EPFL

Secondary Ion Mass Spectroscopy SIMS

SURFACE ANALYSIS

MSE-351

Anna Igual Munoz

Reference book

J. C. Vickerman, I.S. Gilmore

Surface Analysis: The Principal Techniques

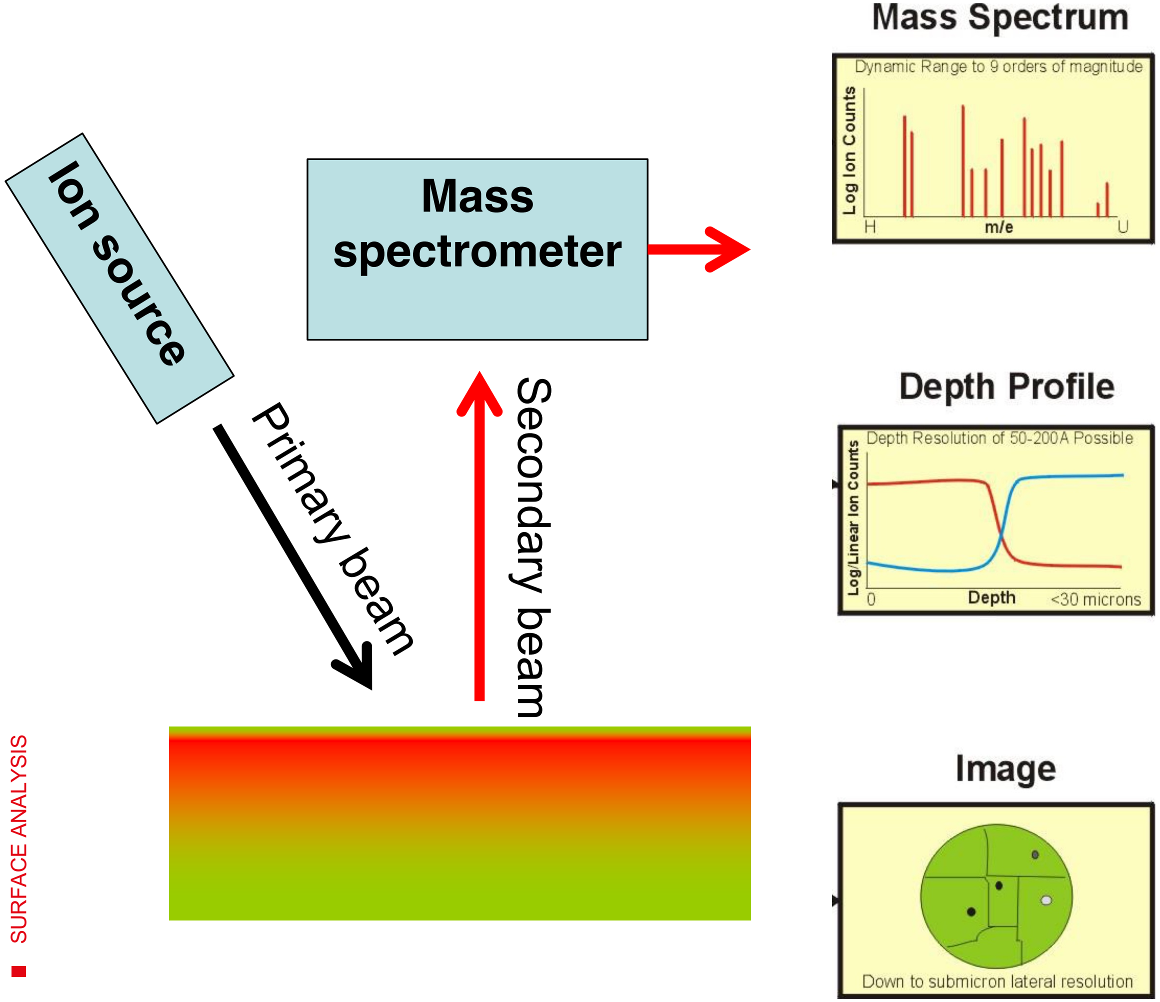
Wiley (2009)

1. Introduction SIMS (sputtering and ionization)

2. Instrumentation

3. Applications

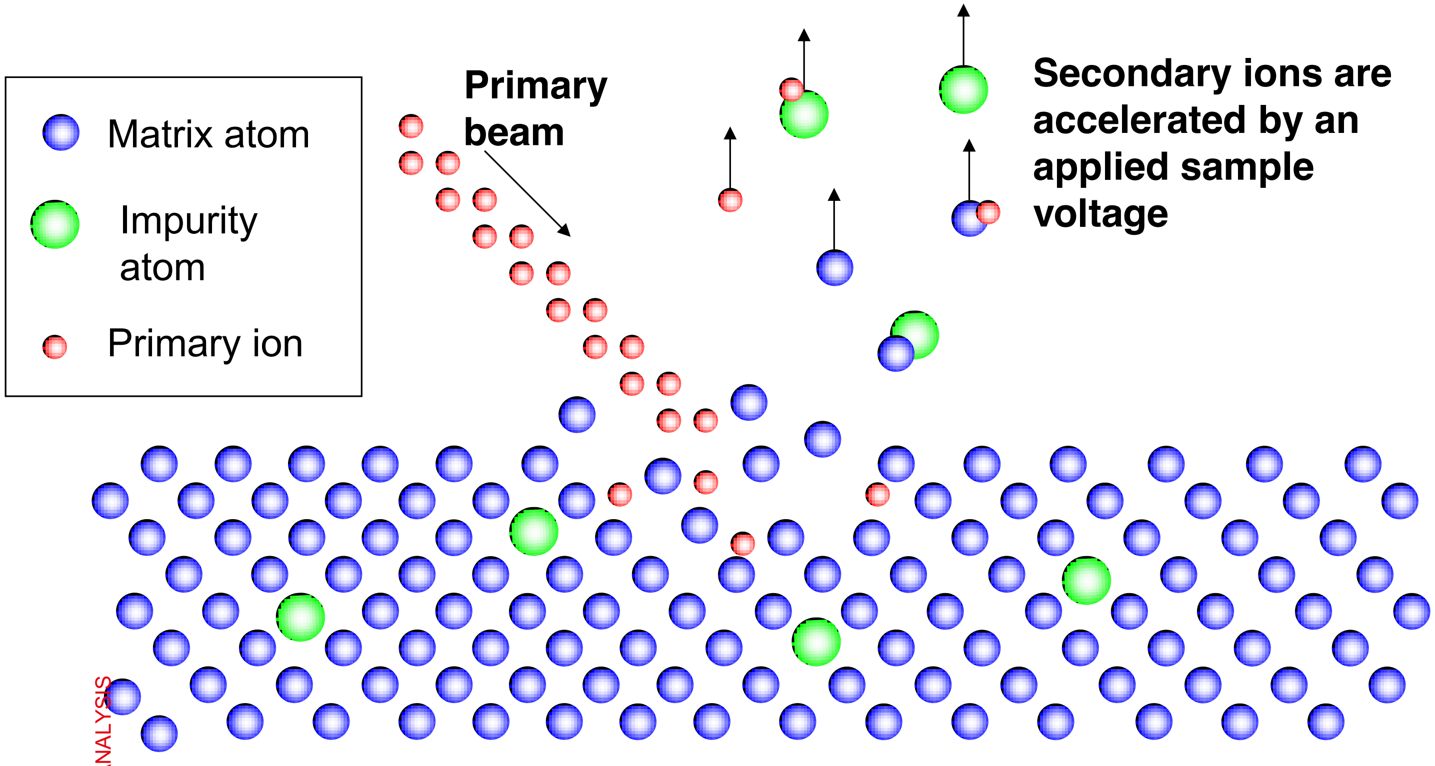
Principle of SIMS



In SIMS the surface of the specimen is sputtered with a focused primary ion beam.

Ejected secondary ions are analyzed with a mass spectrometer to determine the elemental, isotopic, or molecular composition of the surface to a depth of 1 to 2 nm.

Ion-solid interactions



Ion bombardment results in:

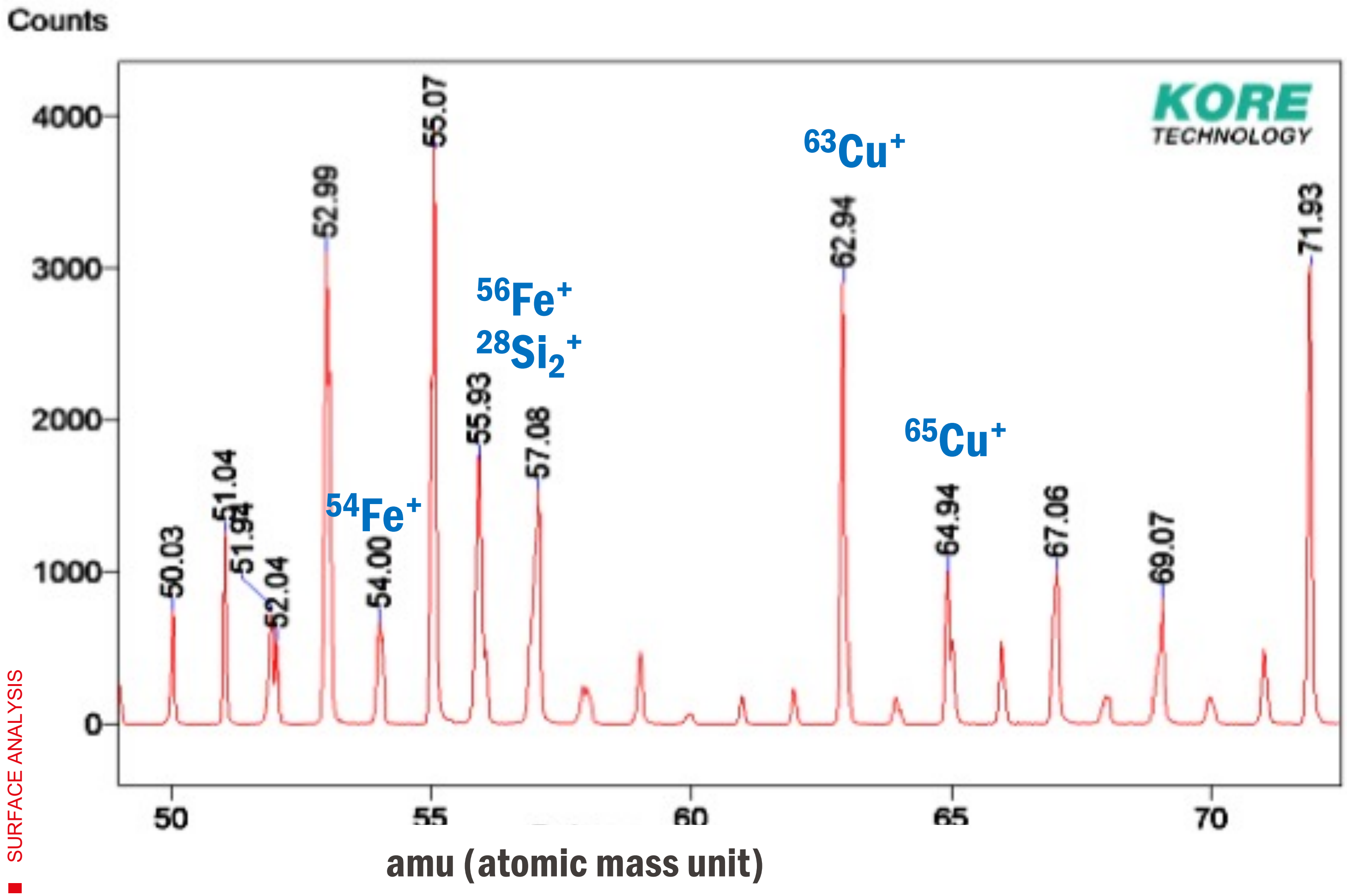
- Ejection of secondary ions (monoatomic or molecular)
- Ejection of neutrals (monoatomic or molecular)
- Implantation of primary ions
- Ejection of electrons and photons
- Surface damage

Secondary ion formation

Secondary ion formation can be divided into two components:

1. The dynamic process by which atoms and polyatomic clusters sputter
2. The ionization process in which a fraction of these sputtered particles become charged

SIMS spectrum: counts vs mass/charge ratio



Silicon wafer contaminated with copper, iron and chromium

Spectral interpretation is complicated by mass interferences

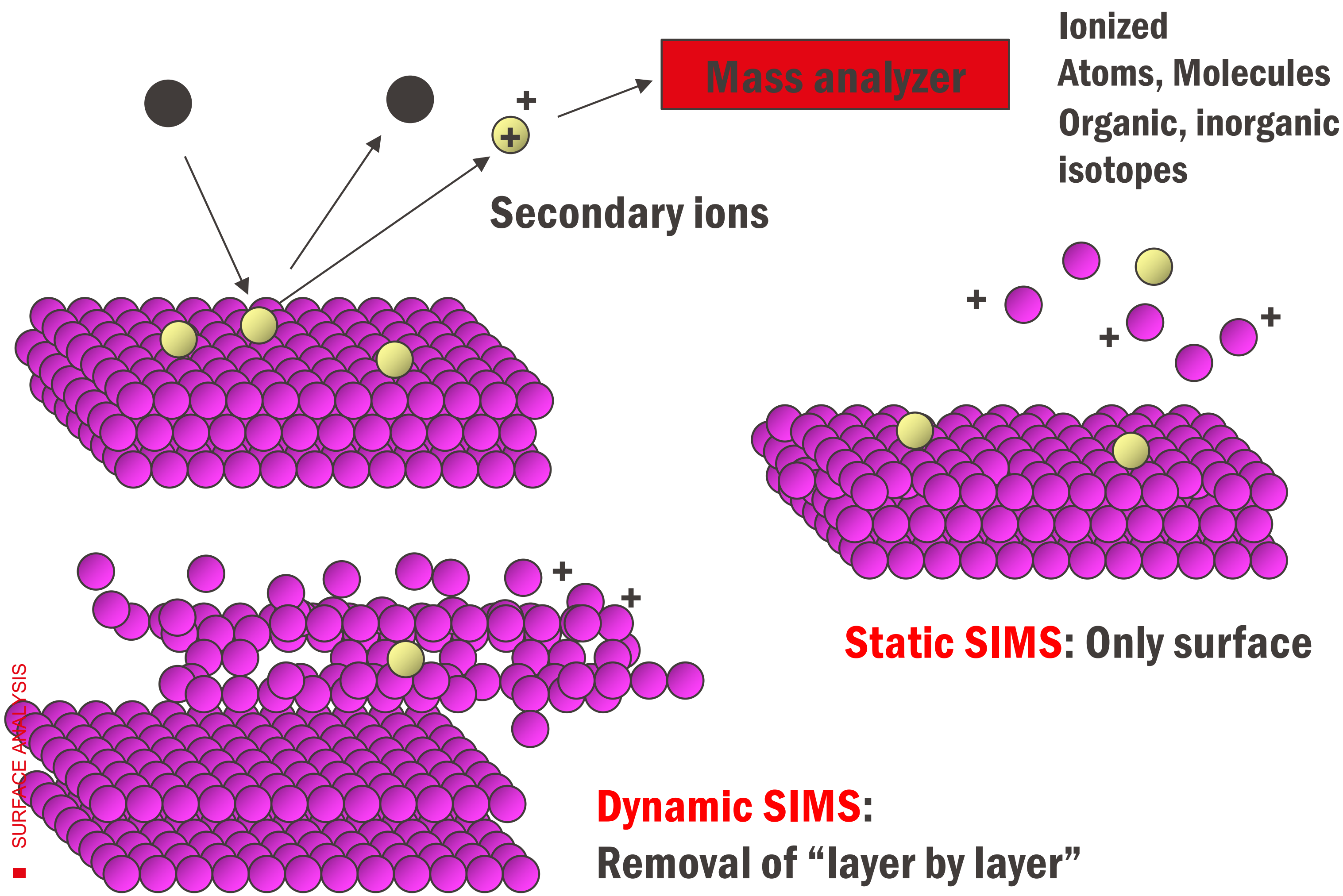
Note the zero background (compare with XPS and AES!)

Mass interference

Several ions/ionic molecules have similar mass to charge ratio:

Interference	Mitigation
^{10}B - $^{30}Si^{3+}$	Monitor 11B
^{75}As - $^{29}Si^{30}Si^{16}O$	Energy selection
^{31}P - $^{30}Si^{1}H$	High mass resolution

Modes of operation in SIMS



Static SIMS:
0.1-10 keV ions, I_p in nA/cm^2 range.

Dynamic-SIMS: 10-30 keV ions,
I_p in mA-mA/cm^2 range.

Static and Dynamic SIMS

Static SIMS

- The essence of the *static* mode is to use an extremely low dose of primary ions (never more than 10^{13} ions/cm2) such that within the time scale of the experiment very much less than 1% of the top surface layer of atoms or molecules receives an ion impact.
- The species generated arise from an area no greater than 10 nm^2 and are remote from the next point of analytical impact.
- Time-of-Flight SIMS (ToF SIMS) is the main experimental variant of static SIMS (SSIMS)

- Whereas **in dynamic SIMS** high elemental sensitivity and rapid erosion rates are required so high primary flux densities of 1µA/cm^2 are used.
- Thus, can be applied to bulk characterization

Comparison

Technique	Dynamic	Static
Flux	10^{17} ions/cm^2	10^{13} ions/cm^2
Information	Elemental	Elemental and molecular
Sensitivity	< 1 ppm	1 ppm
Type of analysis	Depth, mass spectrum, 3D profile	Surface mass spectrum 2D image
Destructive?	Damaging	Minimum damage

The fundamental SIMS equation:

$$I_s^m = I_p y_m \alpha^{\pm} \theta \eta$$

$I^s{}_m$ = secondary ion current of species *m*

I_p = the primary particle flux which is adjusted to ensure analysis is kept within the static regime

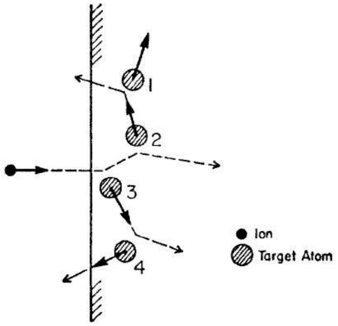
Y_m = **sputter yield** (the number of atomic and polyatomic particles emitted per primary impact)

$\alpha^{\pm}$ = **ionization probability** to positive or negative ions,

θ = *f*ractional concentration of the chemistry giving rise to species *m* in the surface layer,

η = instrument transmission which is obviously crucial to the ability of the technique to detect and analyze the generated ions with good sensitivity

Sputtering yield
(number of sputtered atoms per incoming ion)



Sputtering is a multiple collision process involving a cascade of moving target atoms, this cascade may extend over a considerable region inside the target.

Sputtering yield:

$$S(E_\mathrm{i}) = \frac{K_\mathrm{it}}{U_0} S_\mathrm{n}\left(\frac{E_\mathrm{i}}{E_\mathrm{it}}\right)$$

Nuclear stopping power S_n : Loss of energy of a particle travelling in a solid by unit distance f(radiation, travelled material).

$$S_\mathrm{n}(\xi) = 0.5\ln(1+\xi)\Big/\left\{\xi + (\xi/383)^{3/8}\right\}$$

$$E_\mathrm{it} = (1 + M_\mathrm{i}/M_\mathrm{t}) Z_\mathrm{i} Z_\mathrm{t} \left(Z_\mathrm{i}^{2/3} + Z_\mathrm{t}^{2/3}\right)^{1/2} \Big/ 32.5 \quad [\mathrm{keV}]$$

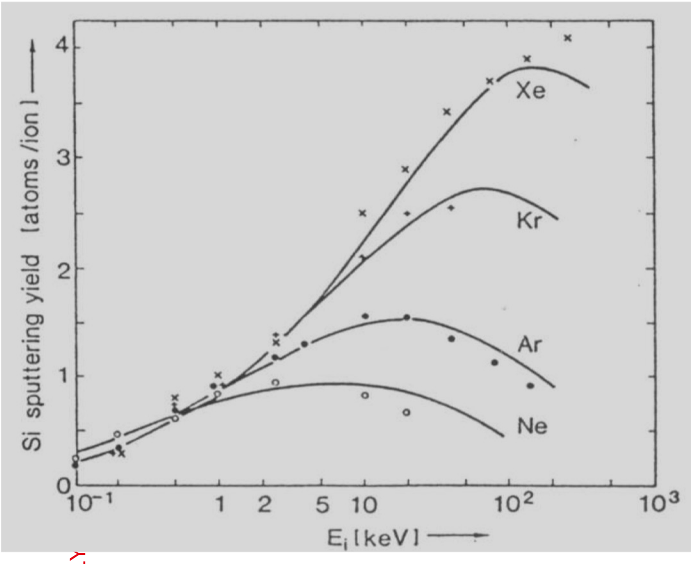
$$K_\mathrm{it} \approx (Z_\mathrm{i} Z_\mathrm{t})^{5/6} \big/ 3 \quad \text{for} \quad 0.05 \le Z_\mathrm{t} Z_\mathrm{i} \le 5$$

M_i, Z_i: Ion mass and atomic number
M_t, Z_t: Target mass and atomic number
U_0 : Surface escape barrier in eV
E_i : Ion energy

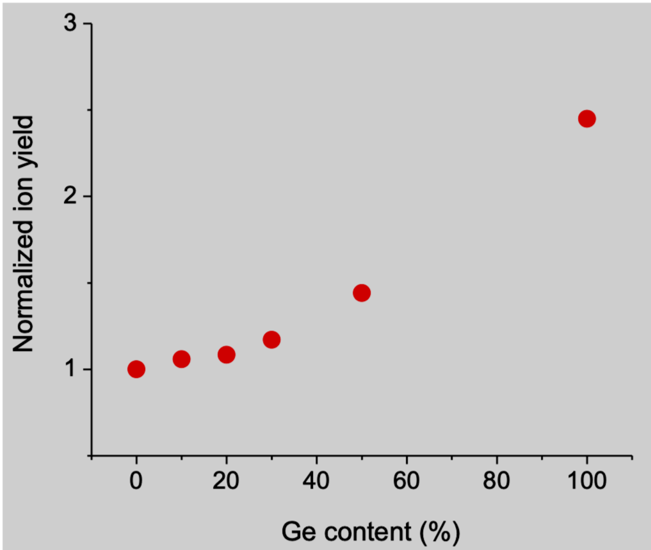
Sigmund P. *Theory of* Sputtering, Phys. Rev. **184**(2), 383 (1969)

Some factors affecting sputter yield

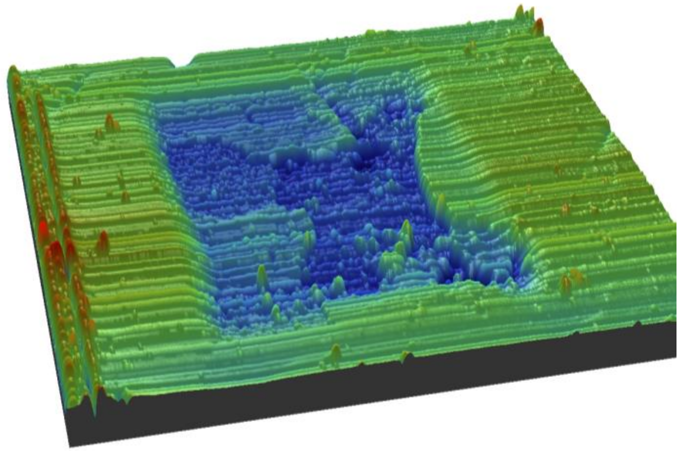
Effect of primary ion and ion energy



Effect of target composition: case of (Si1-xGex)

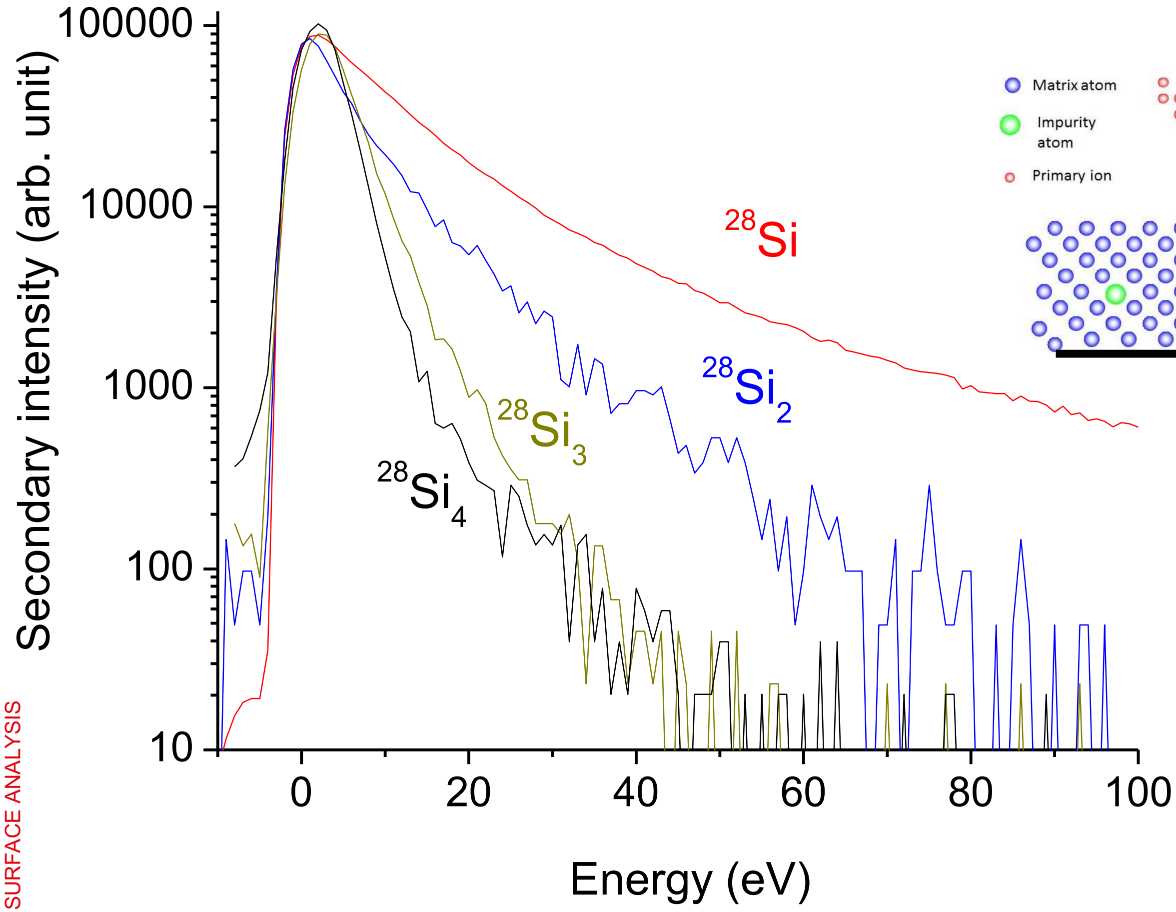


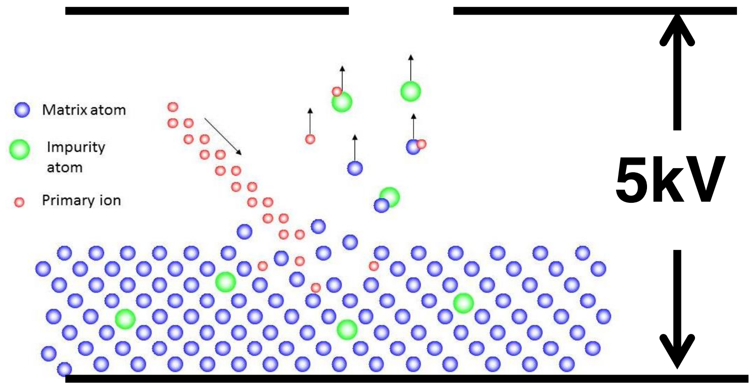
Effect of grain orientation: case of poylcrystalline iron



The erosion rate is different for the different grains: Sputtering yield vary with the crystal orientation

Energy distribution of secondary ions





Secondary ions have low energy insufficient to enter the mass spectrometer. In SIMS they are therefore accelerated by an external field. **The field determines whether positive or negative ions enter the analyser.**

Ionization yield
(fraction of sputtered atoms that becomes ionized)

- Ion yield can generally not be predicted theoretically

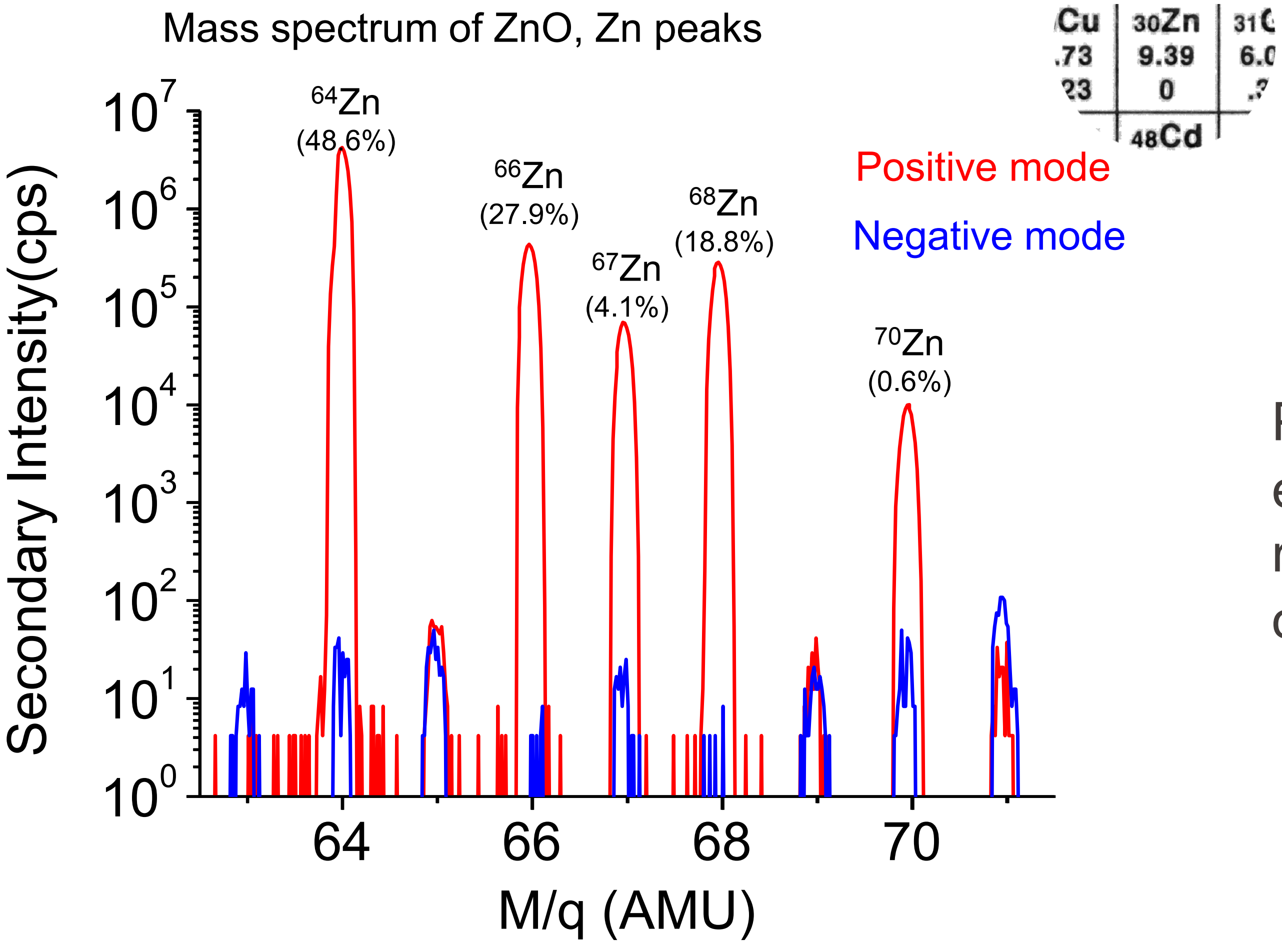
- Ion yield can vary by several orders of magnitude depending on element and chemistry of the sputtered surface
  Example: secondary ion yields from clean and oxidized surfaces

Metal	*Al*	*Ti*	*Cu*
Clean metal	*0.007*	*0.0013*	*0.0003*
Oxidized metal	*0.7*	*0.4*	*0.007*

- Oxygen on the surface will increase positive ion yield

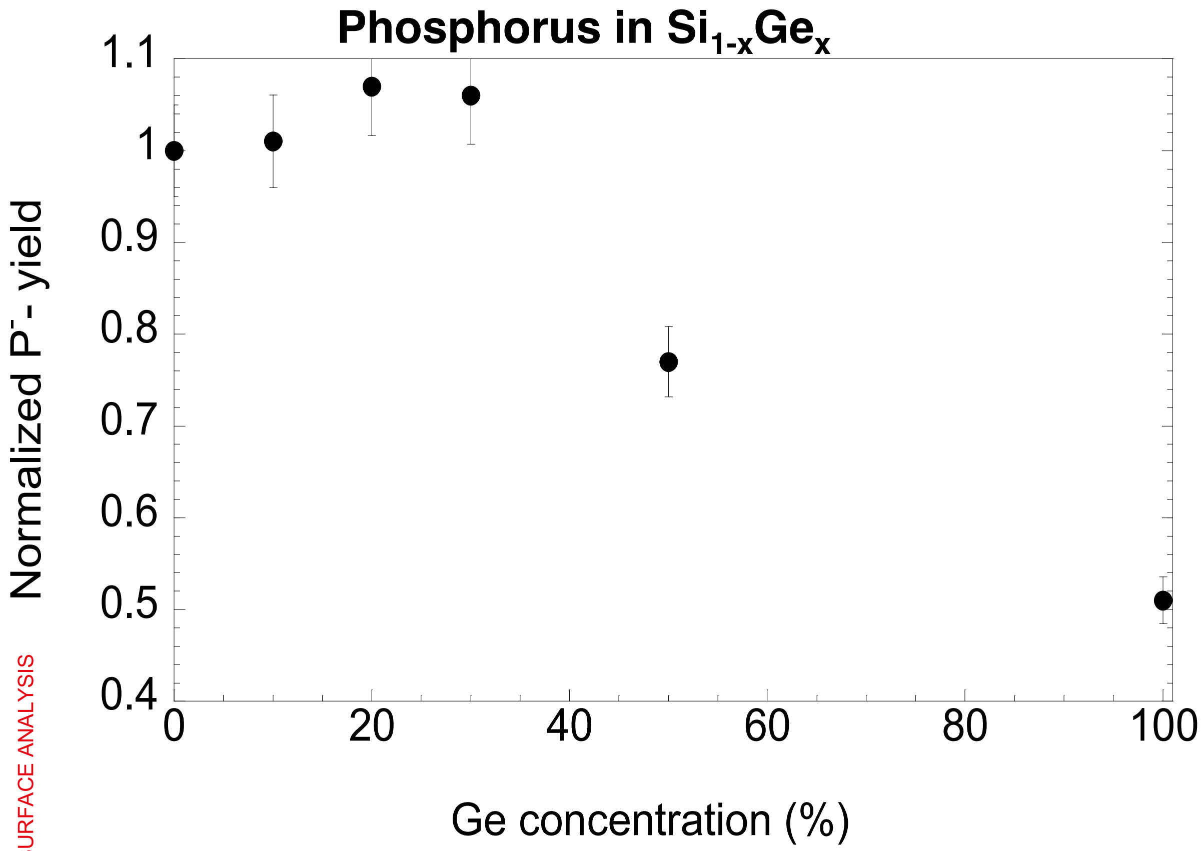
- Cesium on the surface will increase negative ion yield

Ionization of Zinc in Zinc-oxide



Positive Zn ions are emitted preferentially with respect to negative Zn ions on oxidized surfaces.

Ionization yield of P in $Si_{1-x}Ge_x$



The P yield varies depending on the matrix in which it is embedded. This because the ionization probability is highly matrix dependent.
This limits the SIMS quantification possibilities.
SIMS is mainly a tool for measuring small concentrations in a given matrix.

General SIMS Yield for a species t

- Measured intensity I_t for a specific target atom

$$I_t = I_P Y [C_t] \gamma_t T$$

I_P: Primary ion current
Y : Sputtering yield (number of sputtered particles per impinging primary ion)
$[C_t]$: Concentration of species t
γ_t : Secondary ion formation and survival probability (ionization efficiency)
T: Instrument transmission function

γ_t is highly dependent on species and matrix

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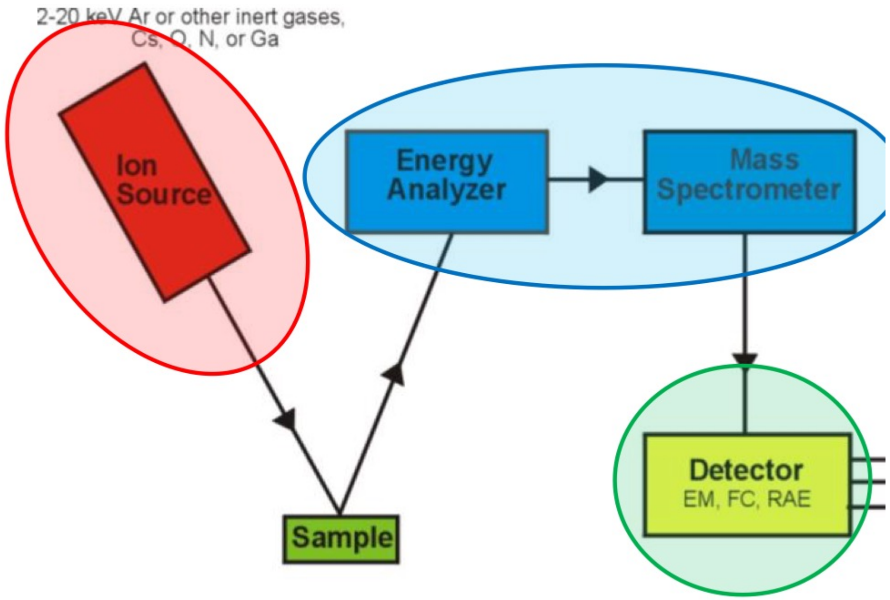
SIMS instrumentation

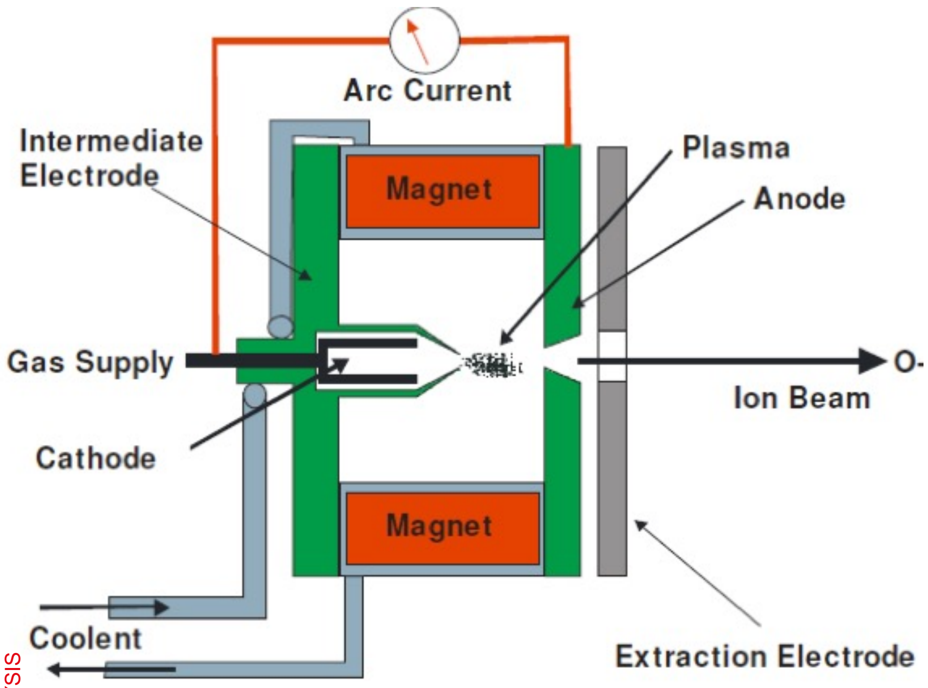
Ion Sources
- Ion sources with electron impact ionization - Duoplasmatron: Ar+, O2+, O-
- Ion sources with surface ionization - Cs+ ion sources
- Ion sources with field emission - Ga+ liquid metal ion sources

Mass Analyzers
- Magnetic sector analyzer
- Quadrupole mass analyzer
- Time of flight analyzer

Ion Detectors
- Faraday cup
- Dynode electron multiplier

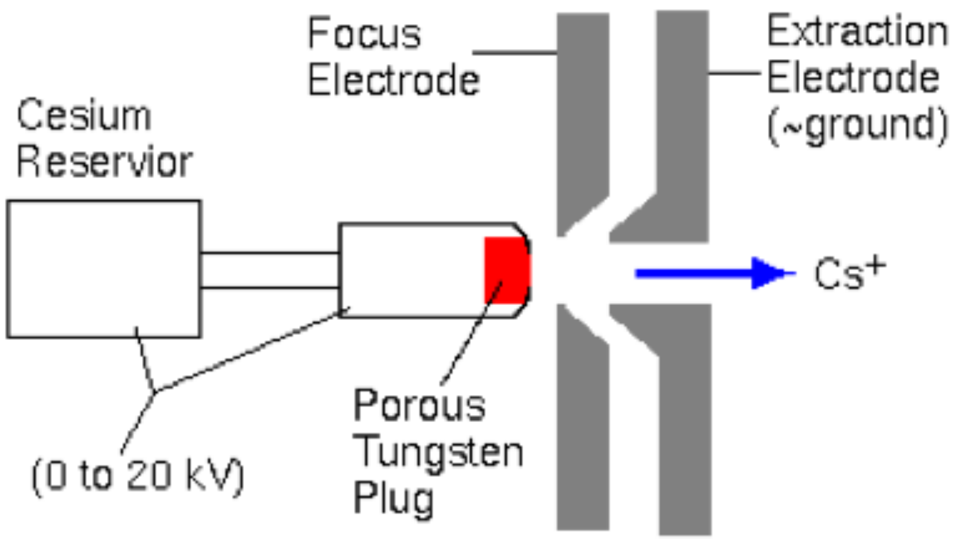


Ion sources: duoplasmatron



- A cathode filament emits electrons into a vacuum chamber
- Small quantity of gas (Ar, O_2, Ne, etc.) leaks into the chamber and interacts with the electrons forming a **plasma**
- The plasma is accelerated through a series of highly charged grids to the desired energy and extracted through the aperture.

Ion sources: Cs^+ source

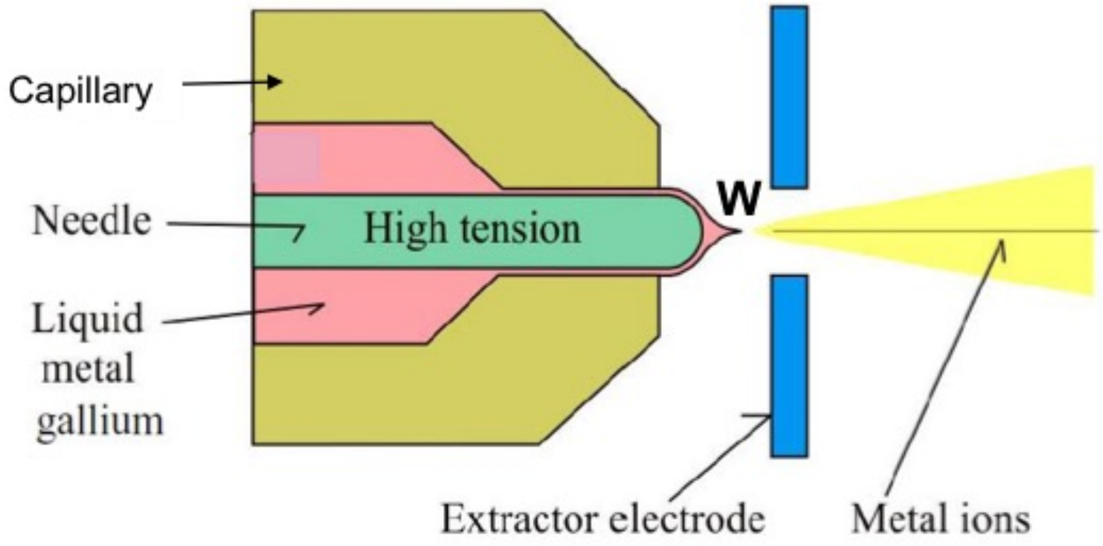


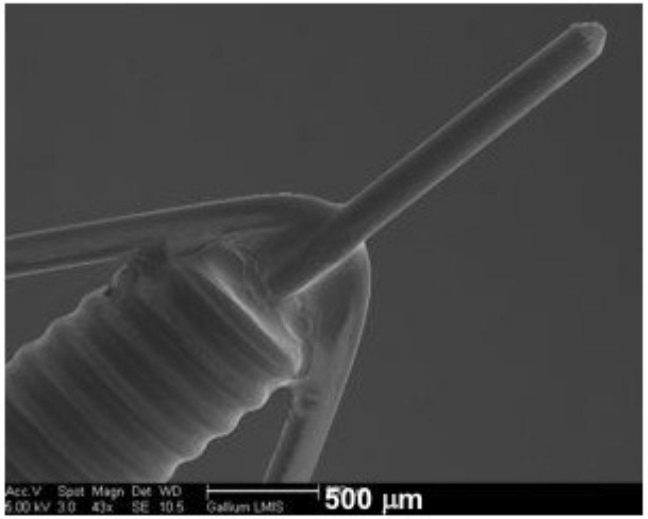
- Cs metal (or compound) is heated in the reservoir (~400°C) forming a vapor
- The Cs vapor flows through a feed tube to a porous tungsten plug
- The Cs vapour diffuses through the pores in the plug to the front of surface which is maintained at >1100°C by the ionizer heater
- The Cs atoms are ionized during evaporation
- The Cs^+ ions are extracted and accelerated to an energy up to 10 keV.

General characteristics *Cs^+ source*

- Cesium guns enhances yield of negative secondary ions under Cs+ bombardment.
- Such systems can produce higher current than LMIS (Liquid Metal Ion Source) type but have lower brightness.
- Low energy spread and small spot sizes 1µm can be attained.

Ion sources: liquid metal ion source



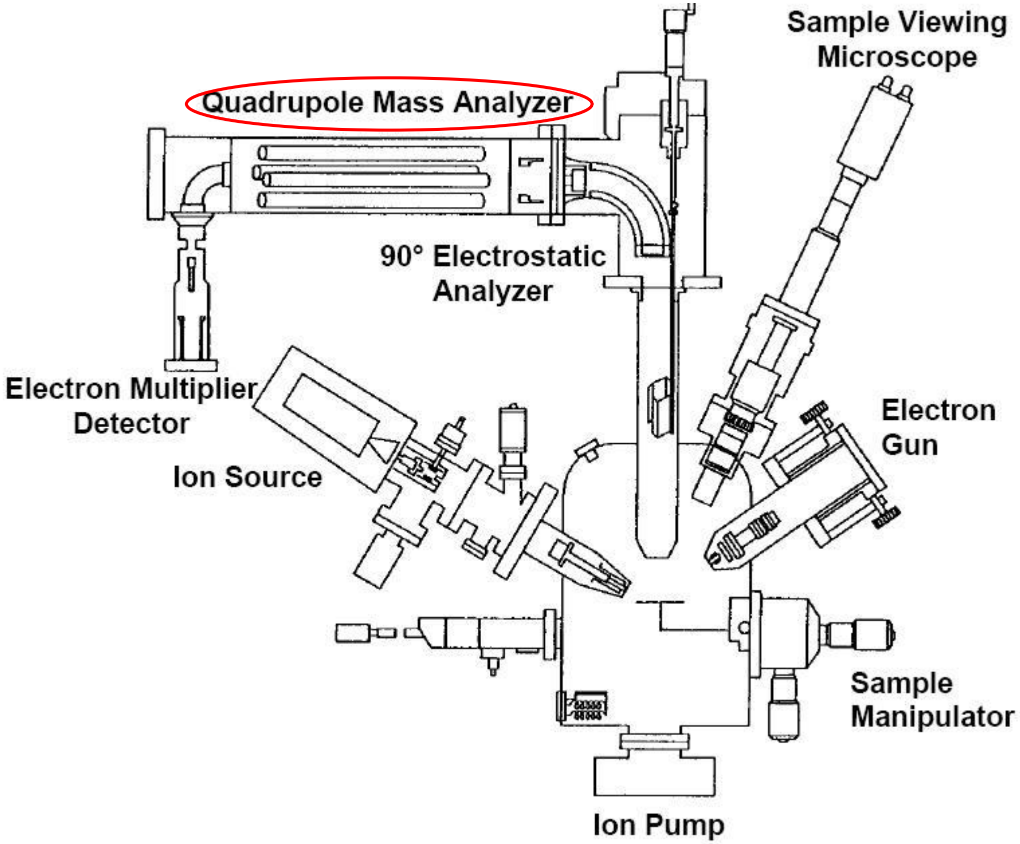


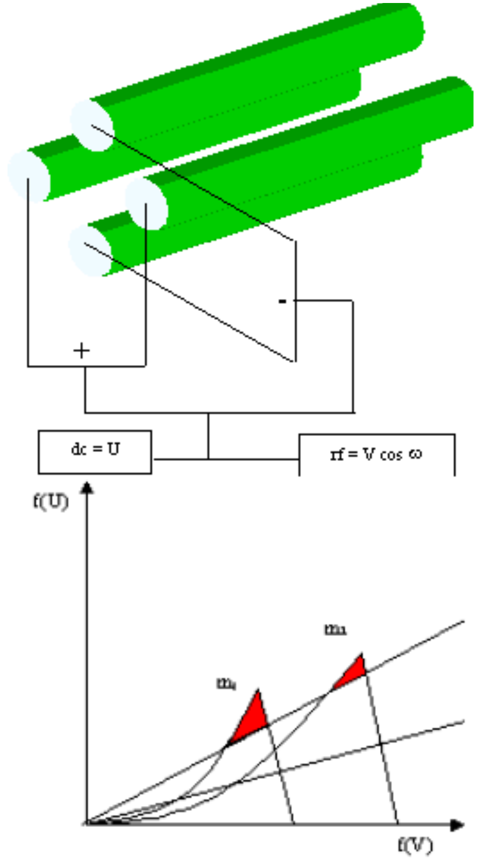
- Operates with low melting point metals or metallic alloys, which are liquid at room temperature or slightly above (Ga, Cs).
- The liquid metal covers a tungsten tip and emits ions under influence of an intense electric field.

General characteristics *Liquid metal ion source*

- The needle and reservoir are coated with gallium– they are welded to the filament which in turn is held on two support legs.
- When the extractor has a potential typically in the range of -5 to -10kV relative to the source, an intense electric field is set up around the tip of the needle. Responding to the electrostatic force, Ga+ ions move to the tip and electrons travel back to the needle.
- High current densities are possible due to small emitter area.

Quadrupole analyser SIMS

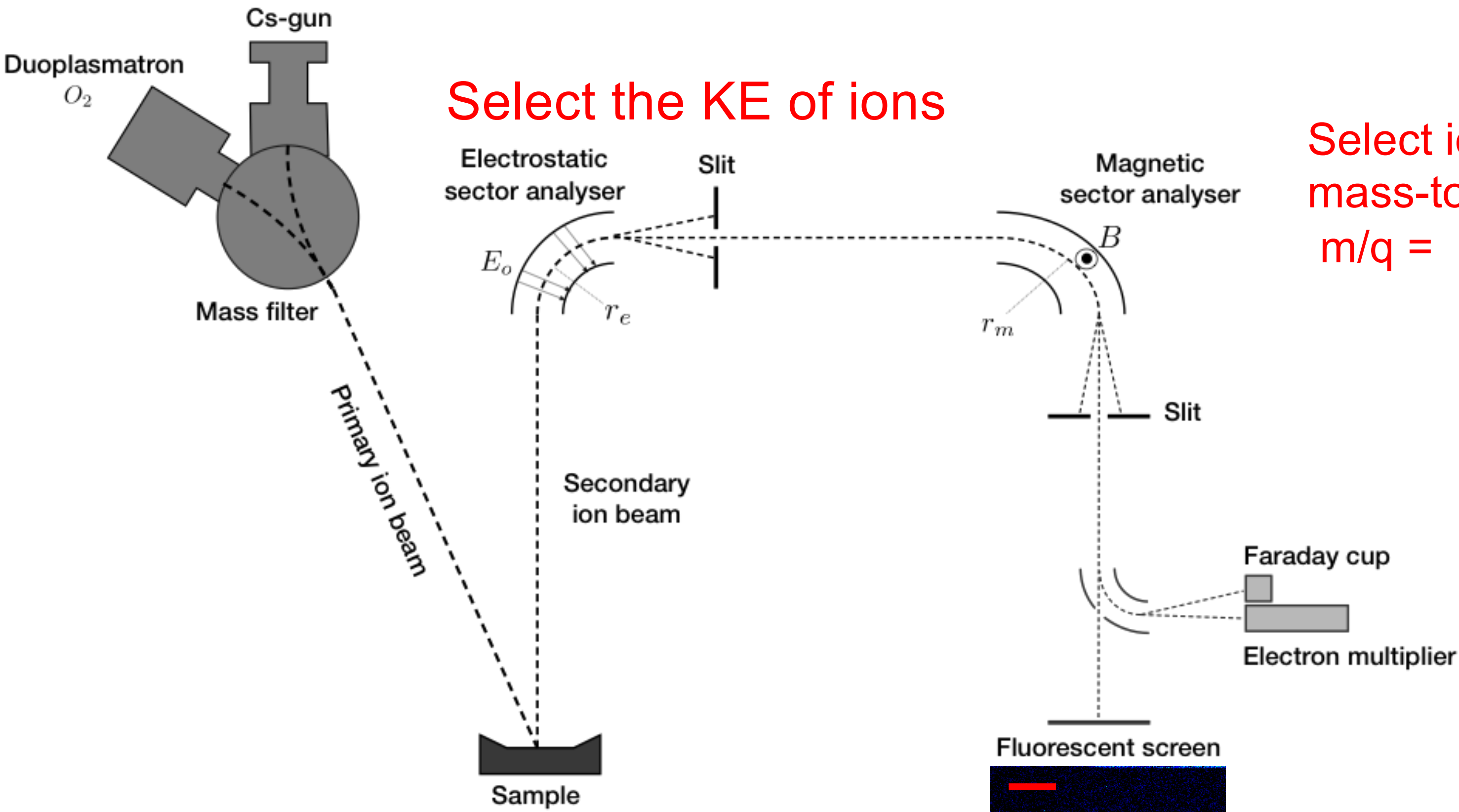


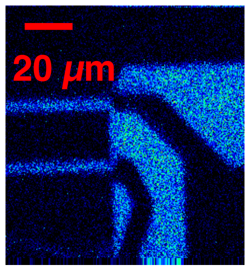


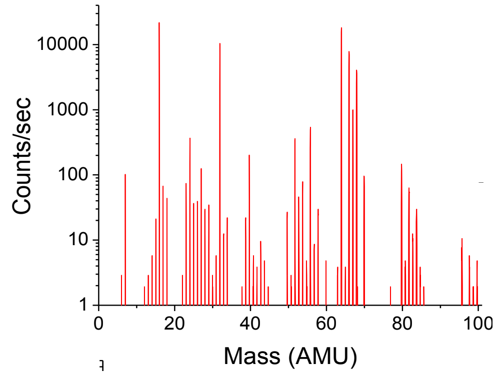
Magnetic sector spectrometer

Select the KE of ions

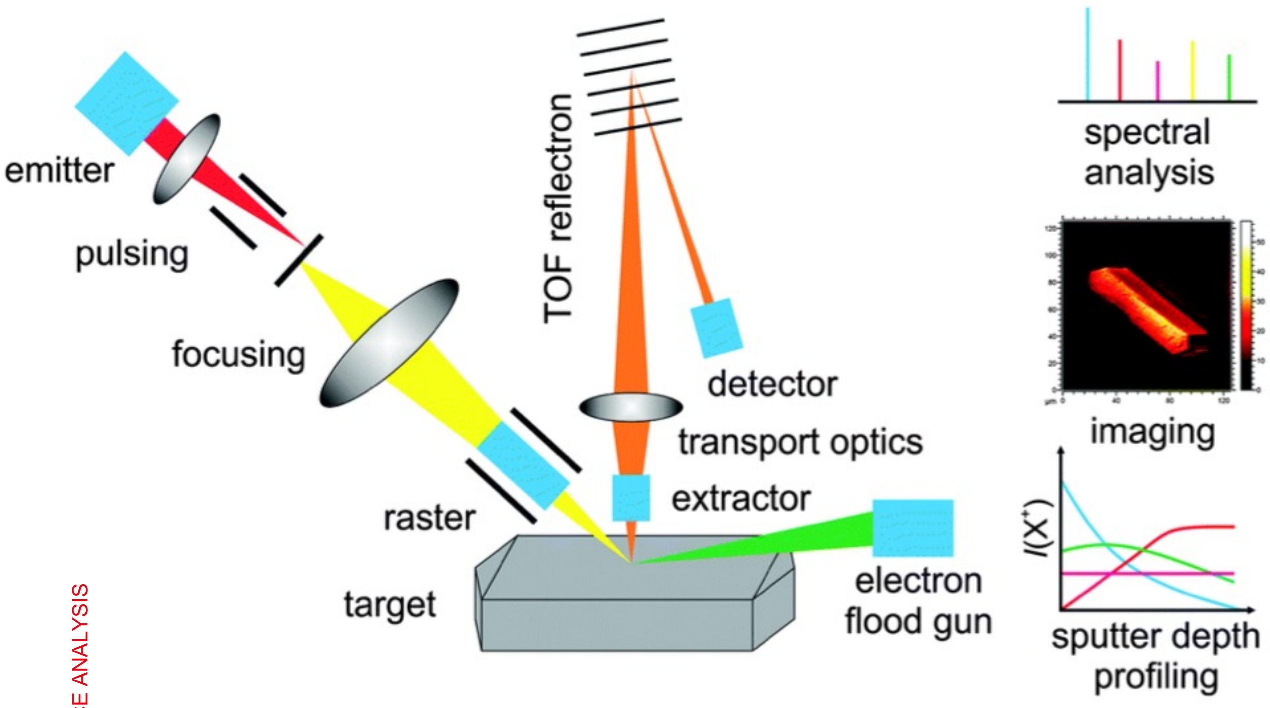
Select ions according to mass-to-charge ratio
$m/q = (r_m B)^2 / (r_e E_0)$







Time of flight SIMS (ToF SIMS)



Time-of-Flight SIMS (ToF-SIMS) uses a pulsed ion beam to remove molecules from the very outermost surface of the sample. These particles are then accelerated into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector (i.e. time-of-flight).

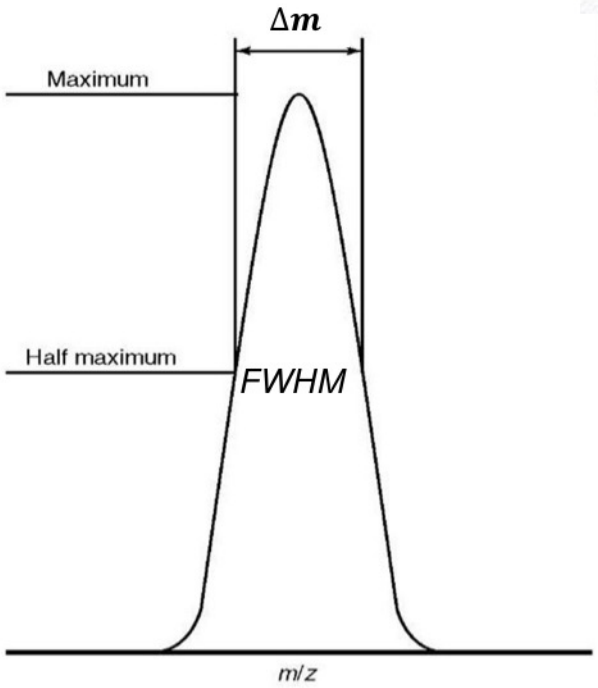
Comparison of SIMS instruments

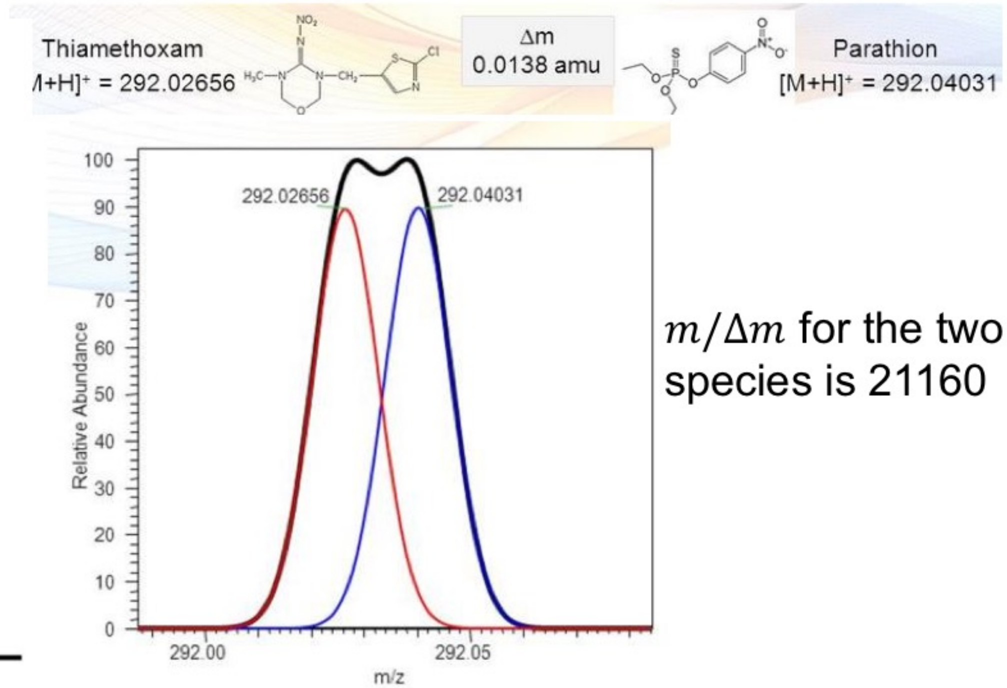
Type	Mass resolution	Mass range (amu)	Transmission	Mass detection	Relative sensitivity
Quadrupole	10^2-10^3	$<10^3$	0.01-0.1	Sequential	1
Magnetic sector	10^4	$<10^4$	0.1-0.5	Sequential	10
Time-of-flight	$>10^3$	$>10^4$	0.5-1.0	Parallel	10’000

Mass resolution

Mass resolution is usually specified in terms of $m/\Delta m$ where m is the mass of the ion and Δm is the FWHM of the detected signal.

– For example, $^{56}Fe^{+}$ and $^{28}Si_2^{+}$ (m/q=55.9349 and 55.9539) require $m/\Delta m$ of
295 for separation while Au and $^{133}Cs^{32}S_2$ (m/q=196.9666 and 196.8496)
0 e $m/\Delta m$ of 1700.





$m/\Delta m$ for the two species is 21160

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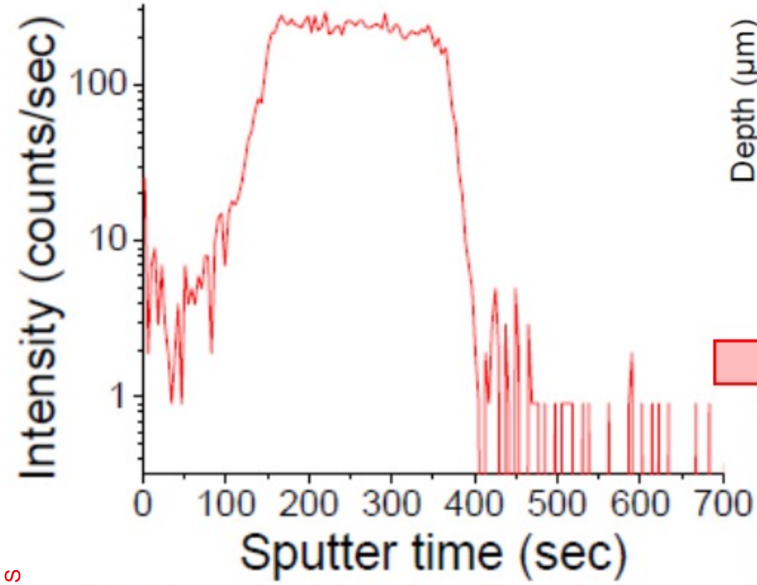
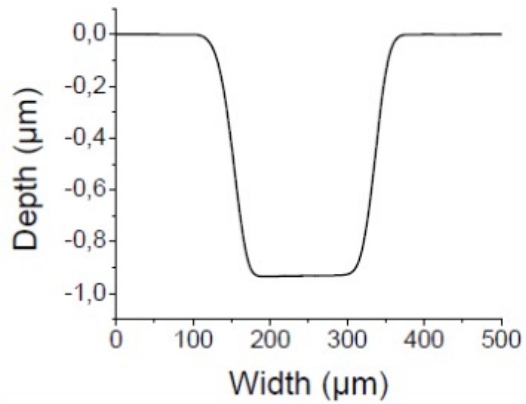
Applications fields of SIMS

- Biology
- Thin film research
- Microelectronics
- Corrosion / Tribology (isotopes)
- ….

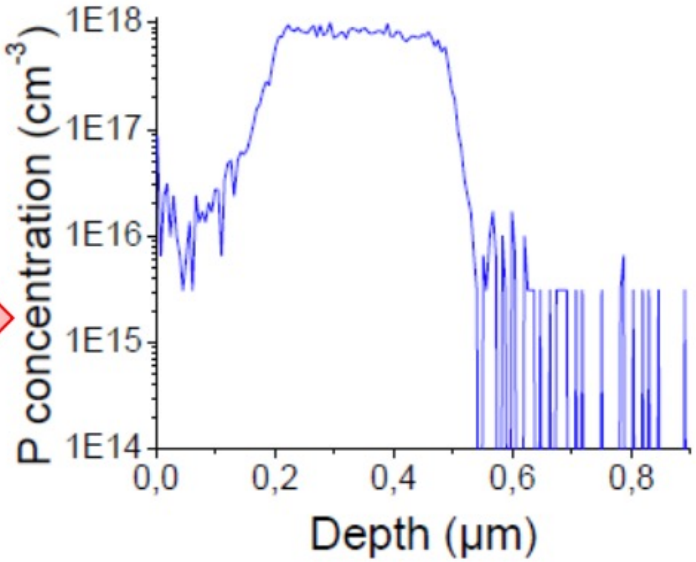
Example of SIMS depth profiling

Phosphorus doped Silicon



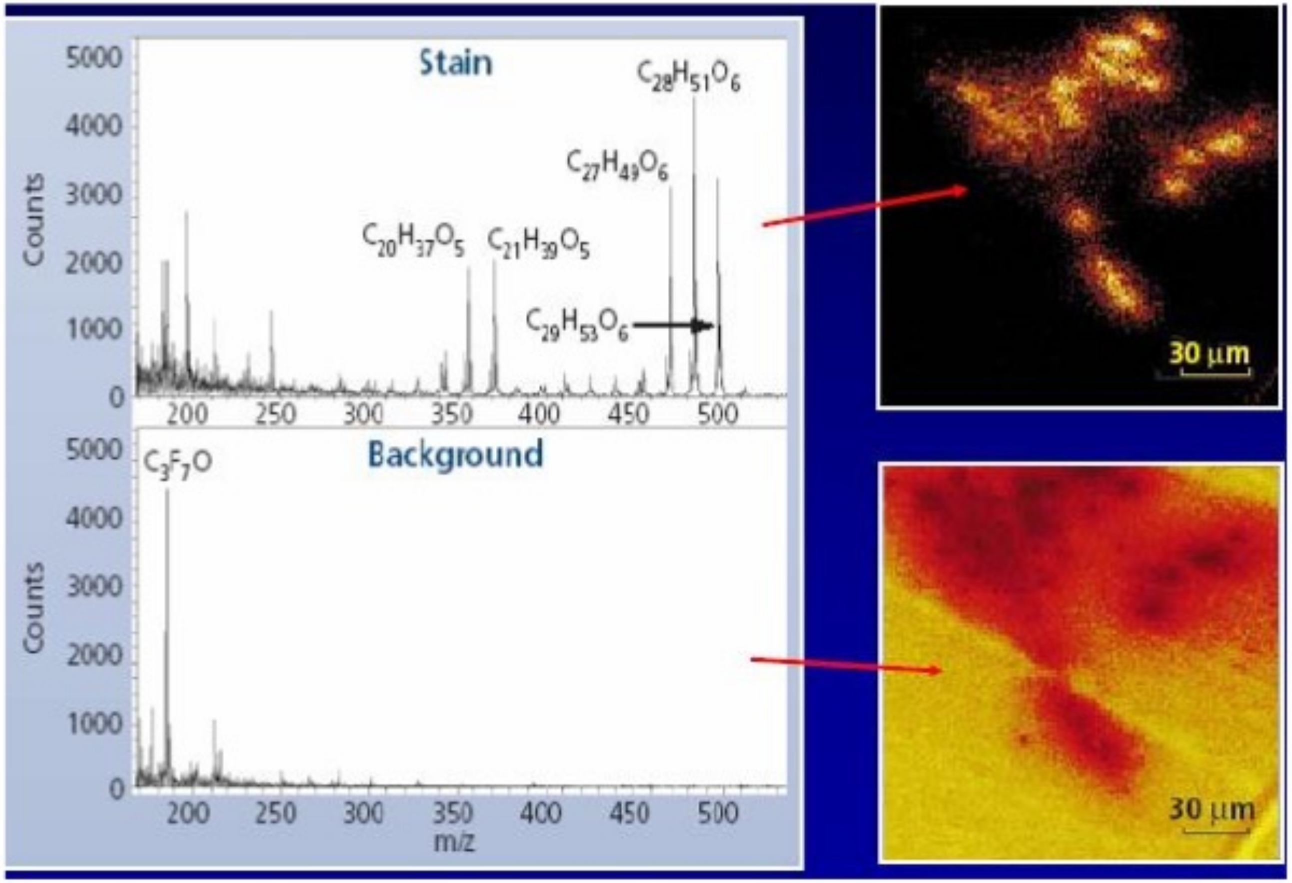


Sputter time: 700 sec
Depth: 9310 Å
Erosion rate:13.3 Å/sec



Conversion of intensity in concentration using RSF calibrated on identical matrix

Example of SIMS surface imaging



Determination of the origin of stains on hard disk.

- SIMS spectrum indicates contamination by lubricant pentaerythritol-tetraoctanoate, $C_{37}\ H_{68}\ O_8$.
- Imaging shows the island of lubricant corresponding to stains
- Background shows residual Freon traces only.

Example of SIMS surface imaging

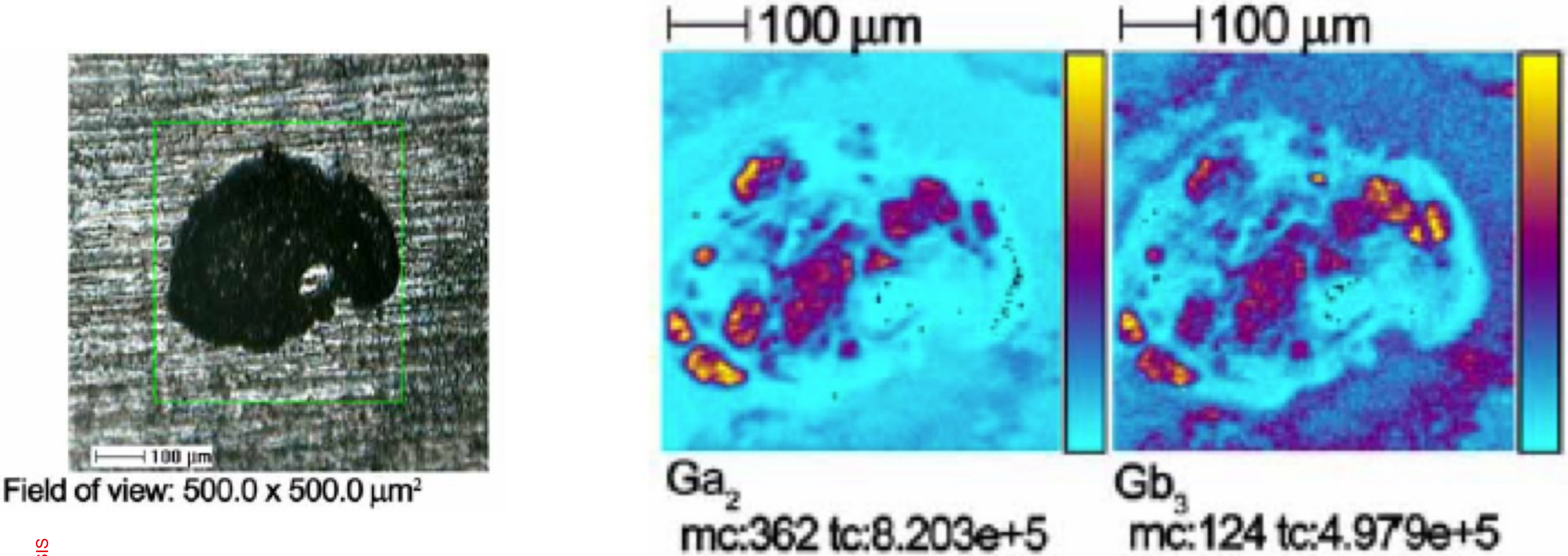


Fig. (11). Optical image and TOF-SIMS images of a section from a kidney biopsy of a patient suffering from Fabry disease showing the accumulations of digalactosylceramide (Ga_2; m/z 880-1030) and globotriaosylceramide (Gb_3; m/z 1040-1200) positive ions. Size 500x500 μm^2, 256x256 pixels, Bi_3^+ primary ions, 10^{12} ions.cm^{-2}.

Current Pharmaceutical Design, 2007, *13*, 3335-3343 3335

Recent Advances in Biological Tissue Imaging with Time-of-Flight Secondary Ion Mass Spectrometry: Polyatomic Ion Sources, Sample Preparation, and Applications

Alain Brunelle* and Olivier Laprévote

More Applications

- In Polymer Technology
- Bio-sciences and bio-materials
- Environmental Sciences
- The monitoring of contamination to the characterization of photographic materials
- Ultra shallow electronic devices

Advantages and weaknesses of SIMS

Advantages

- Excellent sensitivity, especially for light elements
- High surface sensitivity
- Depth profiling with excellent depth resolution (nm) (dynamic)
- Good spatial resolution (<1-25 mm)
- Small analysed volume (down to 0.3mm^3) so little sample is needed
- Information about the chemical surface composition due to ion molecules (static)
- Elements from H to U can be detected with excellent mass resolution

Weaknesses

- Destructive method
- Element specific selectivity
- Standards needed for quantification
- Sample must be vacuum compatible
- Sample must have a flat surface
- High equipment cost (>1M-3M USD)