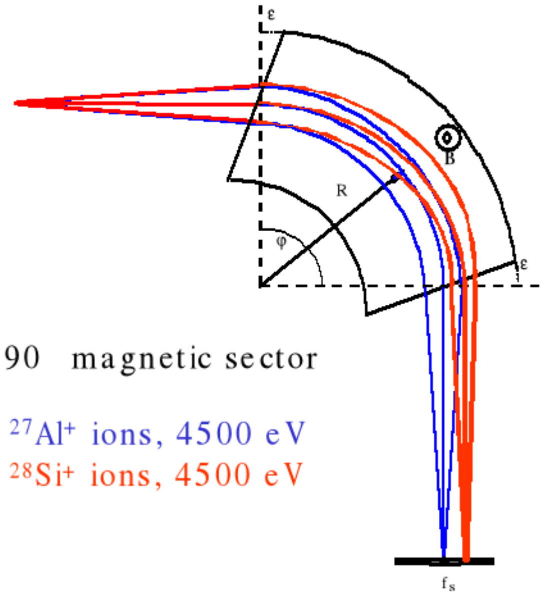
Dynamic SIMS

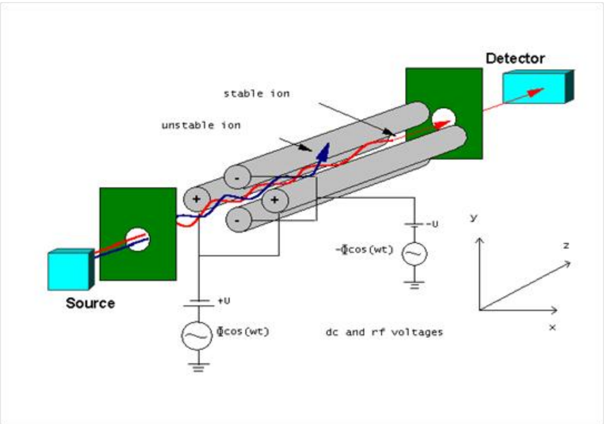
Static SIMS

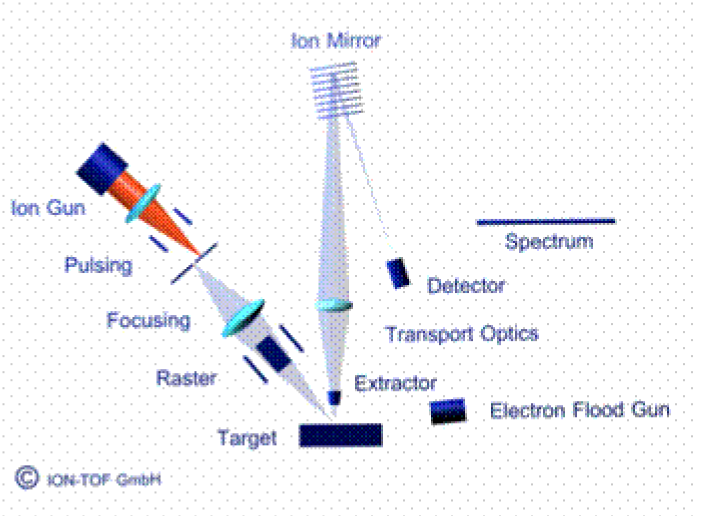
Magnetic sector

Quadrupole

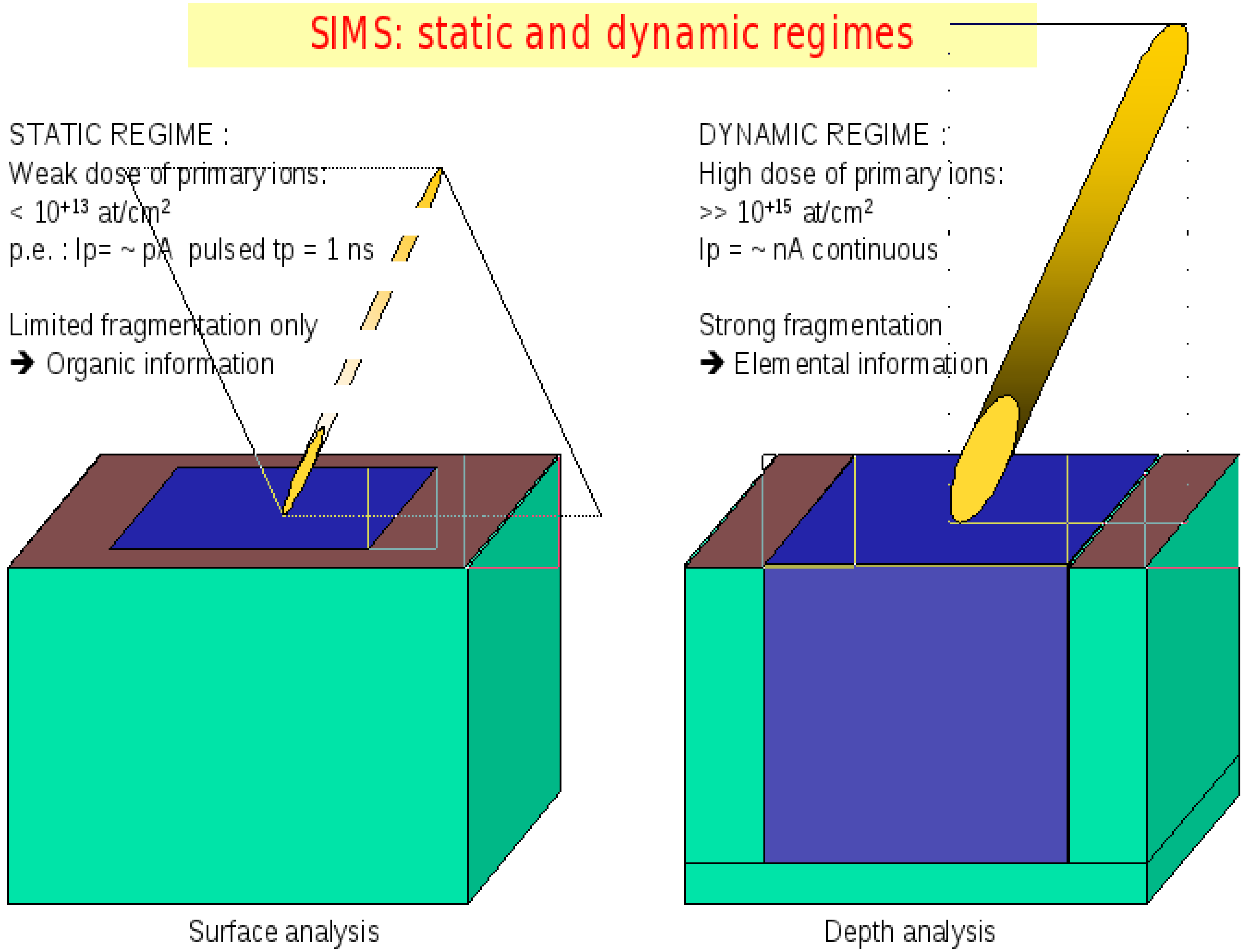
Time-of-Flight







Instrumentation



Static SIMS is the process involved in surface atomic monolayer analysis, usually with a pulsed ion beam and a time of flight mass spectrometer, while dynamic SIMS is the process involved in bulk analysis, closely related to the sputtering process, using a DC primary ion beam and a magnetic sector or quadrupole mass spectrometer.

Instrumentation

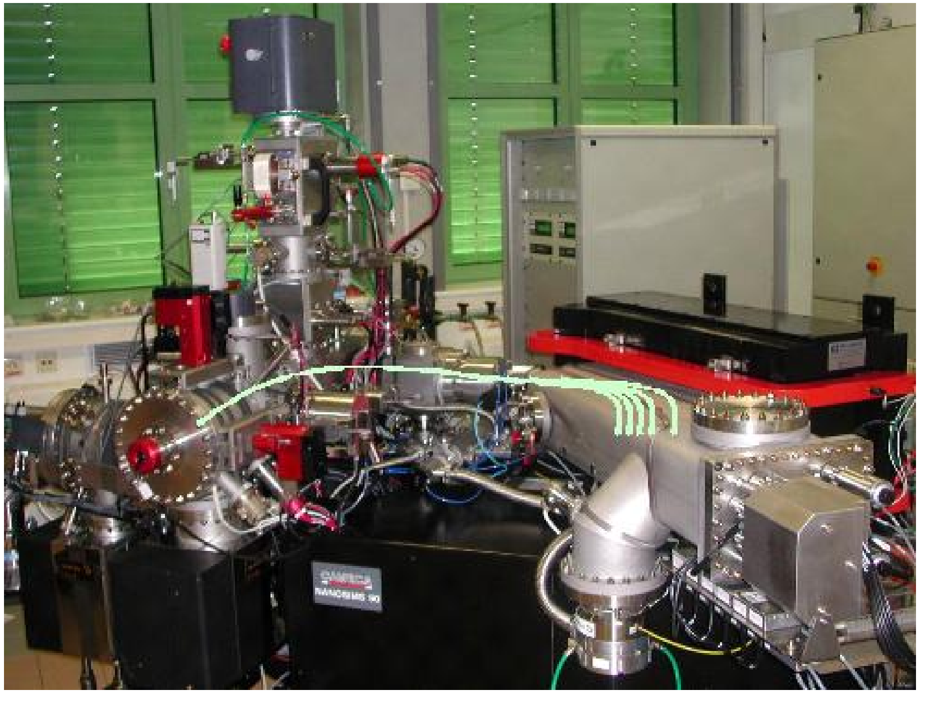
SIMS Manufactures

Dynamic SIMS

- Cameca (France) : magnetic sector and quadrupole
- PHI (USA/Japan) : quadrupole

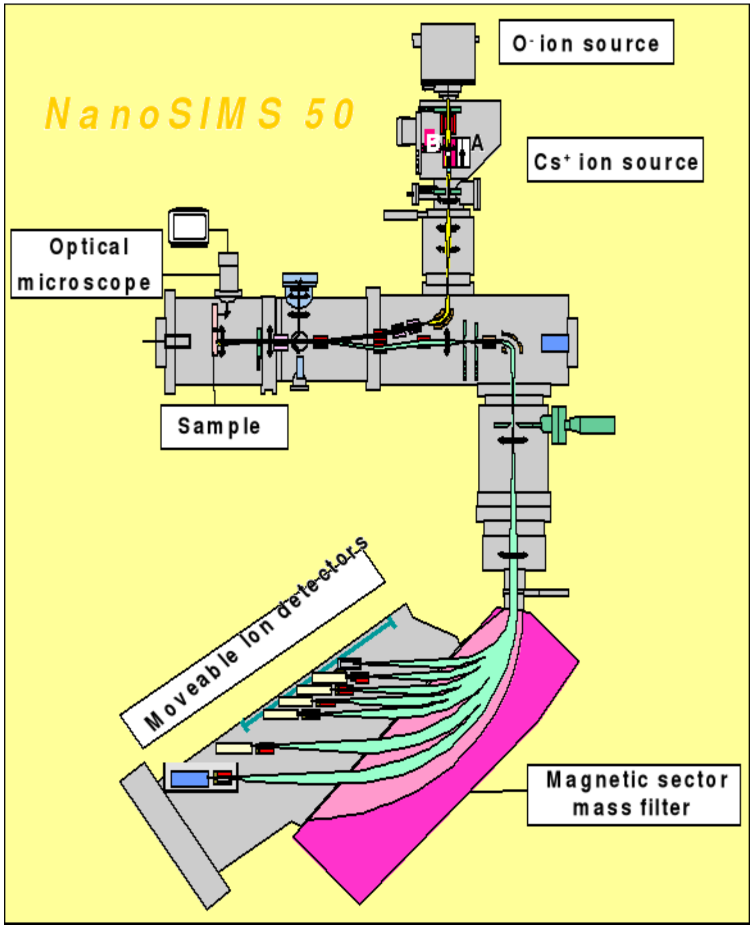
Static SIMS

- Ion-Tof (Germany) : time-of-flight
- PHI (USA/Japan) : time-of-flight



Instrumentation

dynamic SIMS



Cameca NanoSIMS 50

High resolution imaging

Primary ion guns: Cesium, oxygen

Spatial resolution (X,Y): 50 nm (negative secondary ions), 200 nm (positive secondary ions)

Depth resolution: nm range (not optimized)

Detection limits: ppb to ppm until 100%

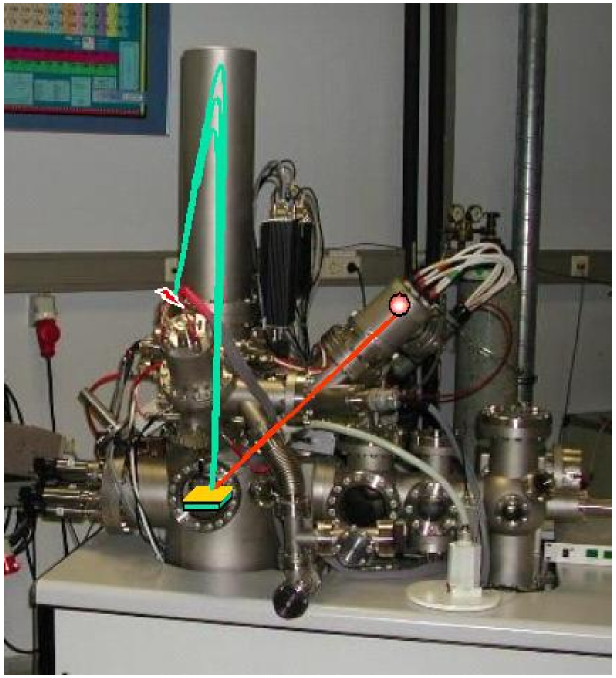
Elemental range: H to U

Unique advantages: High spatial resolution (< 50nm)
High transmission at high mass resolution
Parallel collection of 5-7 ionic species

Instrumentation

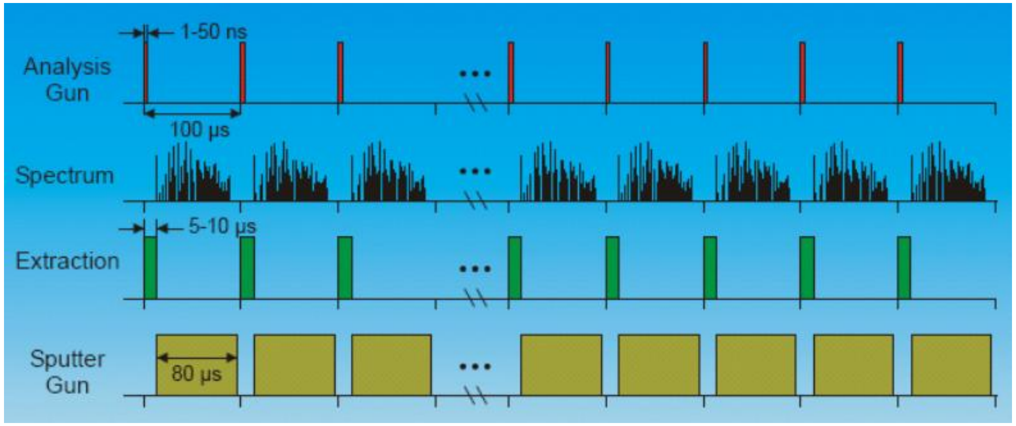
static SIMS

Ion-Tof TOF SIMS 5



Tof-SIMS for extreme surface analysis of organics

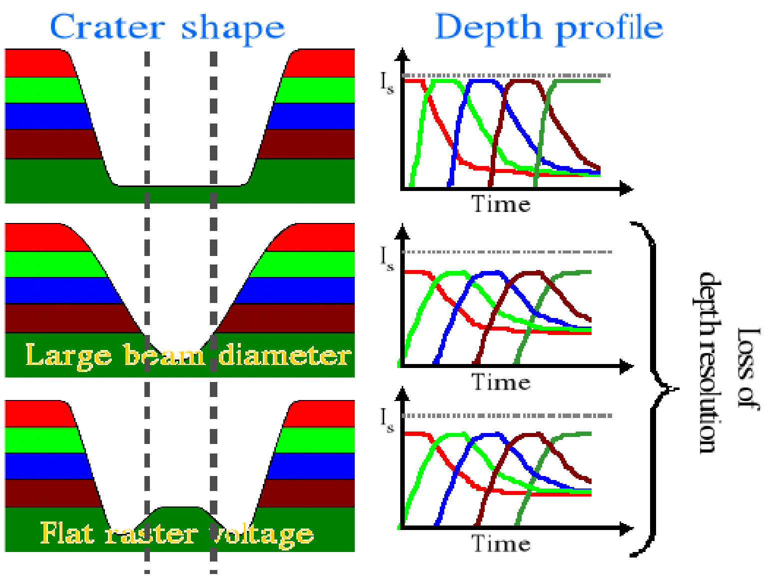
Primary ion guns:	Cesium, argon, gallium, bismuth, C_{60}, Au
Spatial resolution (X,Y):	100 nm
Depth resolution:	1 nm (low-energy ion bombardment)
Detection limits:	less good than dynamic SIMS (matter is lost during sputter-anaylsis cycles



Application

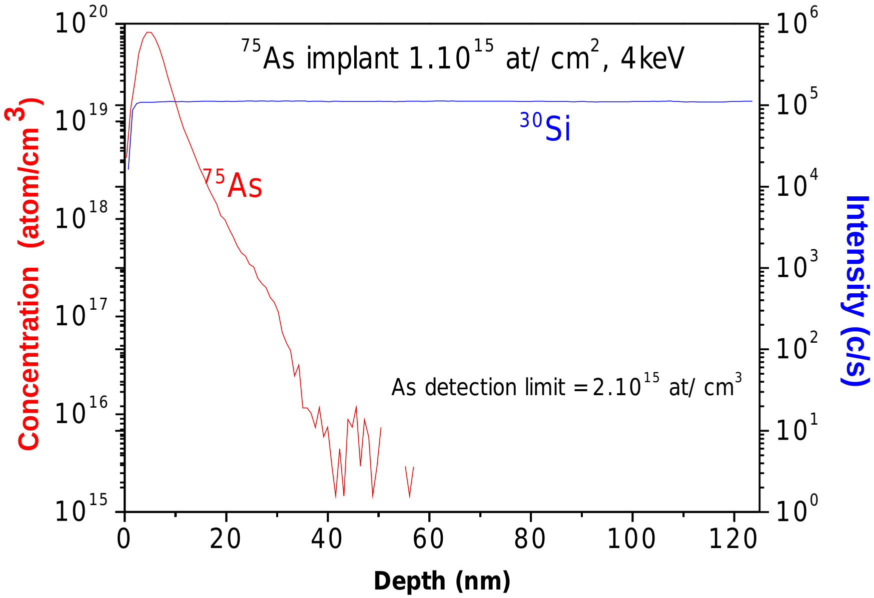
Depth profiling

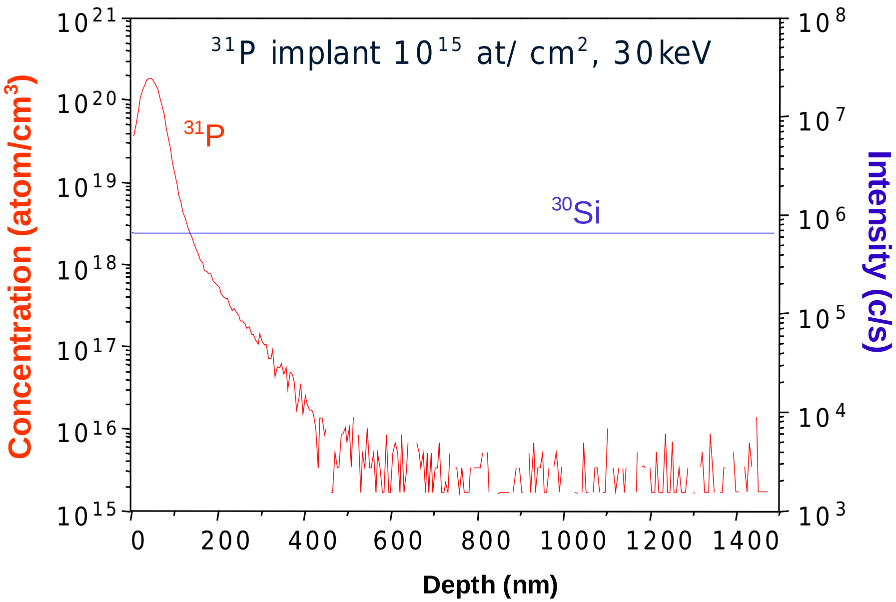
- recording of selected signals with respect to the sputtering time
- parallel detection or cycling between masses
- conversion between sputtering time and depth
  (measurement of the crater depth by profilometry, calculation of the erosion speed, …)
- depth resolution depending on several parameters:
  - sample (chemical composition, cristallinity, surface topography, …)
  - nature of primary ions (light or heavy ions, cluster ions, …)
  - impact energy and angle of incidence of the primary ions
  - sample rotation
  - oxygen flooding
  - focussing and rastering of the ion beam



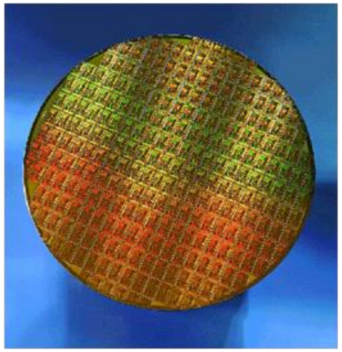
Applications

Si doping





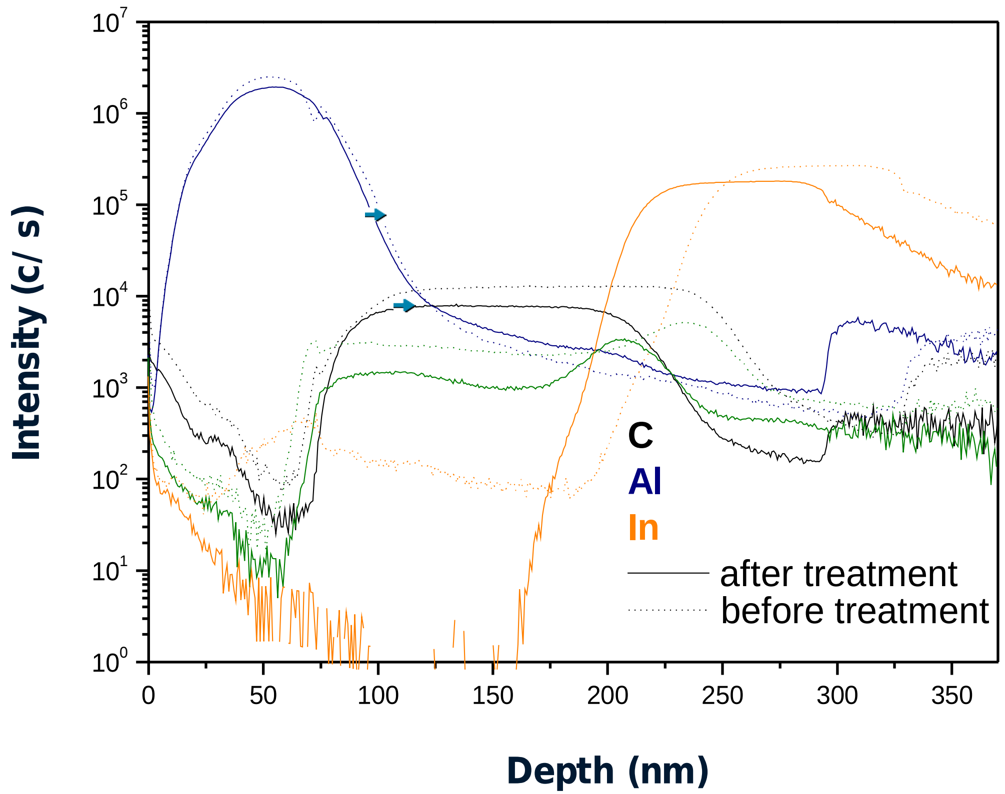
As implanted into Si
Cs^{+} primary ions at 500eV
impact energy

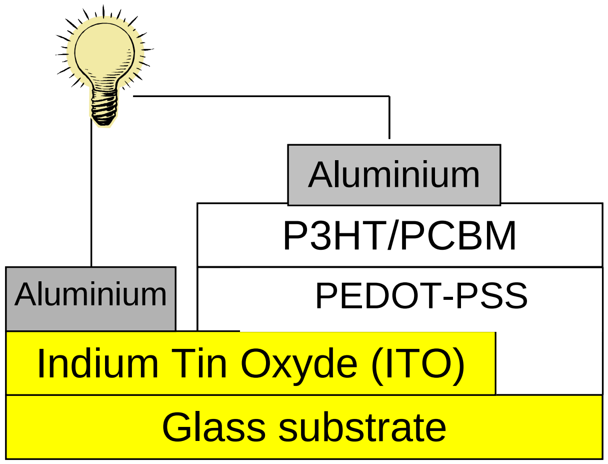


P implanted into Si
Cs^{+} primary ions at 2keV
impact energy

Application

organic solar cell



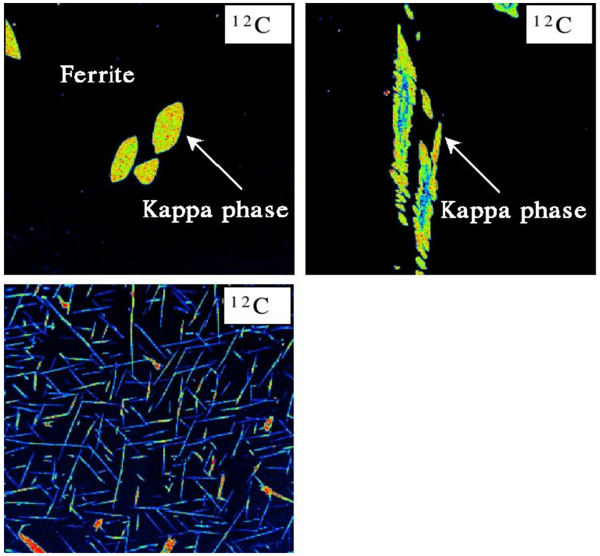


Determination of the diffusion of metallic Al in a polymer layer after heat treatment

Applications

2D imaging

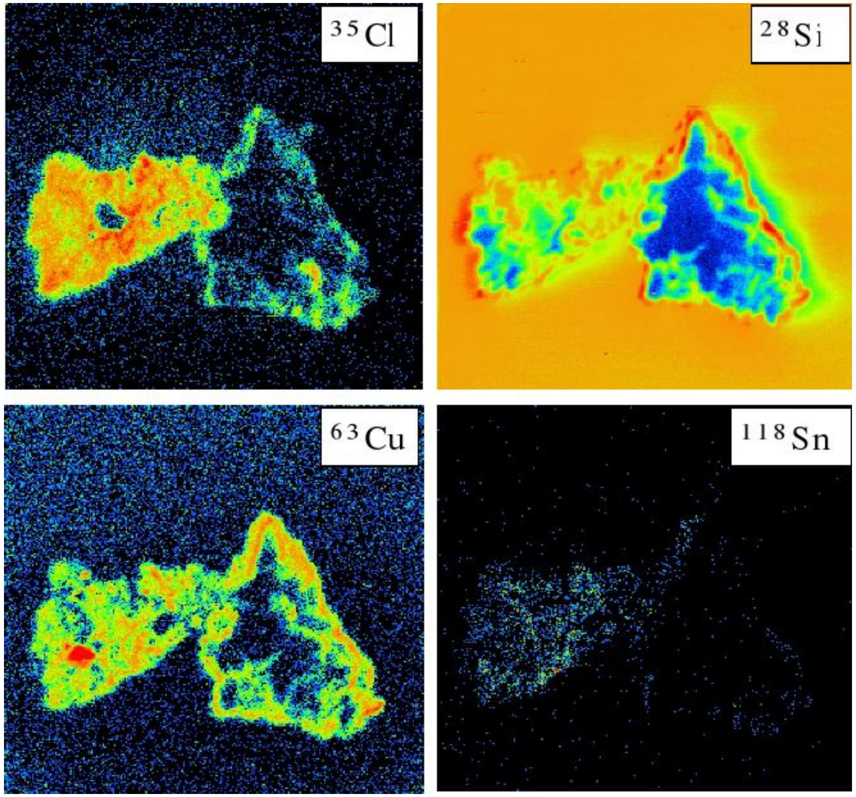
• rastering of the primary ion beam over the area of interest of the sample
• recording of selected signals
• synchronizing the primary ion rastering electronics with the detection electronics > image construction pixel by pixel
• lateral resolution of the ion image depending on two main parameters:
  - diameter of the ion probe (> brightness of the ion source, overall magnification of the focussing column, aberrations of the column)
  - impact energy and angle of incidence of the primary ions (lateral dimension of the collision cascade)



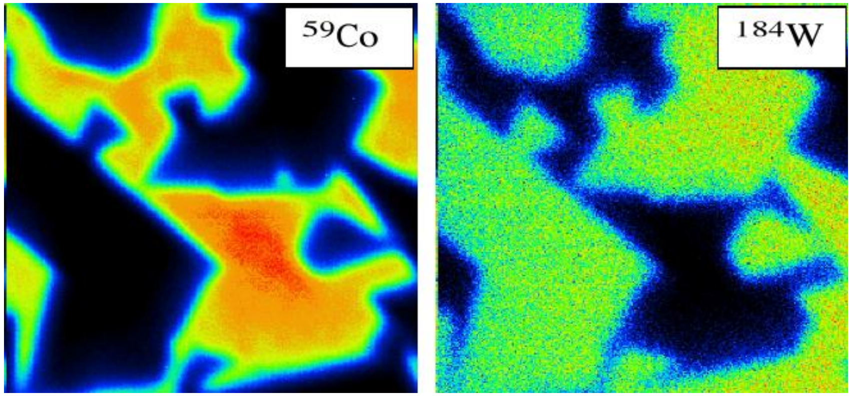
Fe-Al-Mn-C Alloys
Analyzed area : (3 x 3) μm^2

Applications

2D imaging

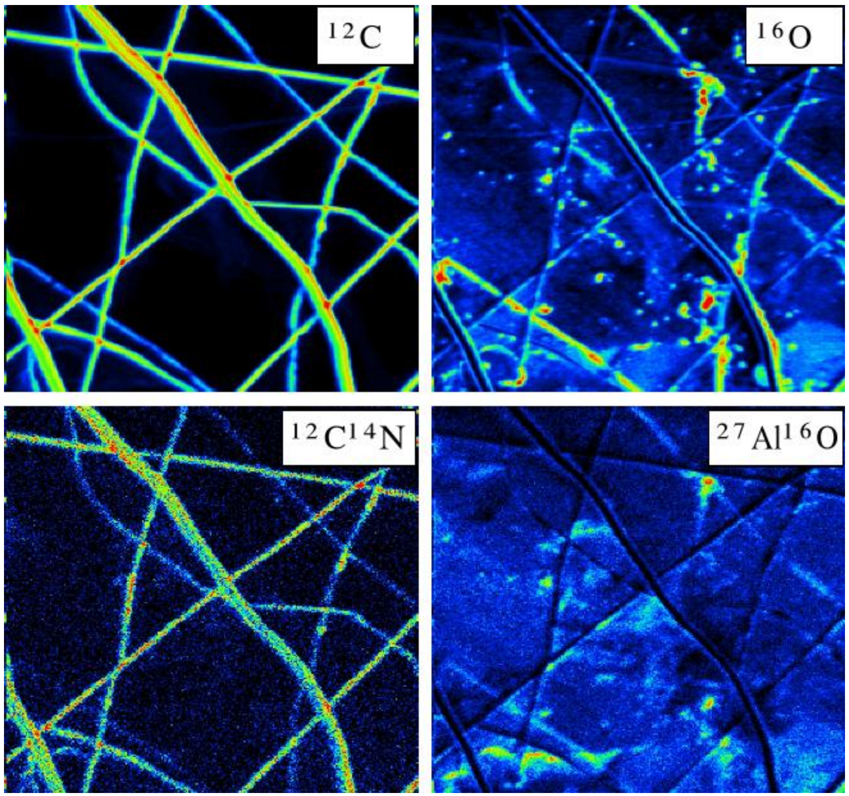


Atmospheric particles
Analyzed area : (12 x 12) μm^2

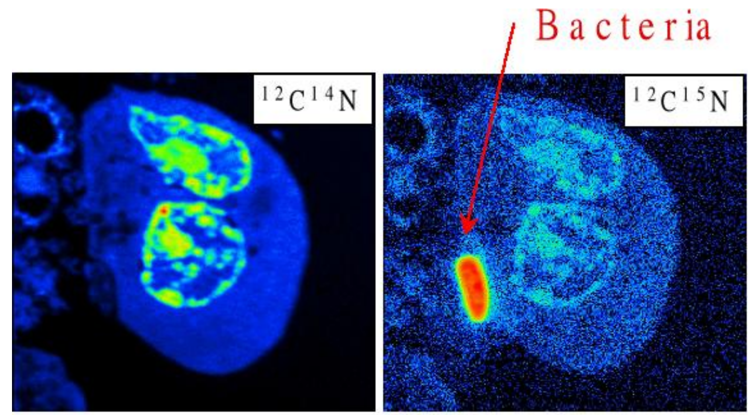


Tungsten carbide
Analyzed area : (10 x 10) μm^2

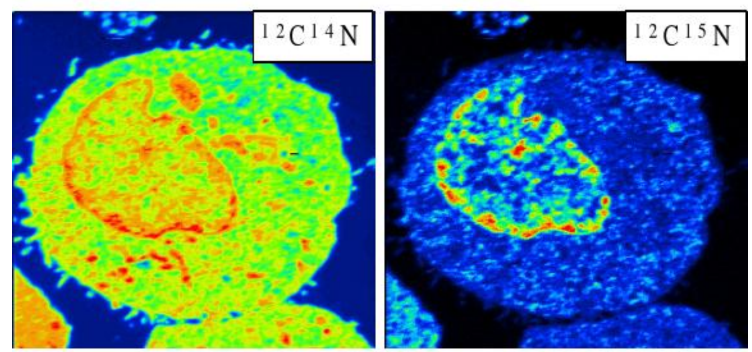
Applications
2D imaging



Nanofibres
Analyzed area : (10 x 10) µm^2



Analyzed area : (12 x 12) µm^2



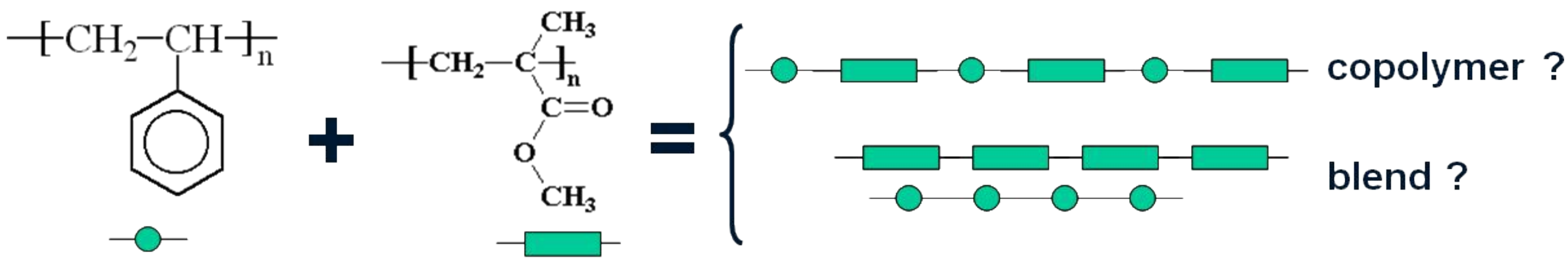
Analyzed area : (13 x 13) µm^2

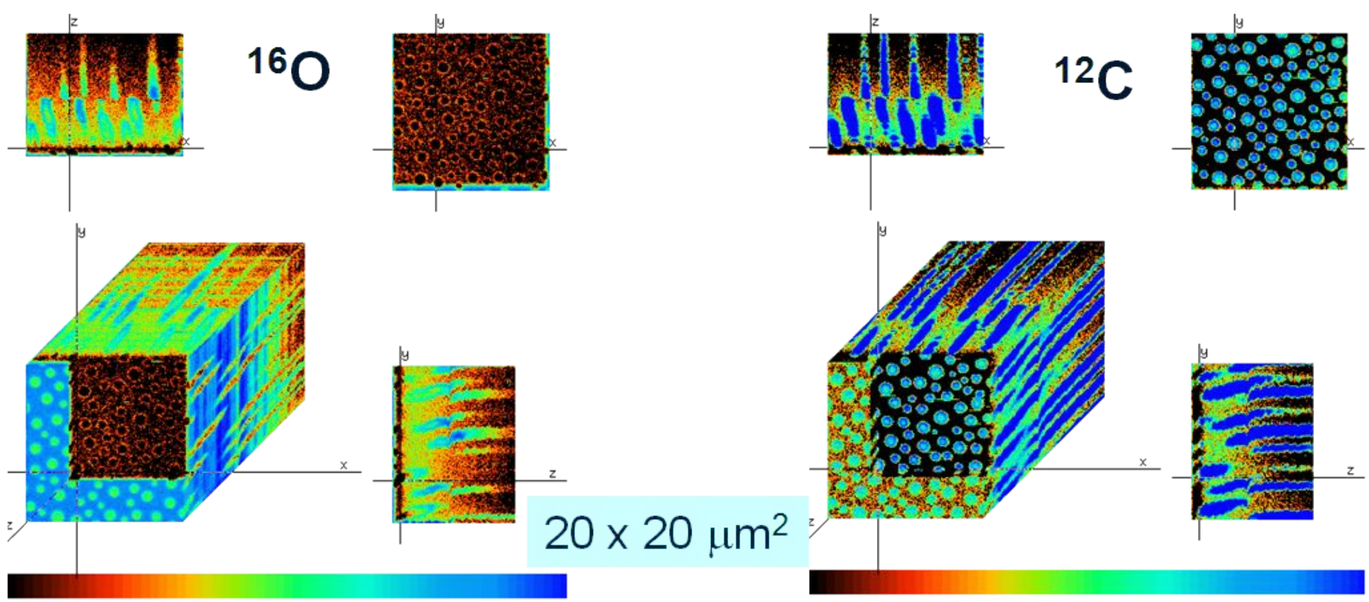
E.coli labelled with ^{15}N, destroyed by the immune system

Applications

3D imaging - Polystyrene – PMMA blend

- acquisition of successive images for selected secondary ions
- depth calibration to determine the depth of origin of the different image planes
- reconstruction of the 3D image





Summary

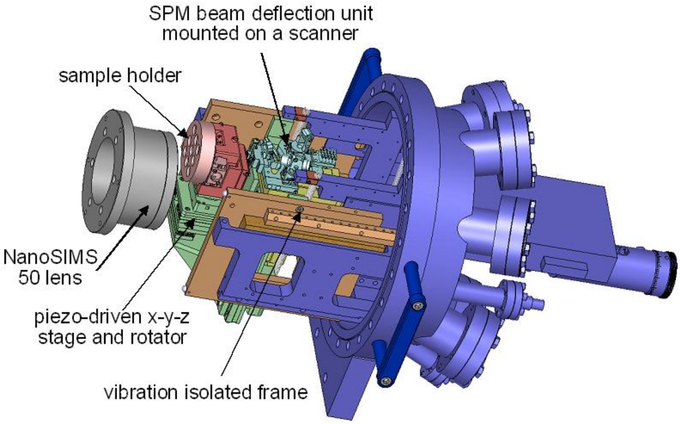
Strong points:

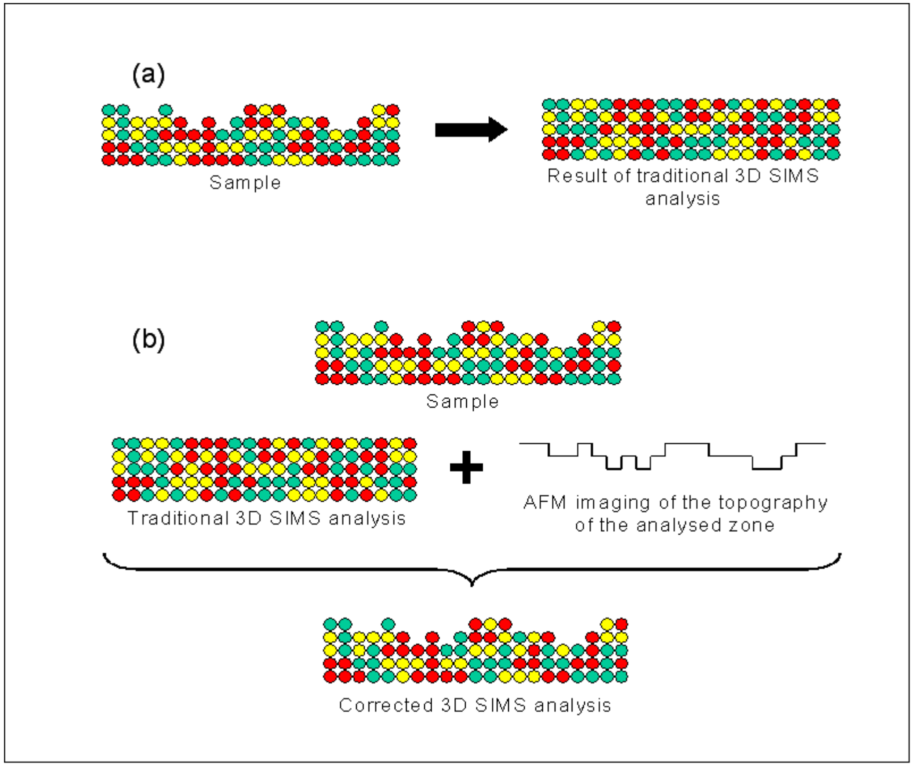
- all elements/isotopes detectable
- excellent sensitivity (ppm – ppb to 100%)
- high dynamic range (intensity variations can be followed over several orders of magnitude)
- high mass resolution (M/DM up to 10.000)
- isotopic measurements
- high depth resolution (1 nm at low-energy ion bombardment)
- high lateral resolution (50 nm on the Cameca NanoSIMS)
- organic information in static mode

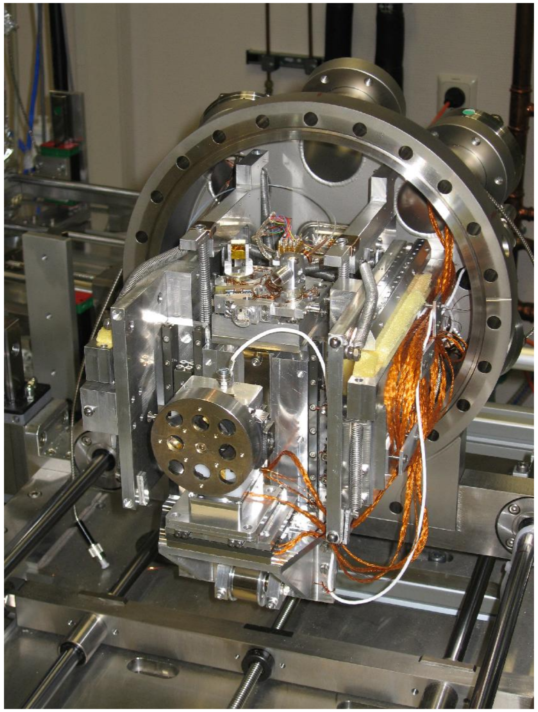
Weak points:

- difficult to quantify measurements (« matrix effect »)

New Instrumentation
combination AFM/KPFM-SIMS!







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