Summer School: Methods in Surface Science

Secondary Ion Mass Spectrometry

Introduction, technology and examples

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SIMS – INTRODUCTION

SIMS - Introduction

Secondary Ion Mass Spectrometry (SIMS)

- **Mass Spectrometry**: Intensity {number of Ions} = f (m)

  note: spectrometry means the **position** of the signal (mass) **is constant** in contrast to spectroscopy where the **position varies** with the sample (e.g. XPS – binding energy)
- Only **Ions** will be detected
- **Secondary Ions** – also primary ions are involved

SIMS – Introduction, History

- J. J. Thomson (1910): Ion beam on solids ➔ Emission of positive secondary
- Francis Aston (Cambridge, 1919): first MS concept, Nobelprice
- F. Viehböck and R. F. K. Herzog (Universität Wien, 1949): first prototype SIMS
- R. F. K. Herzog und H. Liebl (RCA Laboratories, 1963): another prototype, NASA: Analysis of moon rock
- H. Liebl (GCA Cooperation, Applied Research Laboratories (1967): Ion Microprobe Mass Analyser, double-focusing, commercial

SIMS – Introduction, History 2

- G. J. Slodzian and Raimond Castaing (university Paris-Süd, 1960): development of SIMS, commercial (CAMECA, 1968)
- A. Benninghoven develop „static SIMS“ (1970), quadrupol ….. ToF-SIMS, commercial (IONTOF, 1989)
- SIMS + Orbitrap:
  - K.H. Kingdon (1923): Idea Orbitrap
  - A. Makarov (2000): prototype
  - Thermo Fisher Scientific (2005): commercial
  - IONTOF (2020): commercial SIMS+ Orbitrap

SIMS – Introduction, Video

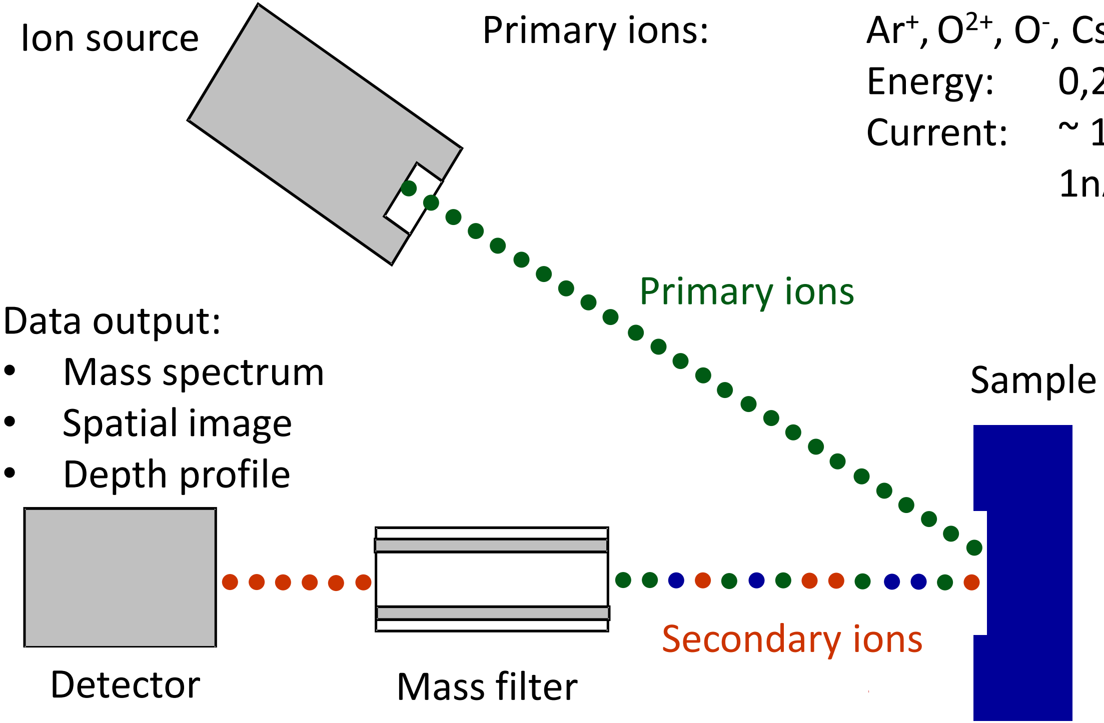
SIMS – Introduction, Basics

Primary ions: Ar^+, O^{2+}, O^-, Cs^+, Ga^+, C_{60}^+ ….

Energy: 0,25 – 30 keV

Current: ~ 1 pA (Static SIMS)

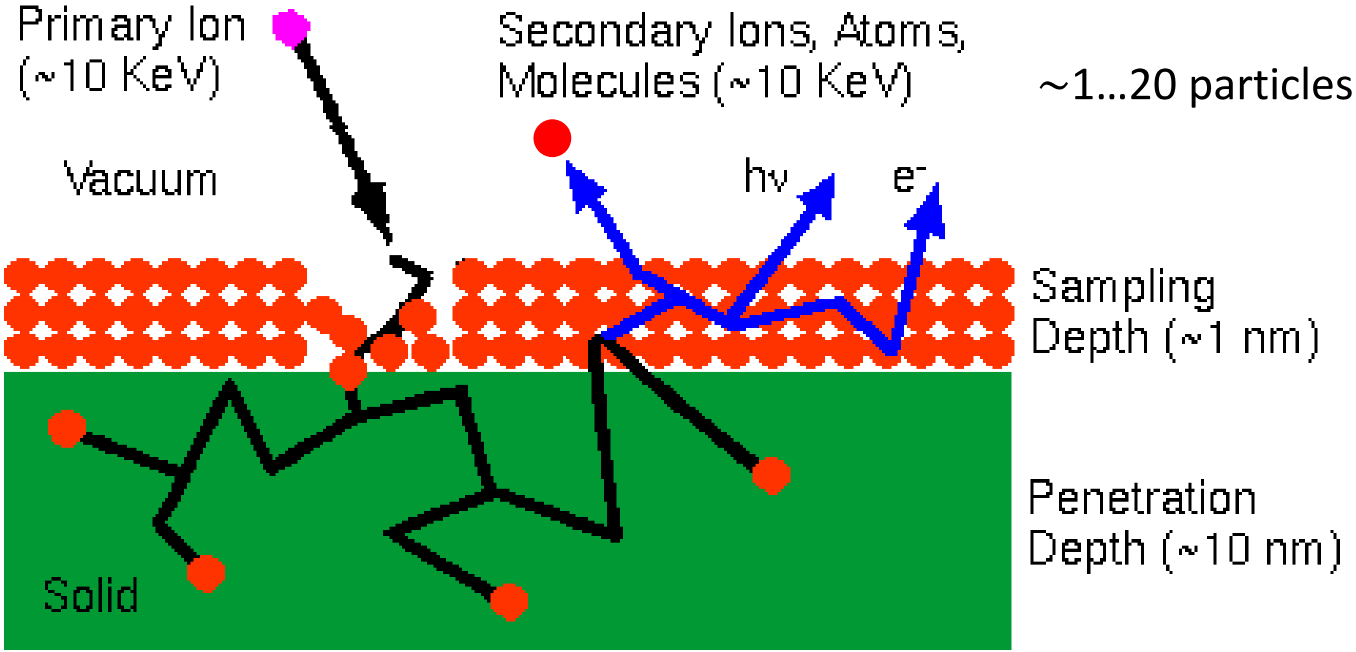
1nA…3 µA (Dynamic SIMS)



Data output:

- Mass spectrum
- Spatial image
- Depth profile

SIMS – Introduction, effects on sample



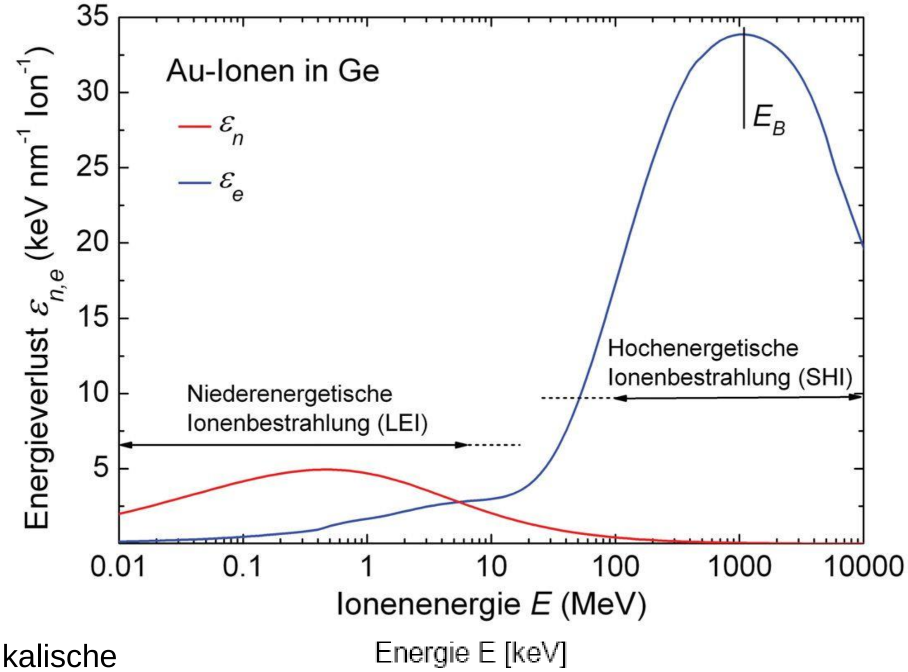
~1…20 particles per Primary Ion

SIMS Theory: Sputtering Effects, http://www.eag.com/mc/sims-sputtering-effects.html (modified)

SIMS – EFFECTS ON SAMPLE

SIMS – Primary ion energy

- *elastic energy transfer* (d*E*/d*x*)$_n$: elastic collisions with atomic nucleus
- *inelastic energy transfer* (d*E*/d*x*)$_e$: inelastic interaction with electrons (excitation and ionization)



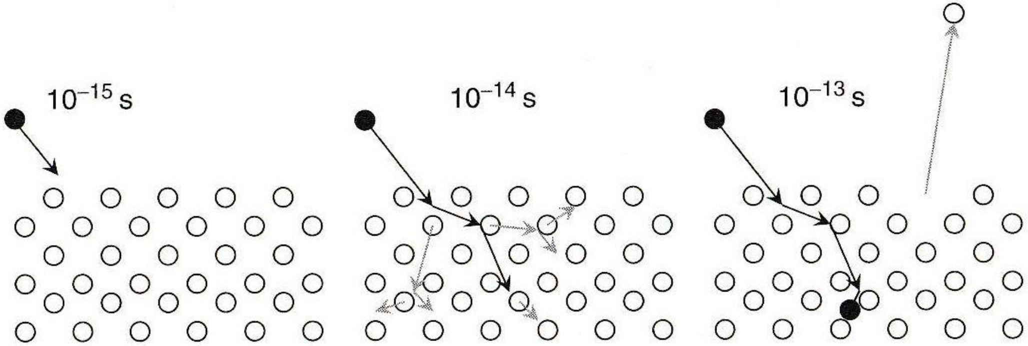
Schatz/Weidinger, Nukleare Festkörperphysik – Kernphysikalische Messmethoden und ihre Anwendungen, Vieweg-Teubener, 1997.
Steinbach, Dissertation, Jena 2012

SIMS – Sputtering, general

Velocity of primary Ions ~ 100…400 km/s (single ion)

Time to overcome 100 nm ~ 0.3…0.8 ps

Average distance of primary ions (100 nA, ideal focus) ~ 100…600 nm



Simplified illustration of sputtering process (timing)

Paul van der Heide, Secondary ion mass spectrometry, Figure 1.3

SIMS – Sputtering regime

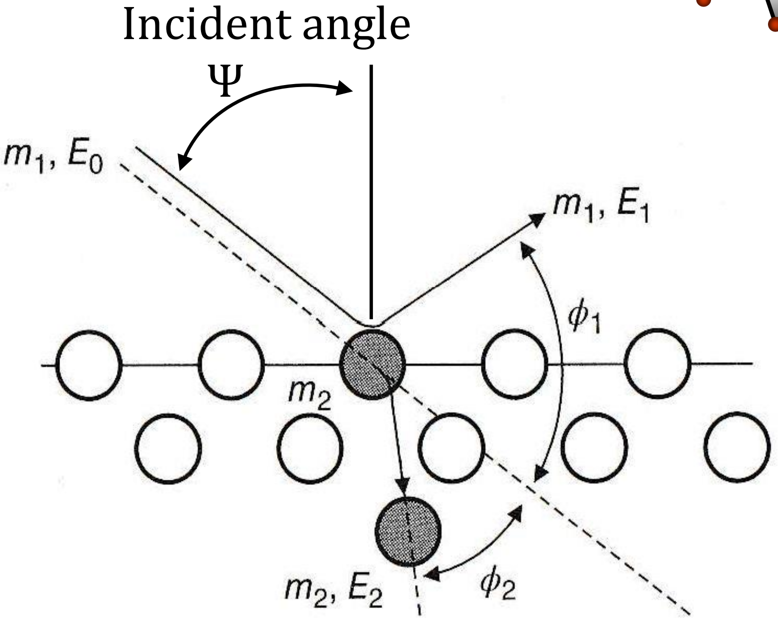
3 regimes depending on energy, mass of primary ion (M_i) and target (M_t):

- knock-on regime: small energy, $M_i << M_t$, very short cascade
- linear cascade regime: medium energy, $M_i << M_t$, collisions between displaced atoms neglectable
- spike regime: high energy and/or heavy ions, many atoms in movement (nearly all in target area), resulting in high temperature, melting or evaporation

→Linear cascade model (Sigmund, useful for atomic or small ion projectiles; other models for big primary ions, multiple charged primary ions, soft material, sputtering of large molecules)

Sigmund P., Phys Rev 1969, 184

SIMS – Sputtering, general



Sputtering depends on:

- Energy dissipated during impact
- Angle Ψ (relative to surface normal)
- Masses (primary and sputtered)
- Surface binding energy
- Density of the target

Elastic collisions ➔ Kinetic sputtering (similar billiard ball game)

Paul van der Heide, Secondary ion mass spectrometry, Figure 3.3 (modified)

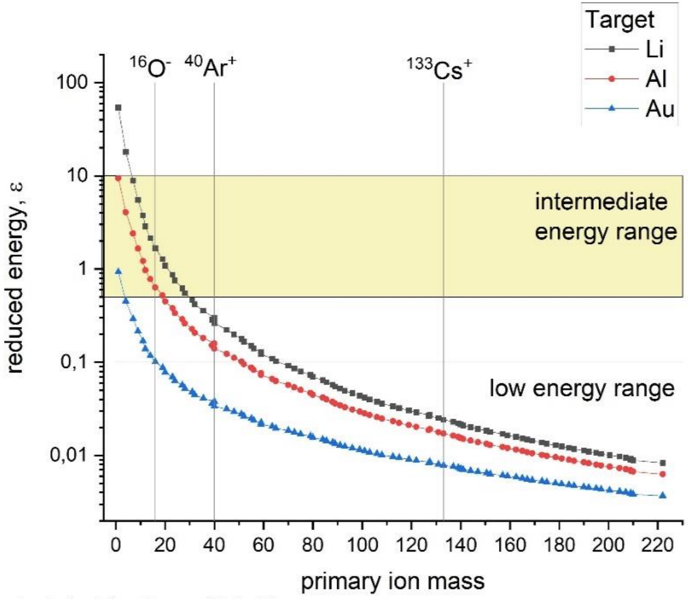
SIMS – Sputtering, mathematical description

Sputtering depends on many parameters

Reduced energy ε (in SI units)

$$\varepsilon = \frac{32.5 \cdot M_t \cdot E_p}{(M_i + M_t) \cdot Z_i \cdot Z_t \cdot \sqrt{\left(Z_i^{2/3} + Z_t^{2/3}\right)}}$$

M	molar mass
Z	atomic number
E_p	primary ion energy (given in [keV])



calculated for Ep = 10 keV

Benninghoven et al, Secondary Ion Mass Spectrometry, ISBN 0-471-01056-1 (1987)

SIMS – Sputtering, mathematical description

$$\text{Sputter Yield: } Y = \frac{\text{Number of secondary particles}}{\text{Primary ion}}$$

$$Y_{tot} = 4.2 \cdot 10^{14} cm^{-2} \cdot \frac{\alpha \cdot S_n(E)}{U_S}, \qquad \alpha \cong 0.15 + 0.13 \cdot {}^{M_t}/_{M_i}, \qquad S_n(E) \cong \frac{{}^1/_2 \cdot ln(1+\varepsilon)}{(\varepsilon + 0.14 \cdot \varepsilon^{0.42})}$$

U_s	surface binding energy, given in [eV]
α	dimensionless factor depending on masses and incident angle, approximation [Zalm] for $\Psi = 0$ (perpendicular to surface) and a wide range of M_t/M_i
$S_n(E)$	nuclear stopping cross section [eVcm^2] , approximation [Wilson]

Benninghoven et al, Secondary Ion Mass Spectrometry, ISBN 0-471-01056-1 (1987), Sigmund, Phys. Rev., 184, 383, (1969)
approximations according to: Zalm, J. Appl. Phys. 54, 2660, (1983); Wilson et al Phys. Rev. B, 15, 2458, (1977)

SIMS – Sputtering, mathematical description

Approximation for small primary energy $U_S < E_p < 1\ \mathrm{keV}$ and $\Psi = 0$

$$Y_{tot} = \frac{2}{3} \cdot \alpha \cdot \frac{M_i M_t}{(M_i + M_t)^2} \cdot \frac{E_p}{U_S}, \qquad \alpha \cong 0.15 + 0.13 \cdot {}^{M_t}/_{M_i}$$

U_s	surface binding energy given in [eV]
E_p	primary ion energy , given in [keV]

➔ $Y \propto E_p$, *sputter yield depends on* M_i

Benninghoven et al, Secondary Ion Mass Spectrometry, ISBN 0-471-01056-1 (1987),
Hamer et al, Anal. Chem., 308, 287, (1981)

SIMS – Sputtering, mathematical description

Alternatively, for $\varepsilon < 0.028$ (smaller) and $0.2 < Z_t/Z_i < 5$

$$Y(E_p) \cong \frac{1.9}{U_S} \cdot \sqrt{\frac{Z_t}{0.5 \cdot \left[\left({}^{Z_i}/_{Z_t}\right) + \left({}^{Z_t}/_{Z_i}\right)^{{}^2/_3}\right]}} \cdot \left(\sqrt{E_p} - 0.09 \cdot \sqrt{U_S}\right)$$

U_s	surface binding energy given in [eV]
E_p	primary ion energy , given in [keV]

➔ $Y \propto \sqrt{E_p}$, almost independent from primary ion, accuracy 10…20 %

Benninghoven et al, Secondary Ion Mass Spectrometry, ISBN 0-471-01056-1 (1987),
Zalm, Vac. Sci. Technol. B 2, 2, (1984)

SIMS – Sputtering, Sputter Yield experimental 1

Sputter Yield,

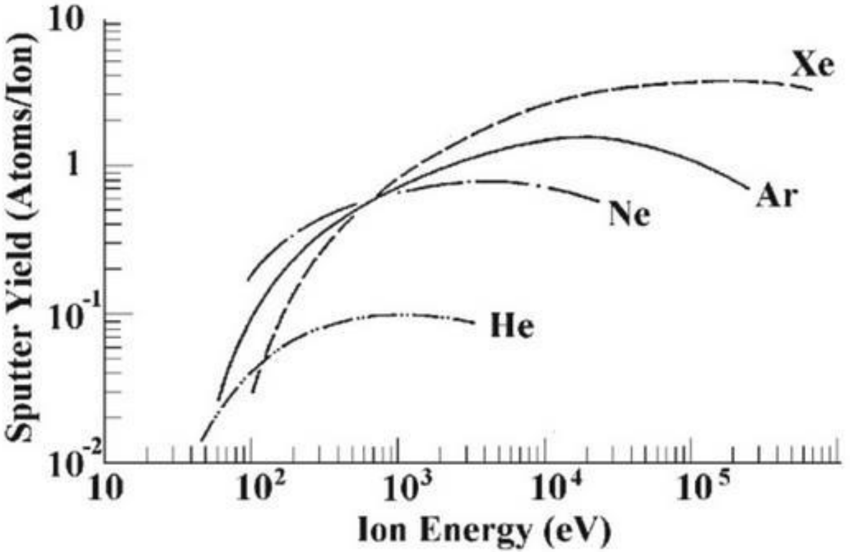
mathematical description difficult

Experimental facts:

Y ↑ if M_i ↑ (if $E_p > \sim 1\ keV$)

Y ↑ if E_p ↑ (up to maximum ~ keV)

Maximum move to higher energy for M_i ↑



Prof YU Kin Man, Instrumental Methods of Analysis and Laboratory Secondary ion mass spectrometry, see also

Paul van der Heide, Secondary ion mass spectrometry

Sputter yields of silicon as a function of ion energy for noble gas ions at normal incidence.

SIMS – Sputtering, Sputter Yield experimental 2

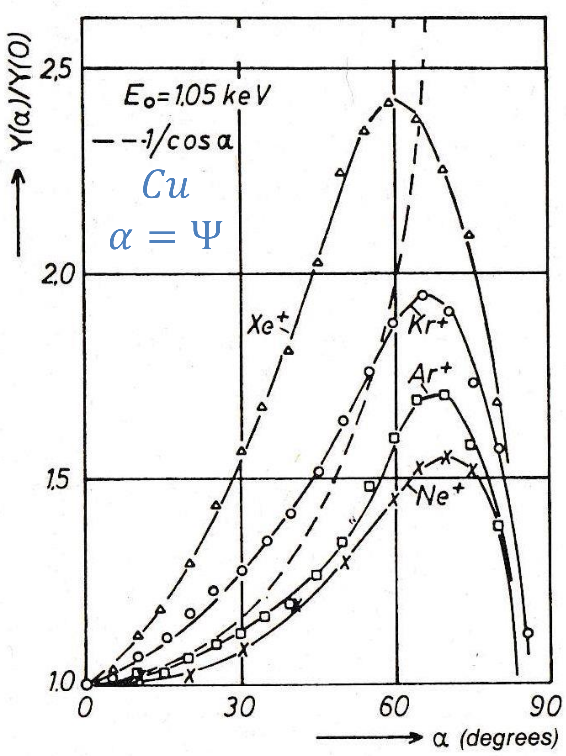
Sputter Yield maximum 60…80°

Depends on M_i and E_p

Polycrystaline or amorph sample

$$Y \propto \frac{1}{\cos\Psi}, \Psi < 75° \text{ (Si) [Mash64]}$$

At high angle reflection of prim. ions



Benninghoven et al, Secondary Ion Mass Spectrometry, ISBN 0-471-01056-1 (1987), Fig. 2.109 modified

E. S. Mashkova et al, Soviet Physics – Technical Physics USSR 9, 1601 (1965)

SIMS – Sputtering, Effects 1

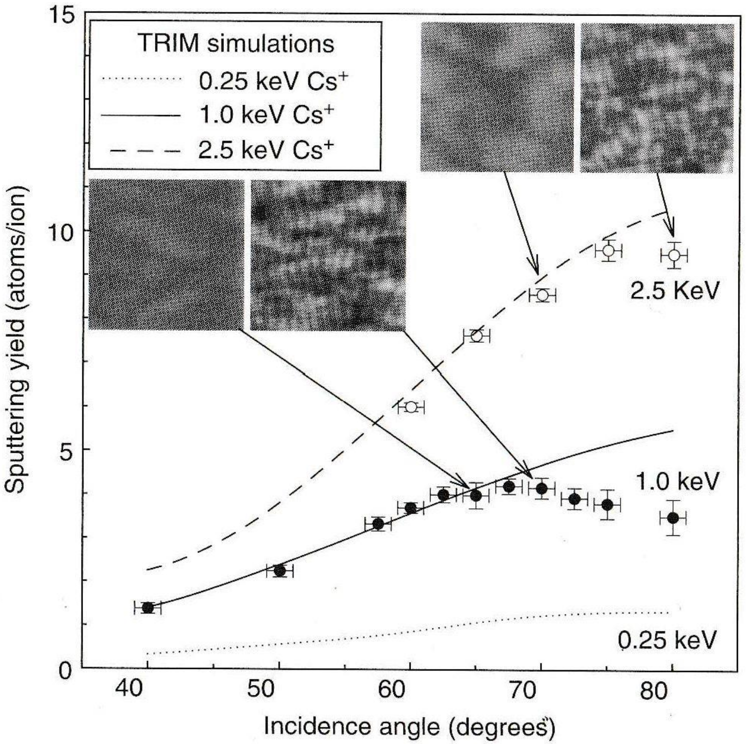
Sputtering –

influence on surface rougthness

Prim. Ion Cs$^+$, Si atomically smooth

Comparison of **TRIM** simulation with Measured data (symbols)

AFM images of crater base for selected measurements



Paul van der Heide, Secondary ion mass spectrometry Figure 3.17

SIMS – Sputtering, Effects 2

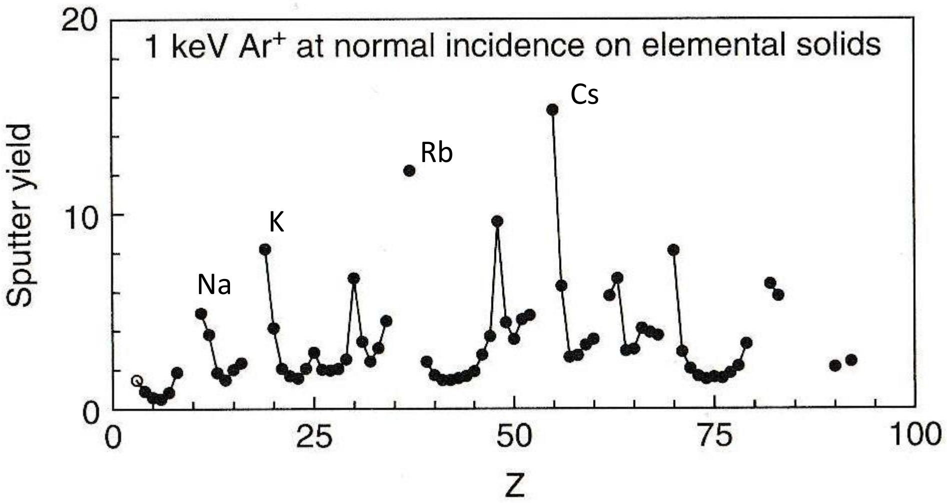
Influence of material

Sputter Yield depends on:

- Masses (both)
- Collision cross section
- Binding energy

➔ Oxides vs. base metal

➔ Preferential sputtering



Prim. Ion Ar^+ , 1 keV, normal incidence, elemental substrates

Paul van der Heide, Secondary ion mass spectrometry
Figure 3.18, modified

SIMS – Primary reflections

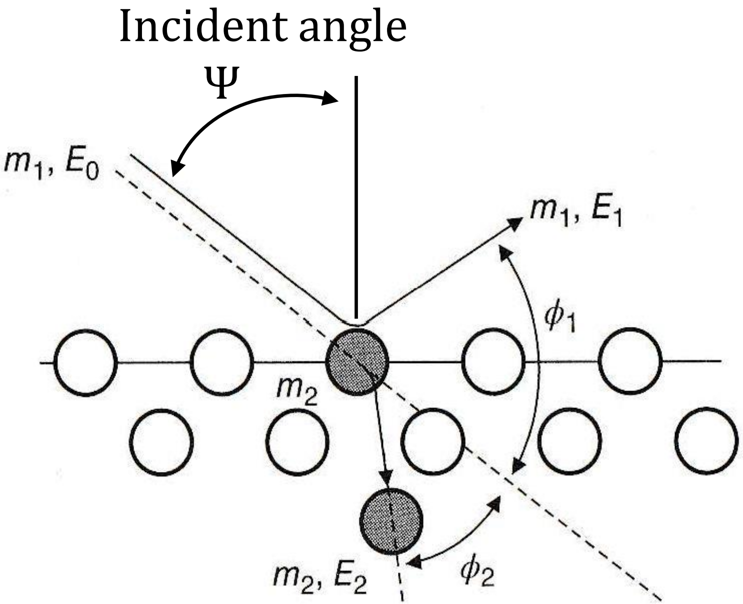
Reflected primary ions

See RBS (eq. Valid for $M_i << M_t$)

Differential cross section, fixed Φ_1

$$\frac{\partial\sigma}{\partial\Omega} = \left(\frac{1}{4\pi\varepsilon_0}\frac{Z_i Z_t e^2}{4E_p}\right)^2 \frac{1}{\left[\sin\left(\frac{\Phi_1}{2}\right)\right]^4}$$

➔ $Y_{refl} \propto E_p^{-2}$



Schatz/Weidinger, Nukleare Festkörperphysik – Kernphysikalische Messmethoden und ihre Anwendungen, Vieweg-Teubener, 1997, Paul van der Heide, Secondary ion mass spectrometry, Fig. 3.3 modified

SIMS – Primary reflections

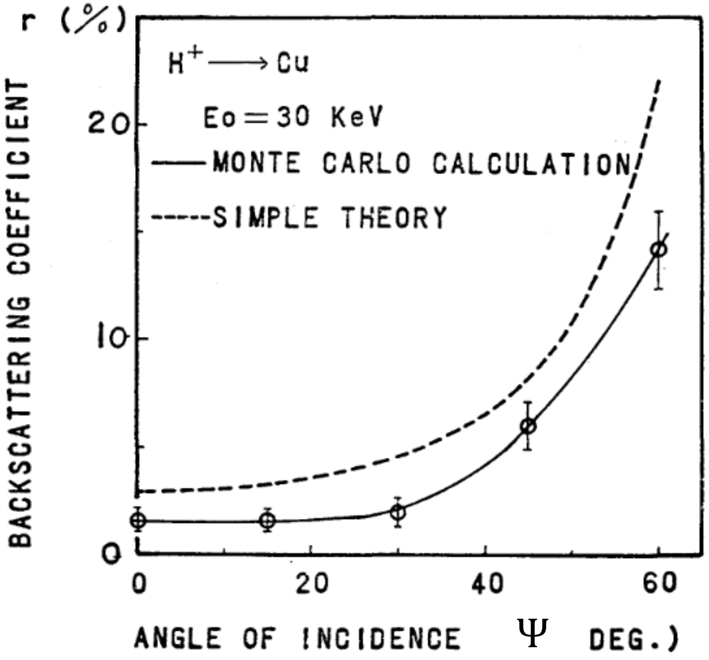
Reflected primary ions

Reflection yield

low for small incidence angle

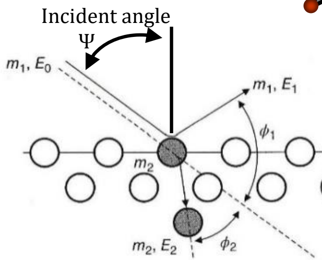
noticeable for > 50° (see sputter yield)

$$r \triangleq Y_{refl} \cdot 100\ \%$$



Ishitani_1972_Jpn._J._Appl._Phys._11_125, Fig.7 modified

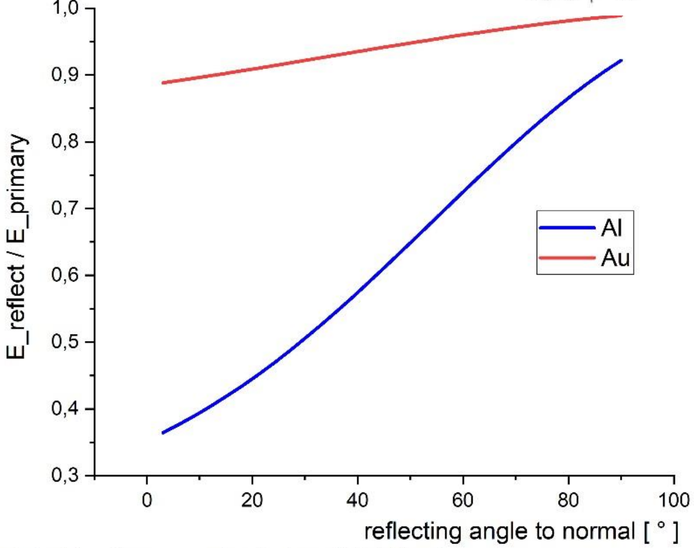
SIMS – Primary reflections, Energy



Reflected primary ions

Energy of the reflected ion (M_r):

$$\frac{E_{reflect}}{E_{primary}} = \left\{\frac{\cos\Phi_1 \pm \sqrt[2]{\left[\left({}^{M_r}/_{M_i}\right)^2 - \sin^2\Phi_1\right]}}{\left[1+\left({}^{M_r}/_{M_i}\right)\right]}\right\}$$



calculated for Oxygen primaly ion, 60° inident angle

Paul van der Heide, Secondary ion mass spectrometry, (3.2)

SIMS – Implantation

Projected Range R_p

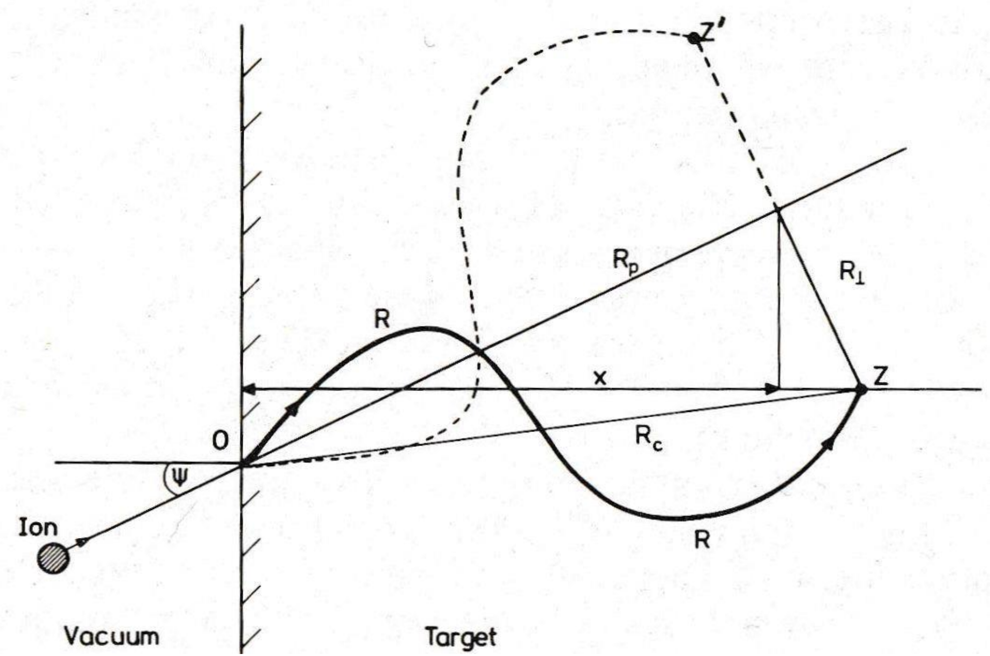
Average depth of implanted ions

$$R_p = f\left(E_p, M_1, M_2, Z_1, Z_2, \Psi\right)$$

LSS theorie

SRIM simulation

$$R_{p,\perp} \propto \cos\Psi$$



LSS: J. LINDHARD, M . SCHARFF AND H . E . SCHIØTT, Mat. Fys. Medd . Dan. Vid. Selsk . 33, no.14 (1963)

Benninghoven et al, Secondary Ion Mass Spectrometry, ISBN 0-471-01056-1 (1987), Fig. 2.6

SIMS – Implantation

Projected Range R_p at **low energy**

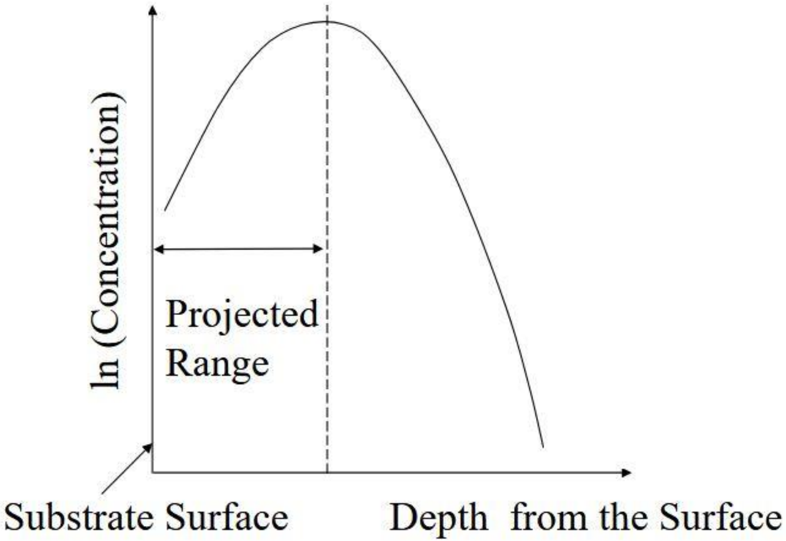
$(0.002 < \varepsilon < 0.1)$

$$R_p = C_l \cdot M_t \cdot \left\{ \frac{\left(Z_i^{2/3} + Z_i^{2/3} \right)}{Z_i \cdot Z_t} \cdot E_p \right\}^{2/3}$$

$C_l = \mathrm{f}\,(M_t / M_i)$, $0.12 < C_l < 0.23$

E_p given in [keV]

R_p results in [µg/cm²] $\propto \boldsymbol{E_p^{2/3}}$



LSS: J. LINDHARD, M . SCHARFF AND H . E . SCHIØTT, Mat. Fys. Medd . Dan. Vid. Selsk . 33, no.14 (1963), Hong Xiao, www2.austin.cc.tx.us/HongXiao/Book.htm, Benninghoven et al, Secondary Ion Mass Spectrometry, (1987)

SIMS – Implantation

Projected Range R_p at **intermediate energy**

($0.5 < \varepsilon < 10$)

$$R_p = C_i \cdot M_t \cdot \frac{\sqrt{\left(Z_i^{2/3} + Z_t^{2/3}\right)}}{Z_i \cdot Z_t} \cdot E_p$$

$C_i = \mathrm{f}(M_2/M_1)$, $0.45 < C_i < 0.9$

E_p given in [keV]

R_p results in [$\mu g/cm^2$] $\propto \boldsymbol{E_p}$

Note:

$$R_p[\,m\,] \cdot 10^{-8} = \frac{R_p[\,\mu g/cm^2]}{\rho\,[\,g/cm^3]}$$

ρ density

LSS: J. LINDHARD, M . SCHARFF AND H . E . SCHIØTT, Mat. Fys. Medd . Dan. Vid. Selsk . 33, no.14 (1963),
Benninghoven et al, Secondary Ion Mass Spectrometry, (1987)

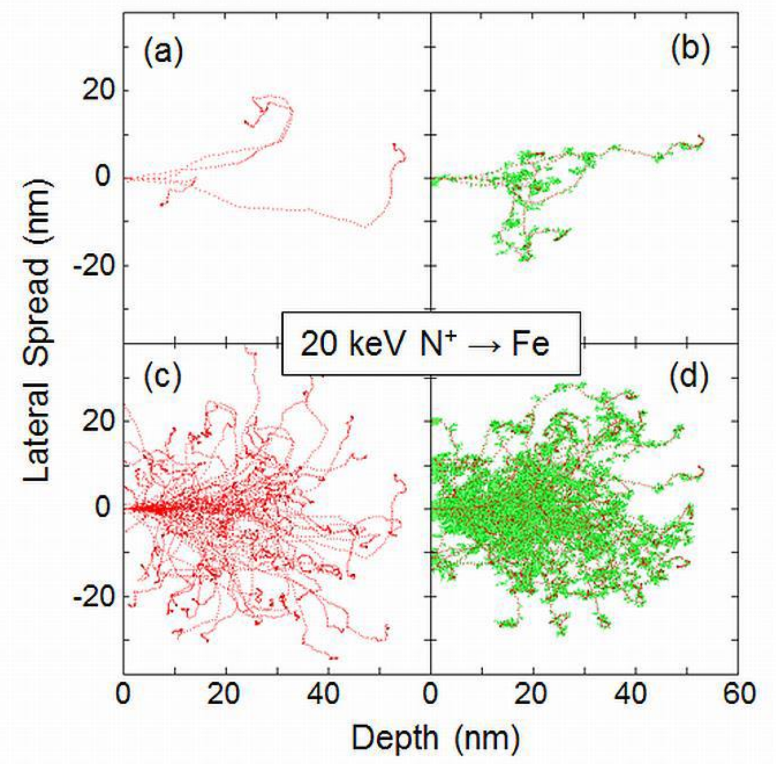
SIMS – Implantation and mixing

Projected Range of N^+ Ions and

Recoils (mixing) of target material (Fe)

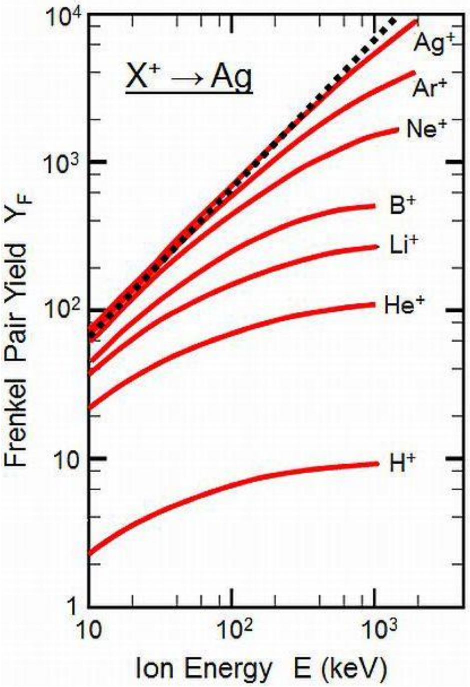
Simulations using TRIM[69], $\Psi = 0°$

Also surface contaminations involved!



Wolfhard Möller, FUNDAMENTALS OF ION-SOLID INTERACTION - A Compact Introduction, HZDR-073 . ISSN 2191-8708

SIMS – Damaging



Frenkel pair (displaced atom, resulting in interstitial and vacancy)

Simple model, hard-sphere collisions by Kinchin and Pease

$$Y_{FP} \cong \frac{E_p}{2U_D} \propto E_p \qquad E_p < 100\,keV,\ Z_i > 20$$

U_D displacement threshold energies, ~ 7…50 eV

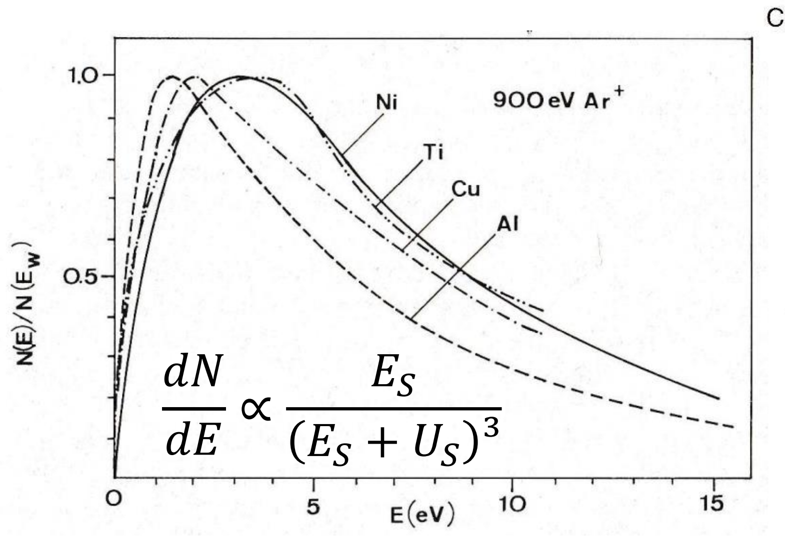
Calculated for $\Psi = 0$

$Y_{FP}\downarrow$ if $M_i\downarrow$ and if $\Psi\uparrow$

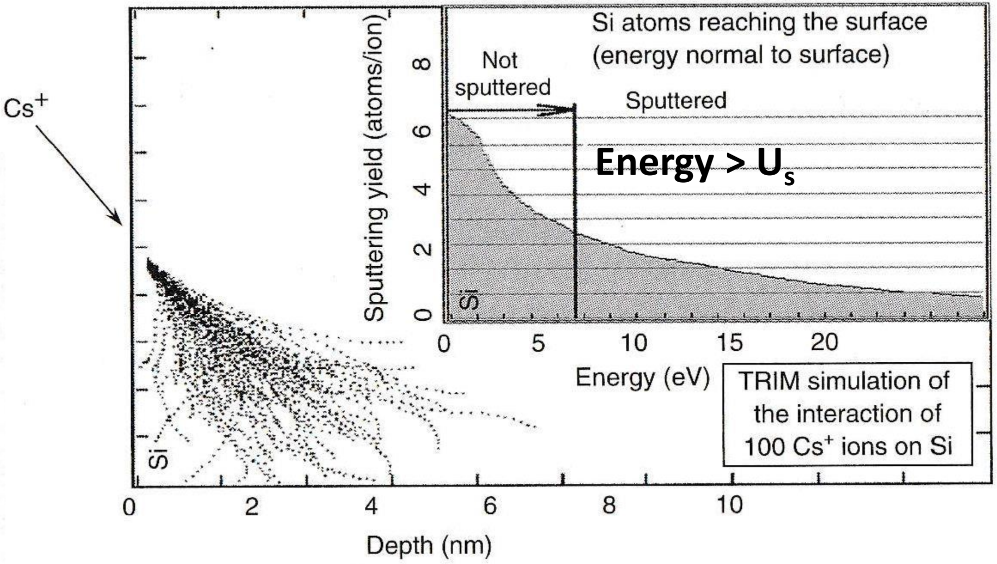
Kinchin, G.H., Pease, R.S.: The displacement of atoms in solids by radiation. Rep Prog Phys 18, 1-51 (1955), Konobeyev et al. / Nuclear Energy and Technology 3 (2017) 169–175, Möller, FUNDAMENTALS OF ION-SOLID INTERACTION - A Compact Introduction, HZDR-073 . ISSN 2191-8708

SIMS – Sputtering, sputtered particles

Energy distribution of sputtered particles



$$\frac{dN}{dE} \propto \frac{E_S}{(E_S + U_S)^3}$$



TRIM simulation, 100 Ions, 1keV Cs$^+$, 60°

Inset: energy distribution Si recoils,

surface binding energy U_S (Si) = 4.7 eV

Benninghoven et al, Secondary Ion Mass Spectrometry, (1987), Fig. 2.113 modified, Oechsner, Z. Phys. **238**, 433 (1970),

Paul van der Heide, Secondary ion mass spectrometry, Figure 3.8

SIMS – Sputtering, other effects

Channelling (crystalline samples)

Swelling

Diffusion

Segregation

Amorphization

Re-crystallization

Paul van der Heide, Secondary ion mass spectrometry

SIMS – Sputtering, conclusions 1

“best sputtering conditions for SIMS”

	Sputter yield (large)	Projected range (small)	Damaging (small)	Reflection (small)
Angle Ψ	$\Psi\uparrow, \Psi \lesssim 60^\circ$	$\Psi\uparrow, \Psi < 90^\circ$	$\Psi\uparrow, \Psi < 90^\circ$	$\Psi\downarrow$
Energy E_p	$\text{Near max.}, E_p \sim keV$	$E_p\downarrow$	$E_p\downarrow$	$E_p\uparrow$
Mass M_i	$M_i\uparrow, E_p > 1\ keV$	$M_i\uparrow, \text{weak dep.}$	$M_i\downarrow$	$M_i\uparrow$

Valid for single primary ions

Molecular primary ion (cluster ion) ? ➔ Linear cascade model not valid

SIMS – Sputtering, Molecular primary ion

Molecular primary ion sputtering (simple view, n Number of elemental parts):

E_p in keV range, binding energy in eV range

➔ Cluster separated into n parts with $\boldsymbol{E_{p,single} \cong \frac{E_p}{n}}$ and $\boldsymbol{M_{i,single} \cong \frac{M_i}{n}}$

Assuming small deviations from Linear cascade model (n not to large)

Sputter yield = f(E_p) near maximum, weak dependence on Energy

➔ $\boldsymbol{Y(Cluster) \lesssim n \cdot Y(single)}$

Each elemental part creates own cascade with smaller energy

➔ $\boldsymbol{R_{p,cluster} \cong \frac{R_{p,single}}{n}}$ or $\boldsymbol{R_{p,cluster} \cong \frac{R_{p,single}}{n^{2/3}}}$, depending on energy

Damaging should be smaller (Mass smaller)

Reflection is somewhat higher (Energy smaller)

Note:
simple view,
routh approximation

SIMS – Sputtering, Sputter rate

Depth removed by sputtering divided by time,

depends on sputter yield Y and primary current I_p and sputtered area A_S

number of implanted ions ignored

$$R = \frac{u}{e_0} \cdot Y \cdot \frac{\bar{M}}{\rho} \cdot \frac{I_p}{A_S}$$

u	unified atomic mass unit
e_0	elementary charge
$\bar{M}$	average M of sputtered particles
ρ	density of sputtered material

Example: Si

$M = 28, I_p = 100\, nA, Y \approx 2$

$\rho = \ 2.3\, {}^{g}/_{cm^3}, A_S = (250\ \mu m)^2$

$$R \approx 1400\ {}^{nm}/_{h}$$

SIMS – Sputtering, Ionization rate and Ion Yield

Note: SNMS

M^q, Selected particle M, selected charge q (+ or – n)

Ionization rate $\alpha(M^q)$, Number of ionized particles/sputtered particle M

Ion Yield $Y(M^q)$, Number of ions of a selected ion per primary Ion

$$Y(M^q) = Y \cdot X_M \cdot \alpha(M^q)$$

X_M mole fraction

Note: Effects like preferential sputtering ignored.

"The formation/survival of secondary ions is less well understood. (…) As the secondary ion yield variations can span five orders of magnitude or more, quantification is often difficult." Paul van der Heide, Secondary ion mass spectrometry p. 46

SIMS – Important parameter 1

- Primary ion energy: E_p [keV]
- Primary ion current: I_p [nA], (1 nA ≙ 6.28E9 ions/s)
- Projected Range: Rp [nm]
- Sputter Yield: Y, Number of secondary particles / Primary ion
- Sputter rate: R [Å/s], [nm/min], sometimes given $R^* = R / I_p$ [nm/(min nA)]
- Ionization rate $\alpha(M^q)$: Secondary ions/Number of sputtered particle M^q
- Ion Yield: $Y(M^q)$, $\quad Y(M^q) = Y \cdot X_M \cdot \alpha(M^q)$

SIMS – INSTRUMENTATION

SIMS – Ion source

General requirements

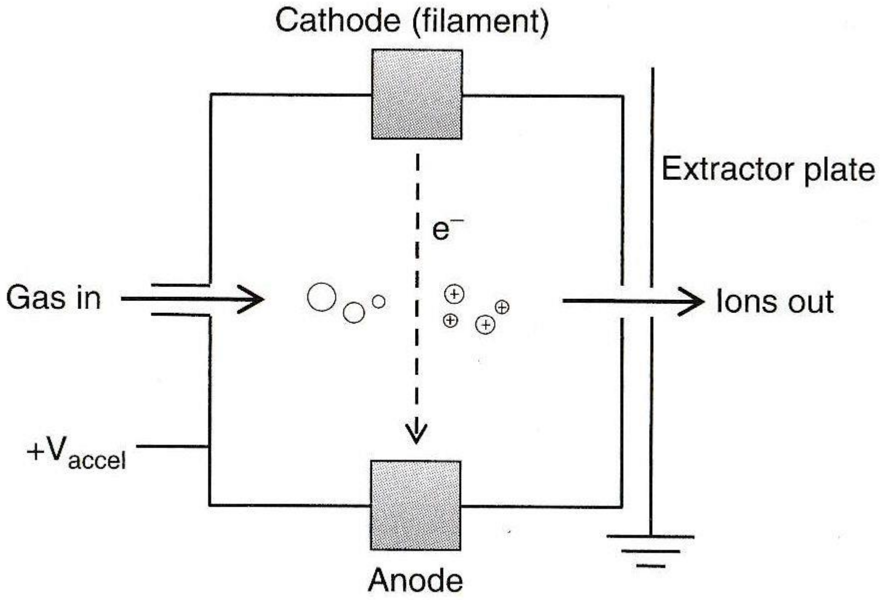
- Tuneable current I_p (pA-range and/or 100 nA-range)
- Stable operation (constant I_p during measurement)
- Small variation in energy (ΔE_p)
- Small source diameter
- (variation of ion type)
- (Pulse mode)
- Long operation time
- Easy maintenance

SIMS – Ion source

Electron impact source

- positive ions
- any inert gas
- molecular ions ($O_2^+, Ar_n^+, C_{60}^+, SF_5^+, C_{24}H_{12}^+$)
- multiple charge (C_{60}^{2+}, C_{60}^{3+})
- long lifetime (hot cathode)

- bad focus

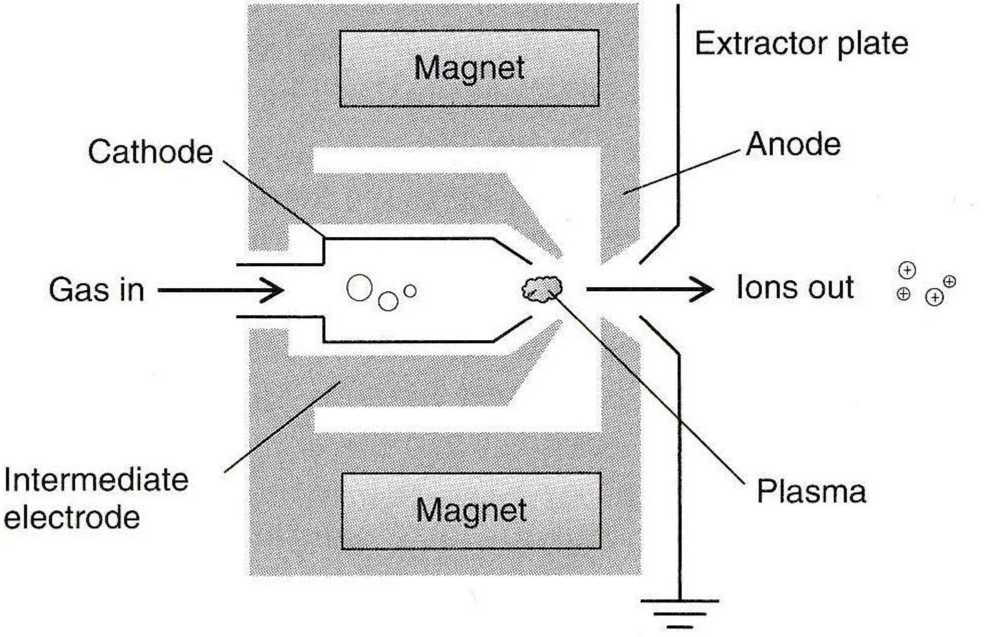


Paul van der Heide, Secondary ion mass spectrometry, Fig. 4.4

SIMS – Ion source

Duoplasmatron

- any inert gas
- oxygen positive and negative (O^-, O_2^+)
- easy maintenance
- short lifetime



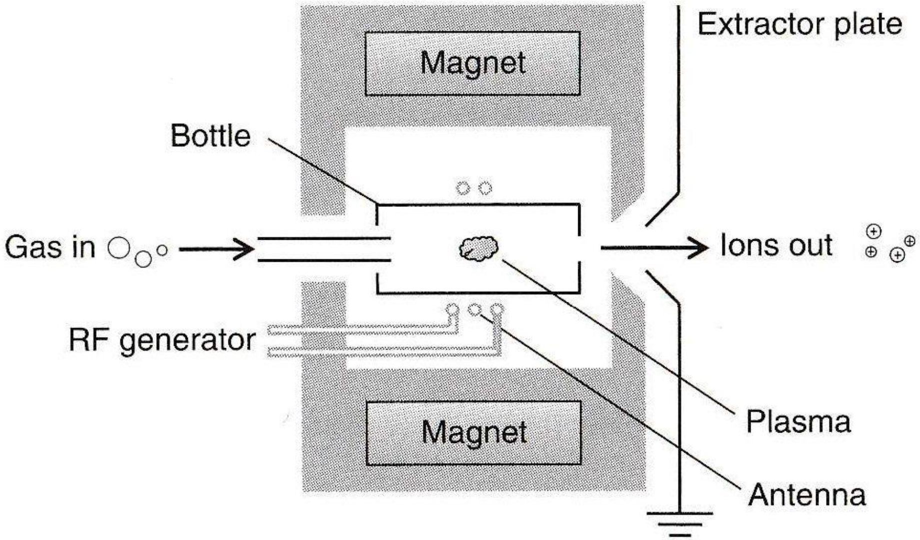
Paul van der Heide, Secondary ion mass spectrometry, Fig. 4.5

SIMS – Ion source

RF source

- any inert gas
- oxygen positive and negative (O^{-}, O_2^{+})
- Spot size < 100 nm (small I_p)
- long lifetime

- complex maintenance

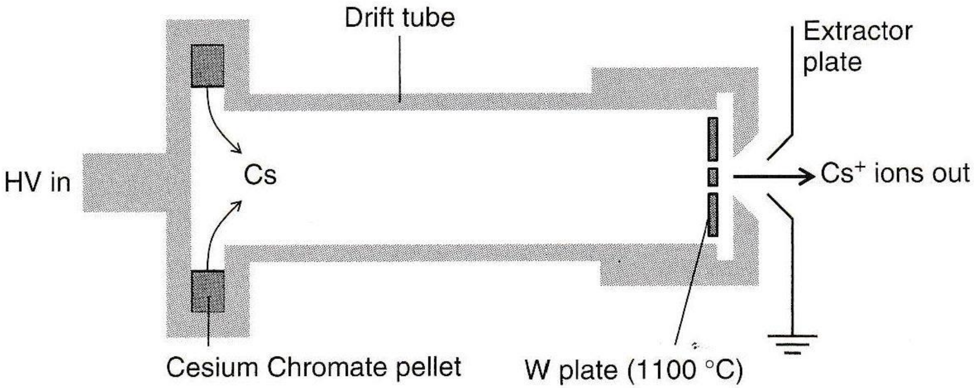


Paul van der Heide, Secondary ion mass spectrometry, Fig. 4.6
Malherbe, Anal. Chem. 2016, 88, 7130−7136

SIMS – Ion source Surface ionization source

Surface ionization source

- positive alkali ion
- mainly Cs^+
- allow cluster analysis
- long lifetime (reservoir)
- small spot



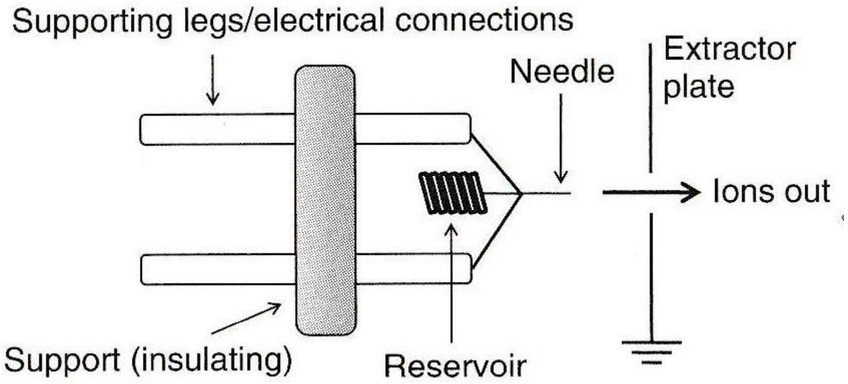
Paul van der Heide, Secondary ion mass spectrometry, Fig. 4.7

SIMS – Ion source, LMIG

Field ionization source (**L**iquid **M**etal **I**on **G**un – LMIG)

- positive ions
- mainly Ga^+, In^+
- molecular ions (Au_n^+, Bi_n^+)
- multiple charge (Bi_n^{q+})
- very small spot

- short lifetime



Paul van der Heide, Secondary ion mass spectrometry, Fig. 4.8

SIMS – Ion source, GCIB

Gas **C**luster **I**on **B**eam source – GCIB

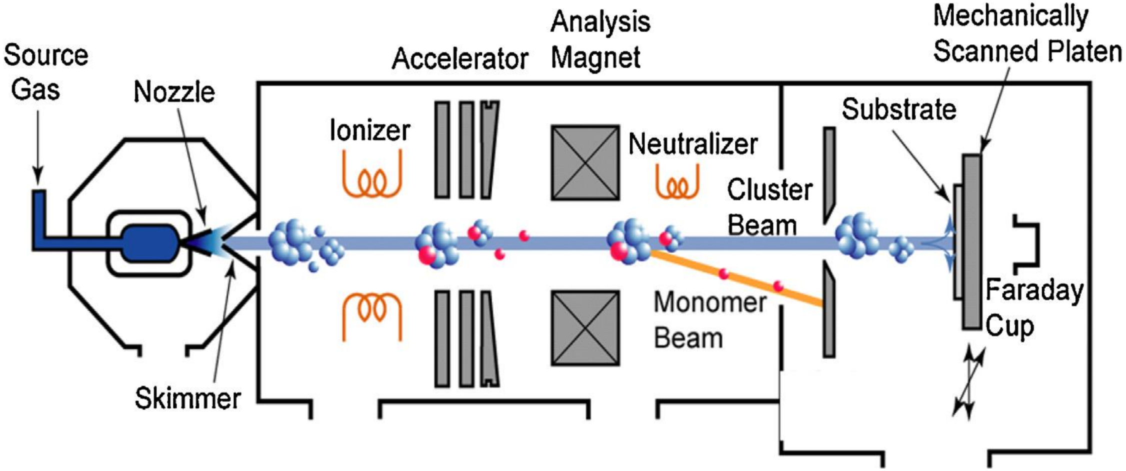
Used in SIMS since ~ 2007

Large positive Cluster

Low implantation depth

Smoothing surface

Large sputter yield



Yamada, Applied Surface Science 310 (2014) 77–88

SIMS – Ion source, Overview

Source	Species	Current (typ.) [nA]	ΔE [eV]	Source [µm]	min. Spot [µm]	Lifetime between Maintenance
Electron Impact	$Ar_n^+, Xe^+, O_2^+,$ SF_5^+, C_{60}^+	…500 …50	< 5	1000	5…30	years
Duoplasmatron	$Ar_n^+, O_2^+,$ $O^-, etc.$	…3000 …300	5…15	200	(0.15)…50 …30	500…1000 h
Radio frequency	$Ar_n^+, O_2^+, O^-,$ $etc.$	0.01…100	< 5	35…50	< 0.1…	… 1 year (difficult service)
Surface ionization	Cs^+	…100 …10000	< 0.5	10	(0.05)… ..50	1000 h or more (dep. on reservoir)
Field ionization (LMIG)	$Ga^+, In^+, Au_n^+,$ Bi_n^{q+}	1…(100)	5	0.003 (virtual)	< 0.01 µm	400…1200 h

Secondary ion beam contains typically different ions and or energies !

SIMS – Primary Ions, empirical facts

- Ar^+, high sputter rate, useful for study oxidation processes, $\ominus$ large mixing
- O^-, O_2^+, increase positive secondary ion yield compared to inert gas
- O^-, useful for insulating samples, $\ominus$ $I_P \sim 10$ times- less than O_2^+
- Cs^+, increase negative secondary ion yield compared to inert gas
- Cs^+, in combination with cluster analysis (MCs^+ for electropositive or MCs_2^+ for electronegative elements) lowers the matrix effect, $\ominus$ lower sensitivity
- Molecular ions increase sputter rate and lower projected range and damaging

Note the influence of primary beam on measurement (interferences).

SIMS – Secondary Ions, empirical facts

- Most secondary ions single charged, some multiple positive charged
- Negative multiple charged ions have a very short lifetime
- Secondary ion energy distribution peak ~few eV
- Single secondary ion energy tail can extend to 500 eV or more
- Molecular secondary ion energy have a much shorter tail
- Secondary ions were influenced by
    - Surface properties
    - Surrounding (matrix)
    - Formed polarity

SIMS – Ion optic

Method used for transport and manipulate ion beams are:

- Electric or magnetic fields (field gradient act as lenses or deflectors)
- Apertures

Wavelength (de Brogli)

$$\lambda = \frac{h}{\sqrt{2 \cdot e \cdot m \cdot U}} < 1\,pm, \qquad m = Ion\ mass, U = excellerating\ voltage$$

➔ Diffraction is not limiting for ion optic

SIMS – Ion optic

Energy of ions in source (before acceleration) ~ eV (see ΔE in ion sources)

Accelerating energy (E_p) ~ keV

➔ collimated beam (approximately parallel trajectories)

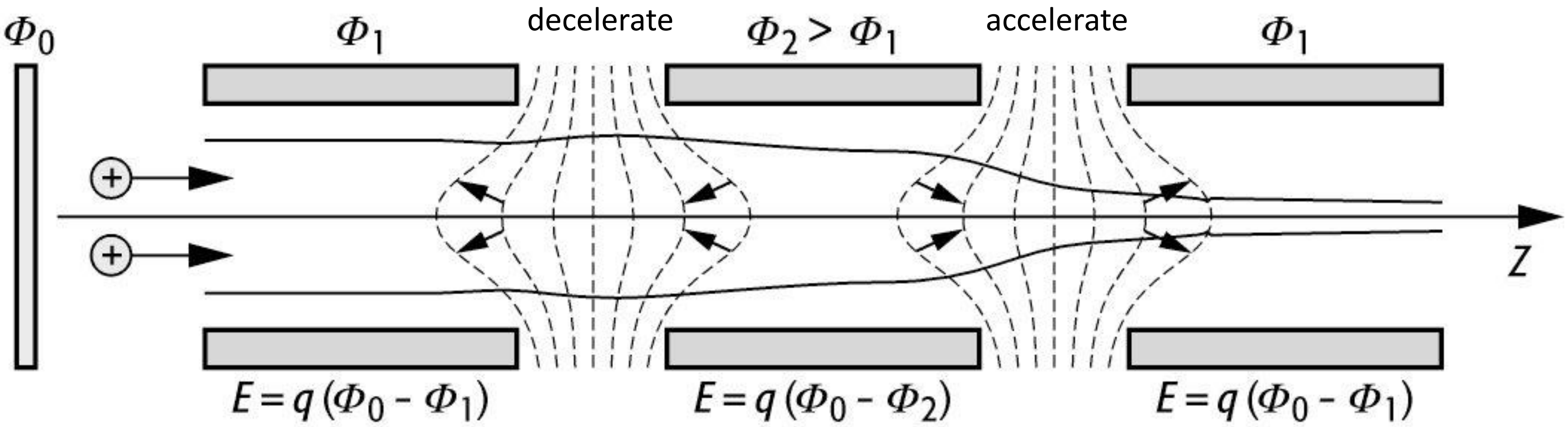
Internal force (coulomb repulsive force)

- more important for fine focus (proportional particle density)
- less important for higher E_p

SIMS – Ion optic, Lenses

Electrostatic lens, three tubes

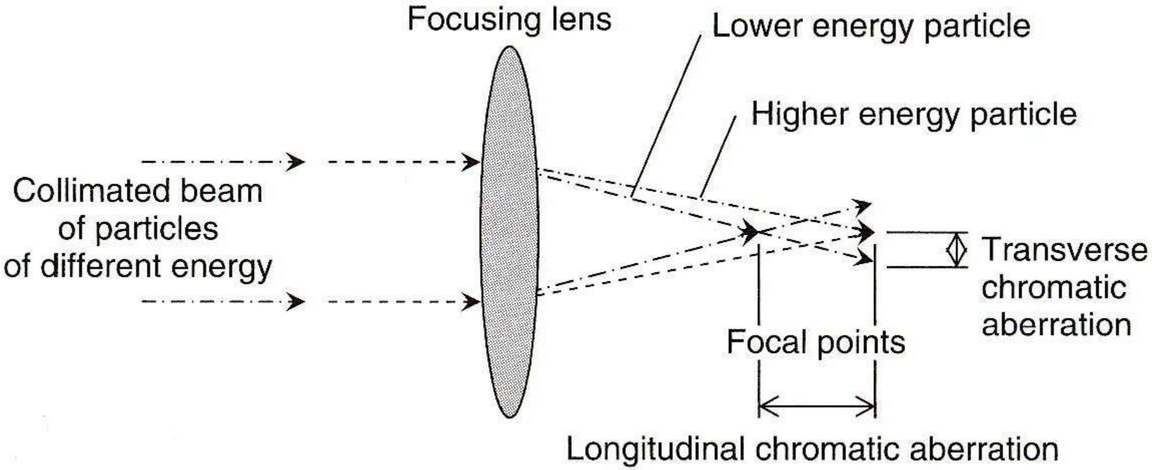
single lens, equipotential lines (dotted), field orientation (arrows), Particle path (solid line)



Spektrum der Wissenschaften, Physik, https://www.spektrum.de/lexikon/physik/einzellinse/3836 27.08.2024

SIMS – Ion optic, Lenses

Chromatic aberration



Ions with:

- Variation in energy
- Entering at same place

→ Different focal points

Paul van der Heide, Secondary ion mass spectrometry Figure A.1

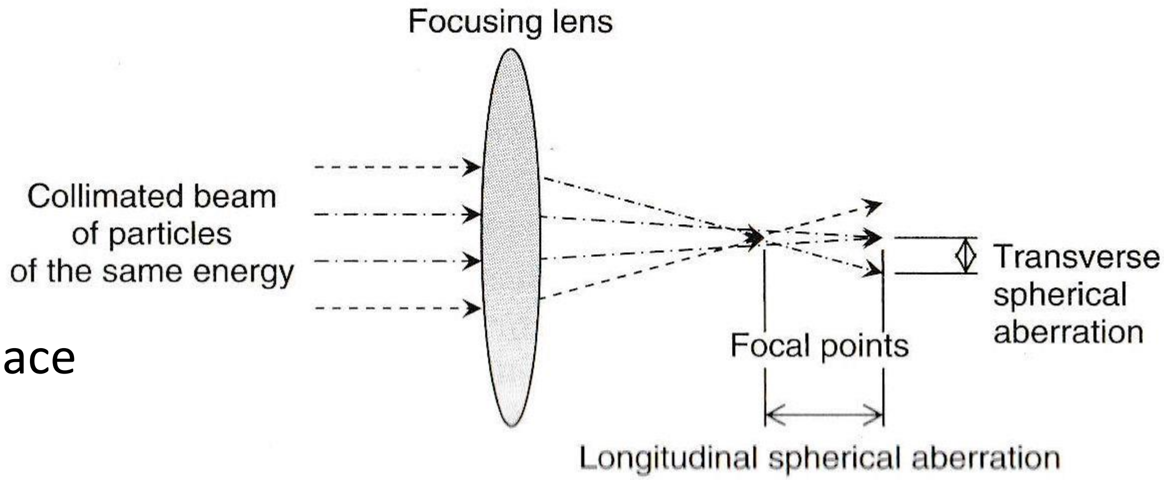
SIMS – Ion optic, Aberrations

Spherical aberration

Ions with:

- same energy
- Entering at different place

➔ Different focal points



Paul van der Heide, Secondary ion mass spectrometry Figure A.2

SIMS – Ion optic, Sector fields

Sector fields for deflect (redirect), filter and analyse ion beams

Homogeneous fields

Magnetic sector field:	B perpendicular to beam B perpendicular to beam
Electrostatic sector field:	E perpendicular to beam E in plane of the beam

SIMS – Magnetic sector field

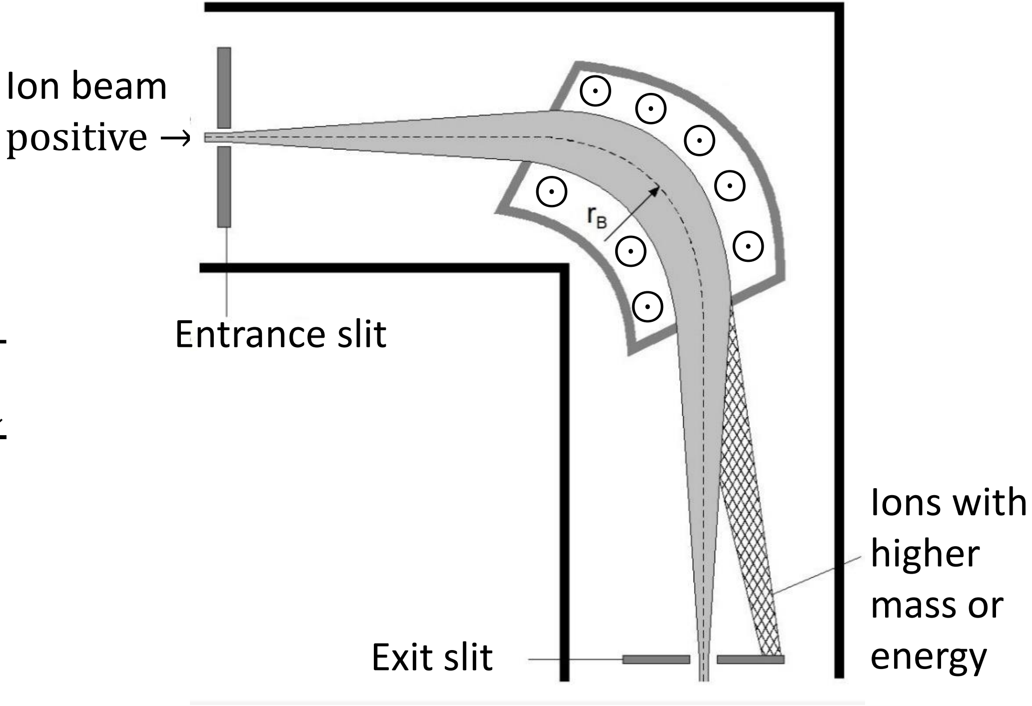
Magnetic sector field

Primary **B**eam **M**ass **F**ilter

$$F_c = \frac{m \cdot v^2}{r} = \frac{2 \cdot E_{kin}}{r}$$

$$F_L = q \cdot B \cdot v = q \cdot B \sqrt{\frac{2 \cdot E_{kin}}{m}}$$

$$r = r_B = \frac{\sqrt{2 \cdot E_{kin}}}{q \cdot B} \cdot \sqrt{m}$$



SIMS – ESA

Electro-**S**tatic **A**nalyser

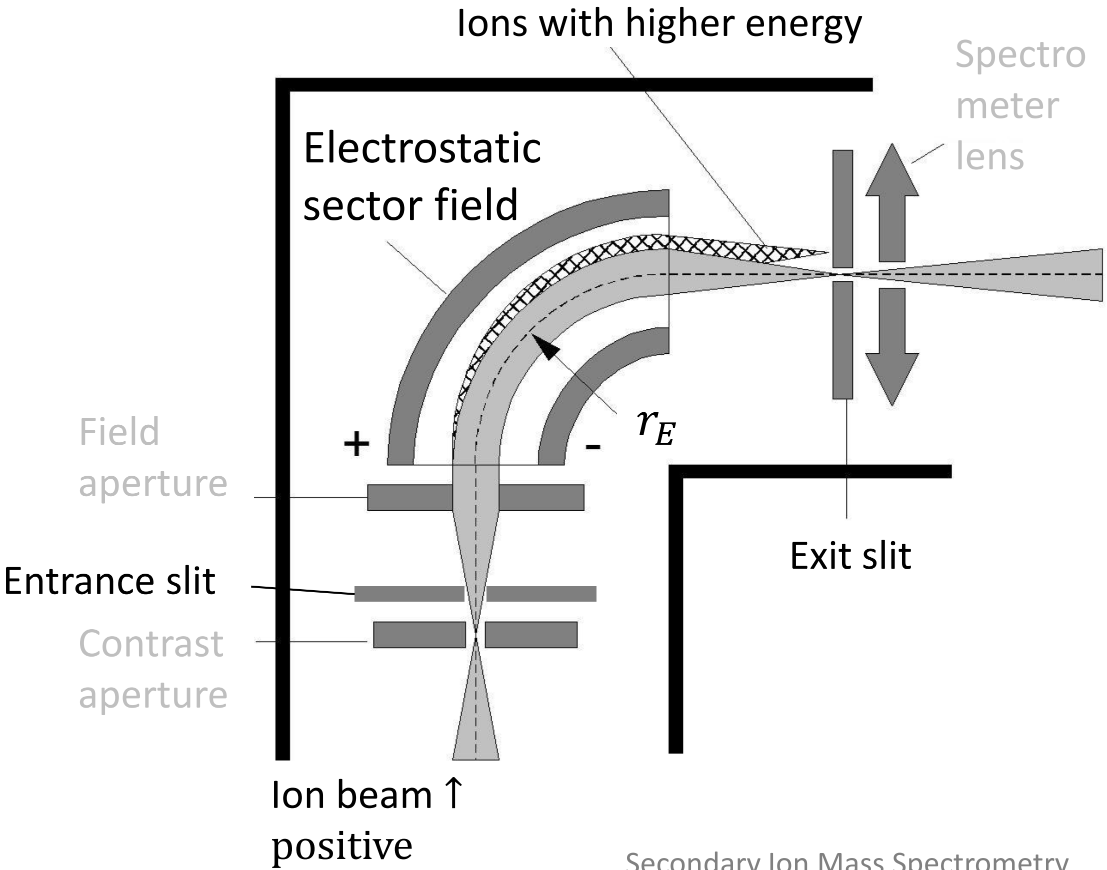
Energy filter

$$F_c = \frac{m \cdot v^2}{r} = \frac{2 \cdot E_{kin}}{r}$$

$$F_E = q \cdot E$$

$$r = r_E = \frac{2 \cdot E_{kin}}{q \cdot E}$$

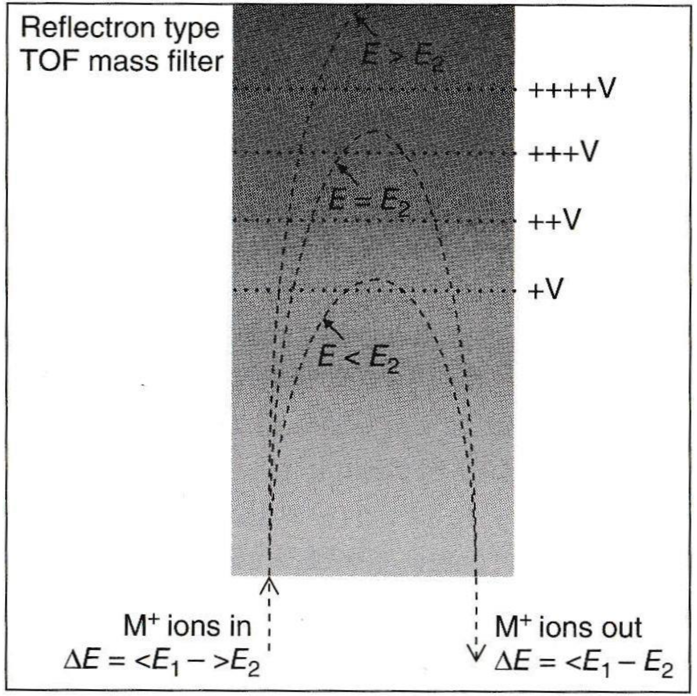
Ions with higher or lower energy removed



SIMS – TOF energy filter

Ion beam filter, lower energy spread (electrostatic mirror)

- Remove ions with high energy
- Match the flight time of ions with different kinetic energy (velocity)



Paul van der Heide, Secondary ion mass spectrometry Figure 4.15 b

SIMS – Wien filter

Primary beam filter, velocity selector

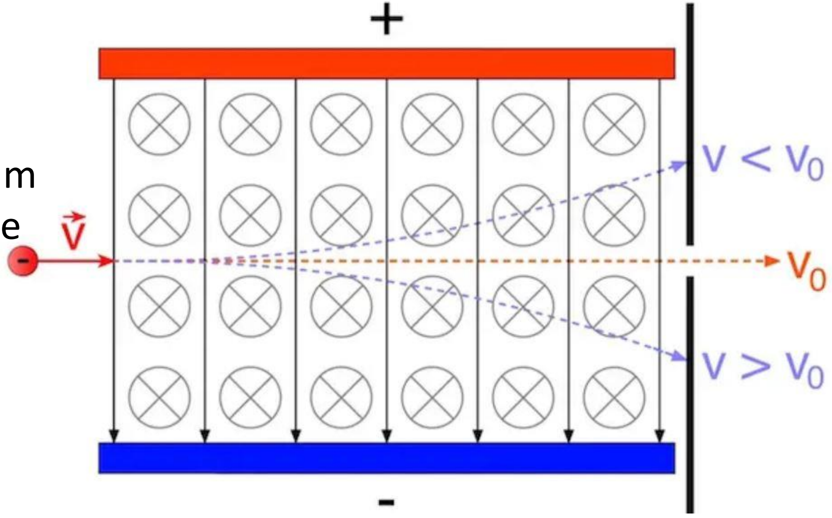
(electric and magnetic fields)

$$F_E = q \cdot E$$
$$F_L = q \cdot B \cdot v$$

$$v = \frac{E}{B} = \sqrt{\frac{2 \cdot E_{kin}}{m}}$$

Ions with higher or lower

mass or energy removed



Ion beam
negative

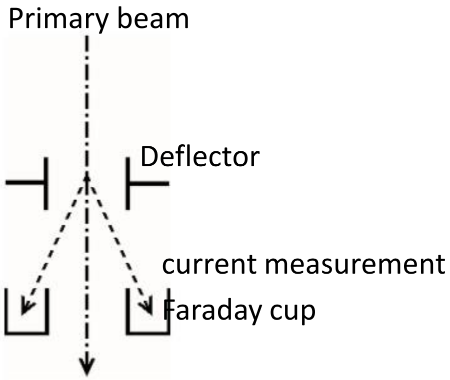
Exit slit

https://physikunterricht-online.de/jahrgang-11/massenspektrometer/

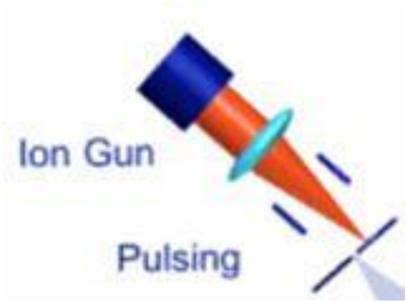
SIMS – Primary beam manipulation

Manipulation of primary beam:

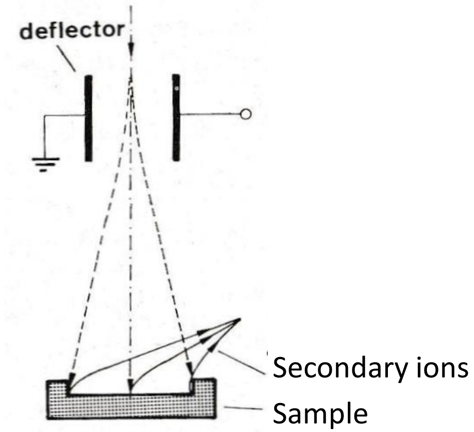
Bend beam to measure current



Pulsing beam for special spectrometer (TOF, TRIFT)



Raster beam for imaging and depth profiling



Benninghoven et al, Secondary Ion Mass Spectrometry, (1987), Fig. 4.88 modified
Pulsing scheme from IONTOF GmbH

SIMS – Sample stage

Primary beam path, Influence of secondary accelerating field

Polarity of primary and secondary ions

① same polarity

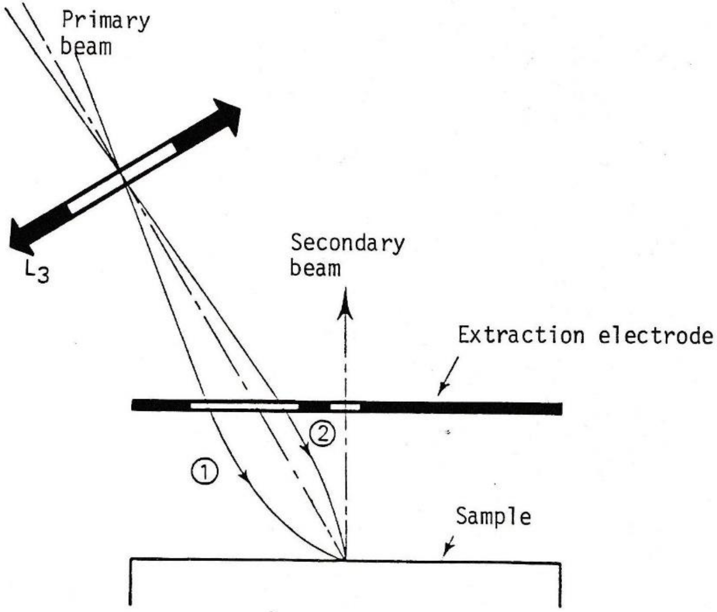
Decelerating of primary ions

Increasing the angle Ψ

② different polarity

Accelerating of primary ions

Decreasing the angle Ψ

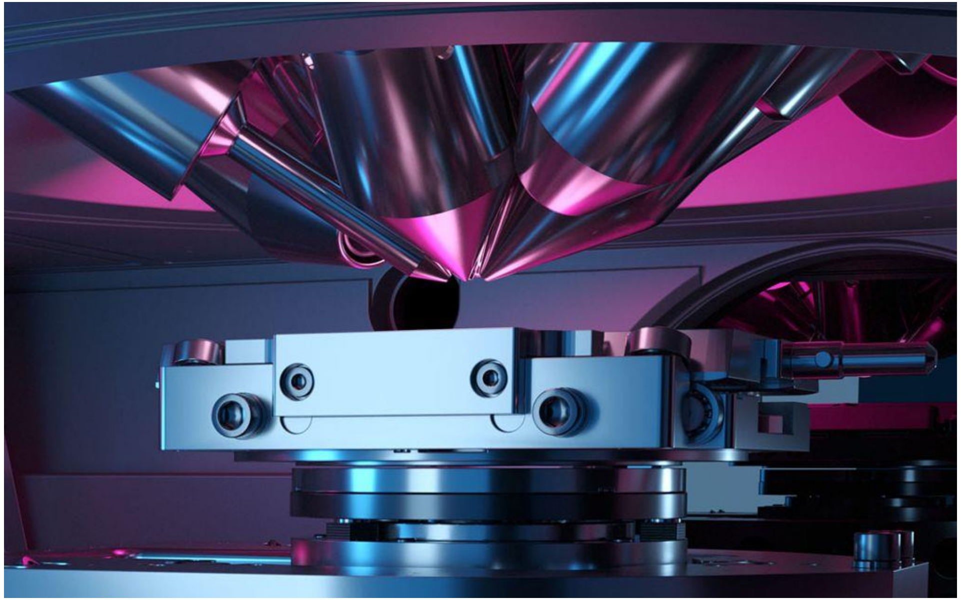


User‘s guide IMS 4f, CAMECA, Fig. 1.45

SIMS – Sample stage

Complex system that contains:

- Vacuum lock
- Positioning x, y, (z)
- (Rotation)
- Primary beam(s)
- Secondary beam(s)
- Lighting
- Optical microscope
- E-gun (charge compensation)



https://www.iontof.com/ M6 Plus sample stage

SIMS – Mass filter and detector

In most cases two separated units

- Mass filter sort the secondary ions according to mass/charge ratio
- Detector count the number of sorted ions (or measure the current)

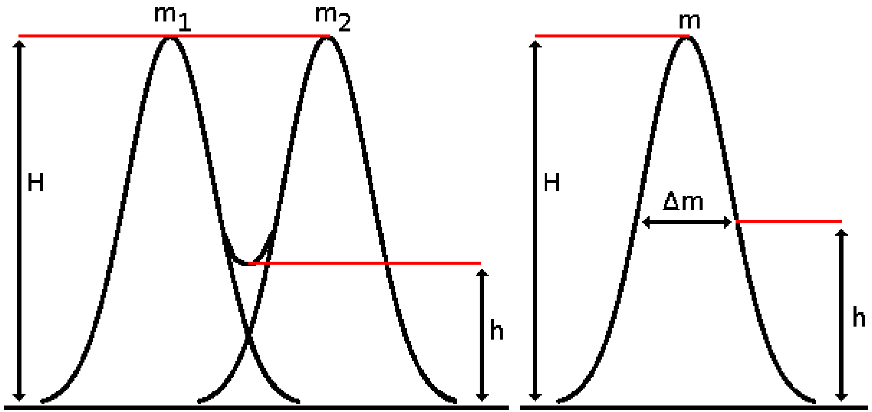
Orbitrap and FT-ICR combine both
(measure ac-signal, Fourier transformation), typically need preselection

SIMS – Mass filter, General

Important parameters:

- Mass resolution $R_{mass} = \frac{\bar{M}}{\Delta M}$,

  (different definitions h = (0.1, 0.5, 0.9)*H
- Mass range
- Mass accuracy [ppm]
- Transmission T_t, (number of ions reaching detector / generated ions)
- Parallel or sequential



https://de.m.wikipedia.org/wiki/Massenspektrometrie, 13.09.2024

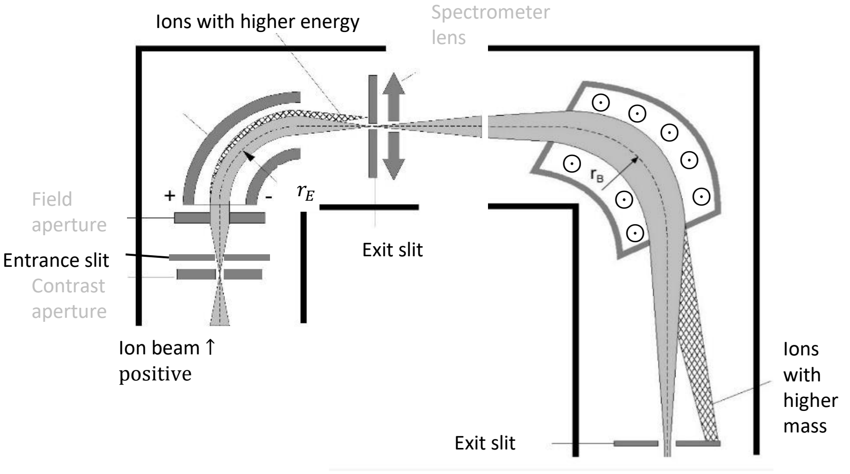
SIMS – Mass filter, ESA + Magnetic sector

Double focussing mass filter

combined ESA and magnetic sector field

$$r_E = \frac{2 \cdot E_{kin}}{q \cdot E}, \qquad r_B = \frac{\sqrt{2 \cdot E_{kin}}}{q \cdot B} \cdot \sqrt{m}$$

$$\rightarrow \quad \frac{m}{q} = \frac{r_B^2}{r_E} \cdot \frac{1}{E} \cdot B^2 \neq f(E_{kin})$$



- Sequential measurement
- $T_t < 0.5$, depends on R_{mass}

SIMS – Mass filter, TOF

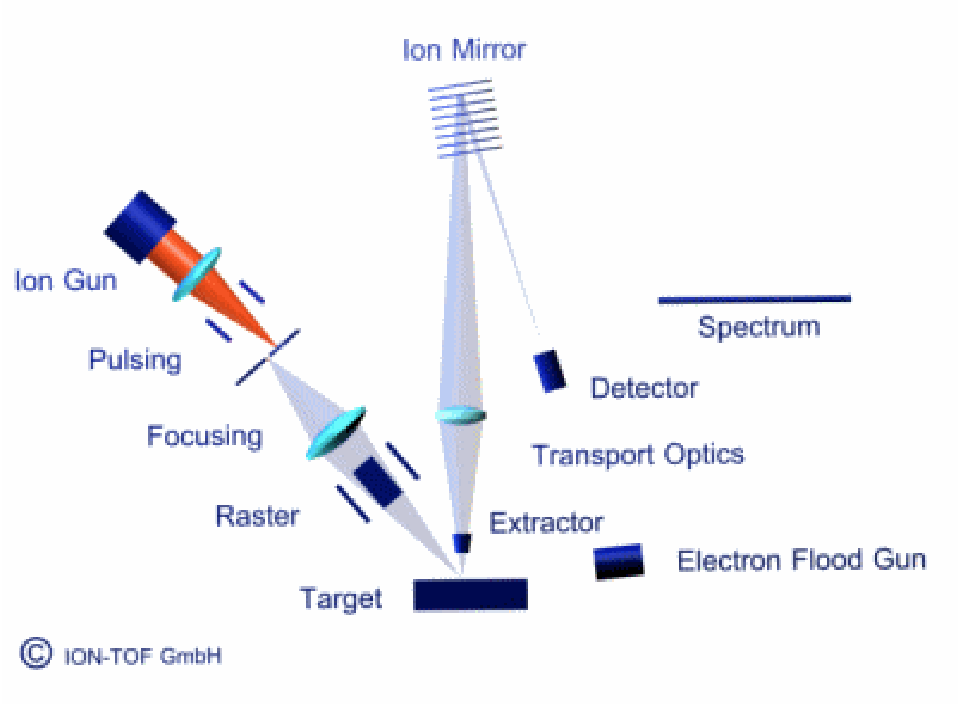
Time Of Flight, TOF

$$E_{el} = q \cdot U = \frac{m \cdot v^2}{2} = E_{kin}$$

$$v = \frac{L}{t}, \qquad \rightarrow \qquad \frac{m}{q} = \frac{2 \cdot t^2 \cdot U}{L^2}$$

U	sec. accelerating voltage
L	Length (sample to detector)
v	Velocity of secondary ion
t	Time of flight

- parallel measurement
- $T_t < 1$



Scheme from IONTOF GmbH

SIMS – Mass filter, Quadrupol

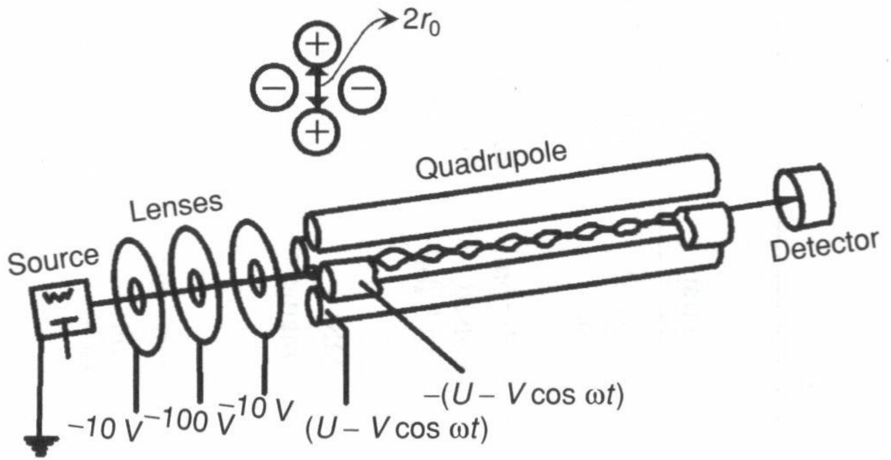
Quadrupol mass filter (QMS)

Two-dimensional time dependence electric field

Movement of ions described by Mathieu function (numerical solution)

Right values of U, V, r_0, ω ➔ stable trajectory

- Limited mass resolution
- Limited mass range
- Poor transmission, $T_t < 0.01$
- Sequential measurement



https://www.ia.uni-bremen.de/Lehre/MS2-2.pdf, 13.09.2024

SIMS – Instrumentation, Ion trap

Ion trap mass filter

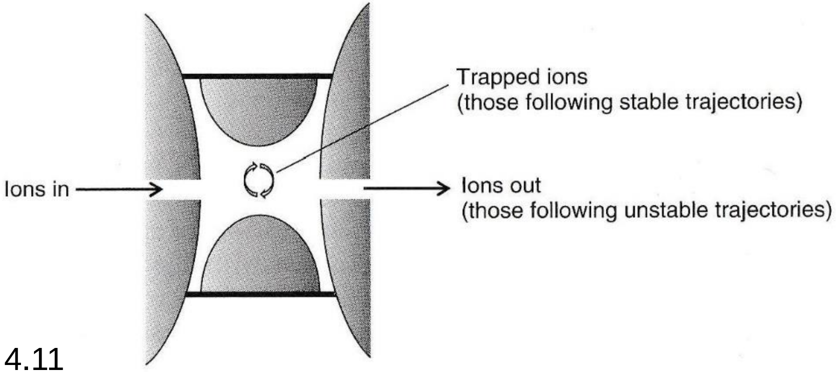
Three-dimensional time dependence electric field

Movement of ions described by Mathieu function (numerical solution)

Trapped all ions (limited capacity $\lesssim 10^6$) until RF potential is adjusted

Outgoing ions were detected

- Limited mass resolution
- Limited mass range
- Better transmission and sensitivity (QMS)
- Sequential measurement



Paul van der Heide, Secondary ion mass spectrometry Figure 4.11

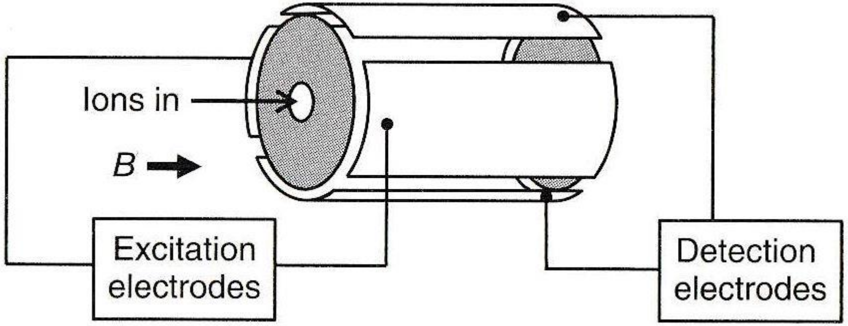
SIMS – Spectrometer, FT-ICR

Ion **C**yclotron **R**esonance (**F**ourier **T**ransformation)

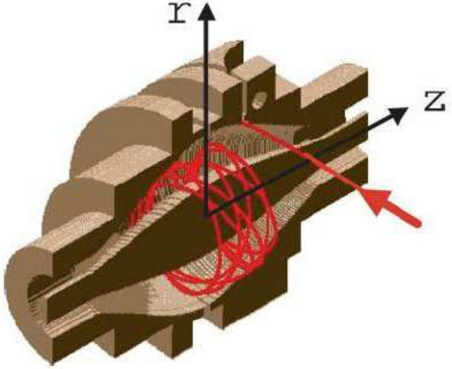
Combination strong magnetic field (7-15 T) with electric field ($\Delta\omega$)

Cyclotron resonance $\omega_C = \frac{q}{m} B_0$

- very high $R_{mass} \geq 10^{6}$
- limited dynamic $\sim 10^{5}$
- high size and weight
  (superconducting magnet)



SIMS – Spectrometer, Orbitrap



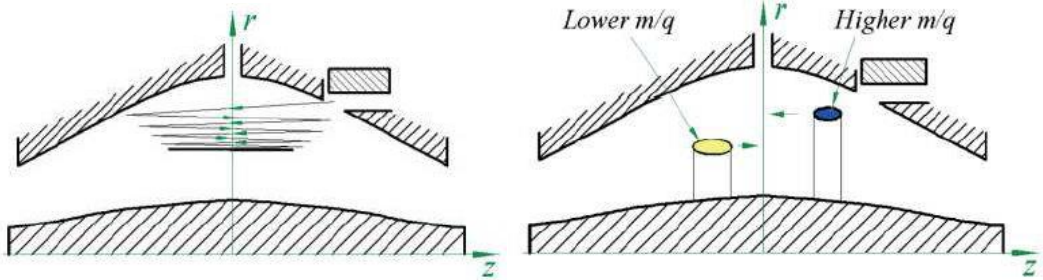
Orbitrap analyser

first publication by Makarov (2000)

$$z(t) = z_0 \cos(\omega t) + \sqrt{\left(\frac{2E_z}{k}\right)} \sin(\omega t)$$

$$\omega = \sqrt{\frac{q}{m} \cdot k}$$

k is field curvature,
geometric determined constant

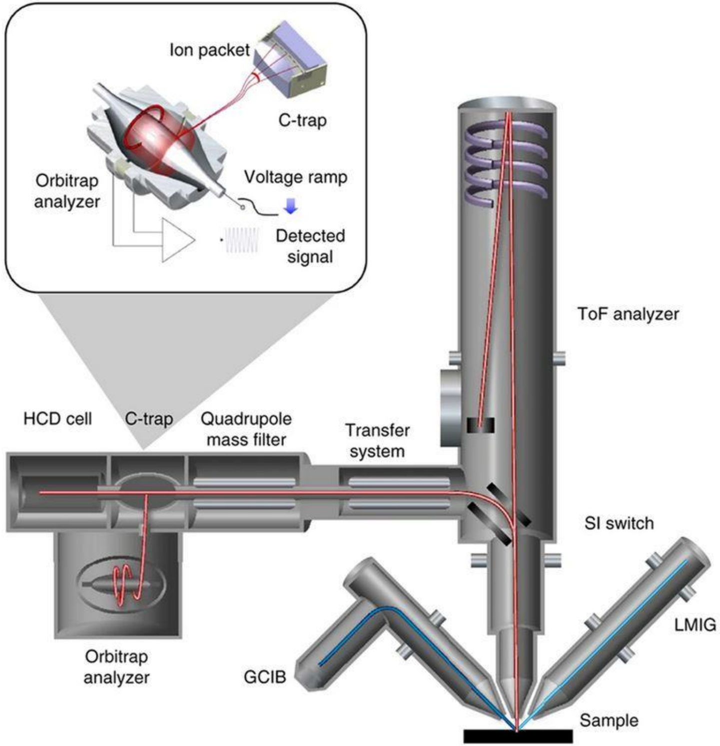


Makarov, Anal. Chem. 72, 1156 (2000)
https://www.ia.uni-bremen.de/Lehre/MS2-2.pdf, 13.09.2024

SIMS – Spectrometer, Orbitrap

Orbitrap analyser, MS/MS analyser
used in SIMS ~ 2017, commercial ~ 2020

- High mass resolution (>10^5, f(t))
- limited load (~10^5 charges)
- limited dynamic (~10^4)
- mass range up to 6000
- pulsed ion load, complex intake system



Pasarelli_Nature Methods volume 14, pages 1175–1183 (2017)

SIMS – Detector, General

Device for counting incoming ions

Important parameters:

- Upper and lower detection limit, given in counts per second [cps]
- Dynamic range,

  typically understood as linear range were signal $\propto \text{Number of ions}$
- Dead time, important for electron multiplier type detectors,

  time after one count event till detector is ready for next one

SIMS – Detector, Faraday cup

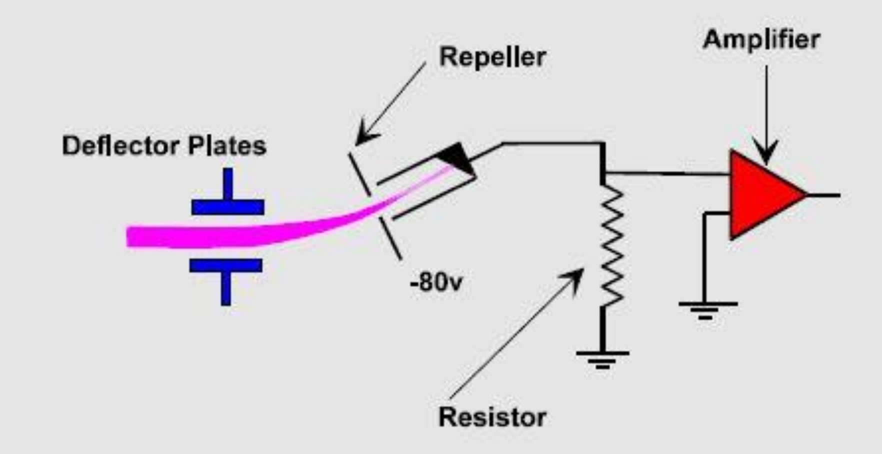
Faraday **C**up (FC)

- Ion beam deposit charge
- Resulting current (measured)

  $I_{meas} = \frac{e}{t}\sum q \cdot N_{M^q}$
- Repeller hold back generated electrons

Upper limit: ~ 10^9 cps

Lower limit: few thousand cps
(depending on noise of amplifier)



Prof YU Kin Man, Instrumental Methods of Analysis and Laboratory Secondary ion mass spectrometry

SIMS – Detector, Electron multiplier

Conversion of ion to electron, followed by multiplying

a) **D**iscrete **D**ynode **E**lectron **M**ultiplier (DDEM)
conversion factor ~10^9, saturation ~10^6 cps (dead time)

b) Channeltron, comparable to DDEM, less robust

c) **M**icro-**C**hannel **P**late (MCP), 2D array microscopic channels, conversion factor ~10^4

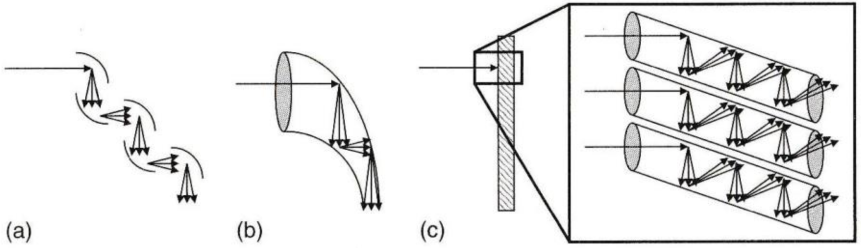
d) Chevron MCP,
MCPs 180° rotated

single ion detection

c and d useful for

ion microscopy

2



Paul van der Heide, Secondary ion mass spectrometry Figure 4.17

SIMS – Spectrometer/detector, Overview

Filter	Detector	m/q	R_{mass}	Min [cps]	Max [cps]	Dynamic	Commercial SIMS
Quadrupol	EM	1…300	< 1000	1	$<10^7$	10^6	Static, dynamic
Ion trap	EM	1…4k					no
Double focus	FC EM	1…500	> 25k	10^4 1	10^9 $<10^7$	$\left.\begin{matrix}10^4\\10^6\end{matrix}\right\rangle 10^8$	dynamic
FT-ICR	-	1…10k	> 2M				no
TOF	MCP	1…10k	> 10k	1 (a)	10^4 (a)	10^4	Static, dynamic
Orbitrap	-	1…6k	> 100k	1	10^4	10^4	Static, dynamic

(a) variable

Paul van der Heide, Secondary ion mass spectrometry

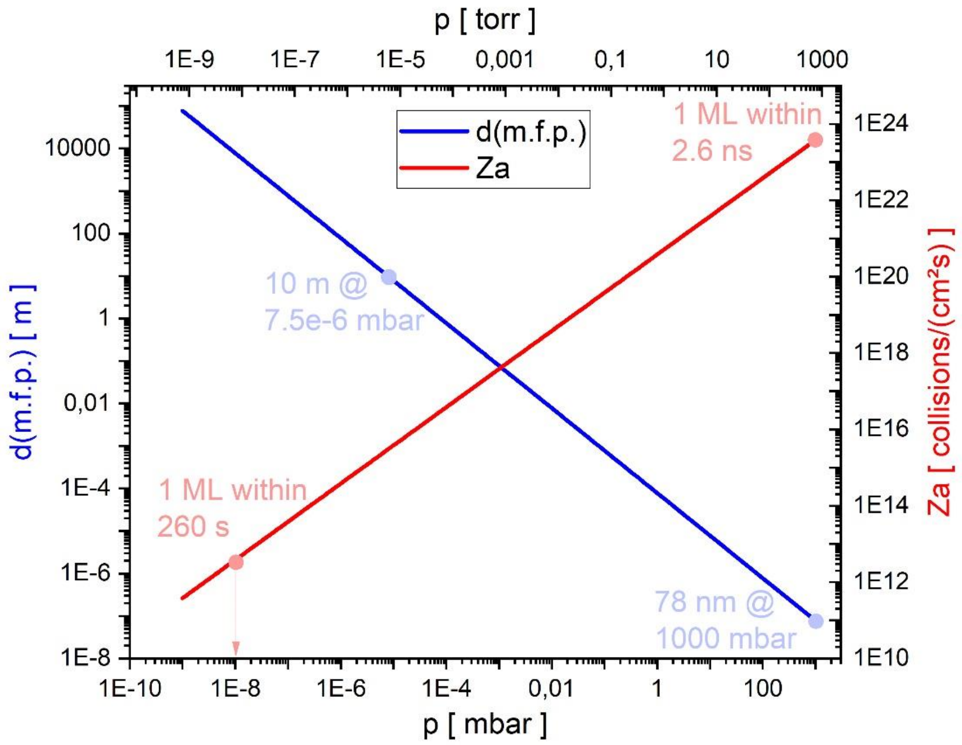
SIMS – Instrumentation, Vacuum

- Mean free path

$$d_{m.f.p.} = \frac{k_B \cdot T}{(\pi\sqrt{2} \cdot d^2 \cdot p)}$$

- Surface covering
  (Collision rate, Z_a)

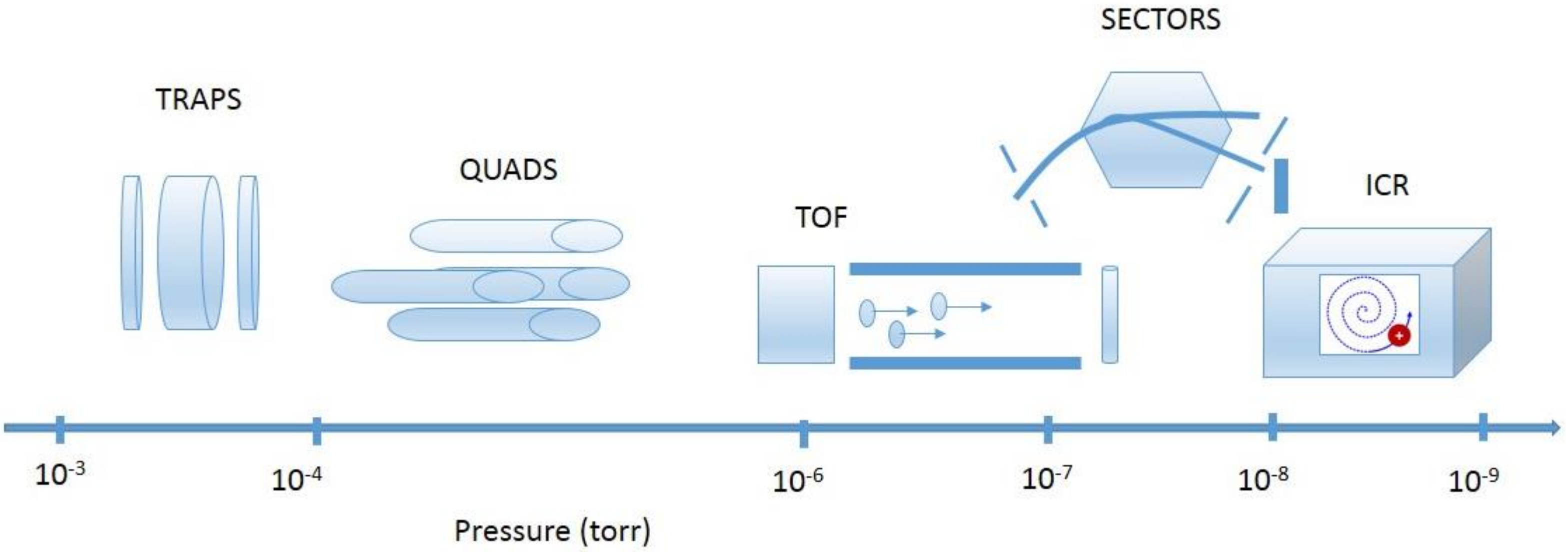
$$Z_a = \frac{p}{\sqrt{(2 \cdot \pi \cdot m \cdot k_B \cdot T}}$$



calculated for oxygen at 300 K

Note:
1 pA @ 10x10 μm² ≙ $Z_a \approx$ 6E12 collisions/(cm²s)

SIMS – Instrumentation, Vacuum



Pressure_in_mass_spectrometer_Huy.hnguyen.png, Huy.h.nguyen, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=39169162

SIMS – Instrumentation, Vacuum

Vacuum pumps used in SIMS (rough overview)

Pump typ	p [mbar]	important	Good for	Worse for	used
Rotary vane pump	10^{-3}	Oil based			pre-vacuum
Scroll pump	10^{-1}	Oil free			pre-vacuum
Turbomolecular pump	10^{-10}		Medium…heavy elements	light elements	Ion source area, air-lock
Cryo pump	10^{-11}	cyclical	H_2O, O_2, N_2	He, Ne, (H_2)	Sample area
Getter pump (NEG)	10^{-11}		H_2	Nobel gas	spectrometer

SIMS – Instrumentation, Vacuum

Outgassing, nearly all materials outgas in a vacuum, important are:

- Plastics, elastomers and adhesives
- Porous ceramics and porous metals
- Greases (lubricating, sealing and heat-conducting)

Aviod such material

Most common outgassed gases and vapors are:

- water vapor
- oil and grease vapors
- solvents and volatile organic compounds
- Hydrogen, carbon monoxide

SIMS – MEASUREMENTS

SIMS – Measurements, General

Samples (and sample holder)

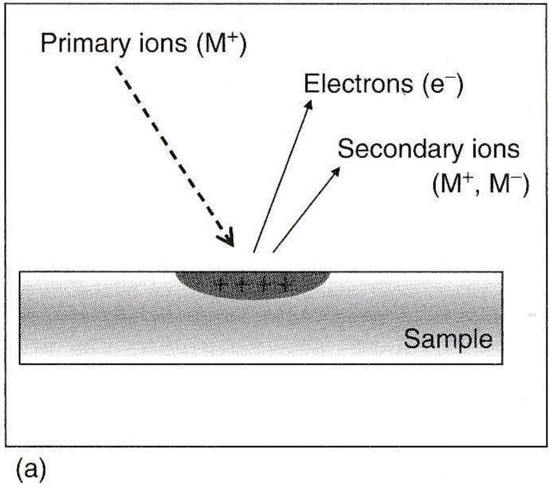
- Clean, do not touch cleaned samples without gloves
- UHV compatible, no evaporation
- Flat and smooth surface without scratches or dust in area of interest
- Conducting sample (avoid charge accumulation)
- In case of isolating samples: conductive thin film or grid may be useful

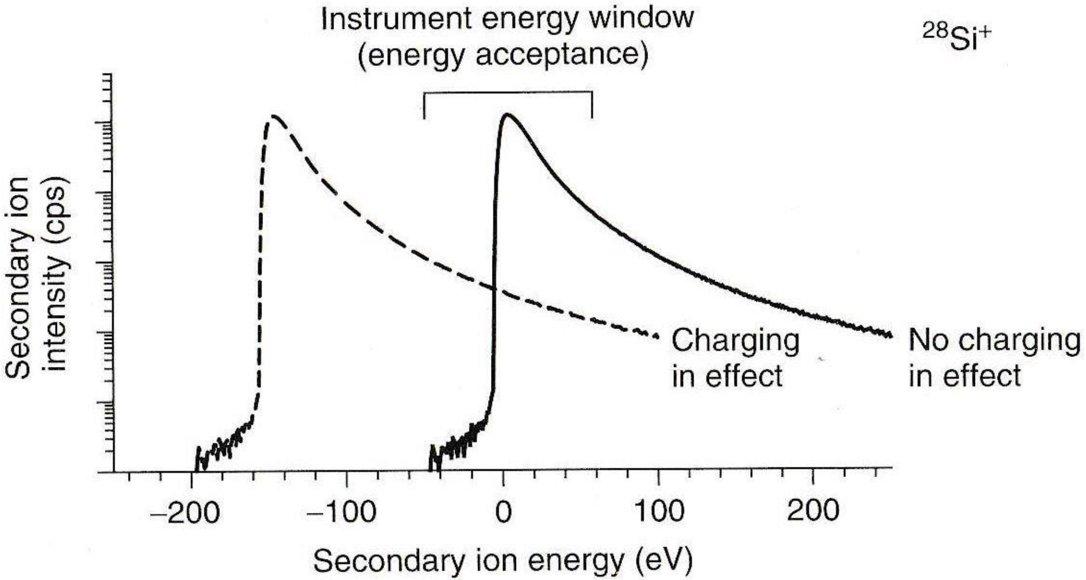
Sample should pump down in instruction chamber min. for 10…15 min

SIMS – Measurements, Charging

Charging affect

- Primary beam
- Secondary ion energy





Paul van der Heide, Secondary ion mass spectrometry Figures 5.9a and 5.10

SIMS – Measurements, General

Measured signal – number of secondary ions (Intensity)

$$I_S = f\left({}^{m}/_{q}\,, t\right), [\,counts/s\,]\ or\ [\,cps\,]$$

$$I_S(M^q) = I_p \cdot T_t \cdot Y(M^q) = I_p \cdot T_t \cdot Y \cdot \alpha(M^q) \cdot X_M$$

$I_S(M^q)$	Detected secondary ion of species M with charge q
I_p	Primary beam [ions/s], $I_p[ions/s] = I_p[A]/(q_p \cdot e)$
T_t	Transmission, depends on instrument
$Y(M^q)$	Ion yield of species M with charge q
Y	Sputter yield, depends on primary ion and sputtered material
$\alpha(M^q)$	Ionization rate for M to charge q, depends on species and matrix ….
X_M	mole fraction

Note:
$T_t \cdot Y(M^q)$
called useful yield

SIMS – Measurements, General

Interesting quantity of species M

- Mole fraction $X_M\ [-]$
- Surface concentration $c_{M,S}\left[{}^{atoms}/_{cm^2}\right] = {}^{X_m}/_{(\bar{M})} \cdot N_A \cdot \rho_A$
- Bulk concentration $c_{M,B}\left[{}^{atoms}/_{cm^3}\right] = {}^{X_m}/_{(\bar{M})} \cdot N_A \cdot \rho$

$\bar{M}$	Medium molar mass of the sample
N_A	Avogadro constant, 6.022e23 mol^{-1}
ρ_A	Surface density of the sample
ρ	Density of the sample

SIMS – Measurements, Limits

Sensitivity and detection limit (for singe isotopic element M)

Absolut sensitivity $S_a(M) = I_p \cdot Y \cdot \alpha(M^q) \cdot T_t(M^q)$

$Y \propto R \cdot A_S$, **best sensitivity: sputter rate R, ionization rate and area large**

Detection limit $c_{min} = \frac{I_{min}(M^q)}{S_a(M)}$, [atomic fractions],

$I_{min}(M^q)$ min. detectable current, mainly caused by detector noise

Comparison with other highly sensitive methods next page

Benninghoven et al, Secondary Ion Mass Spectrometry, (1987), p.284, p.768

SIMS is most sensitive method for probe based micro volume or surface analysis

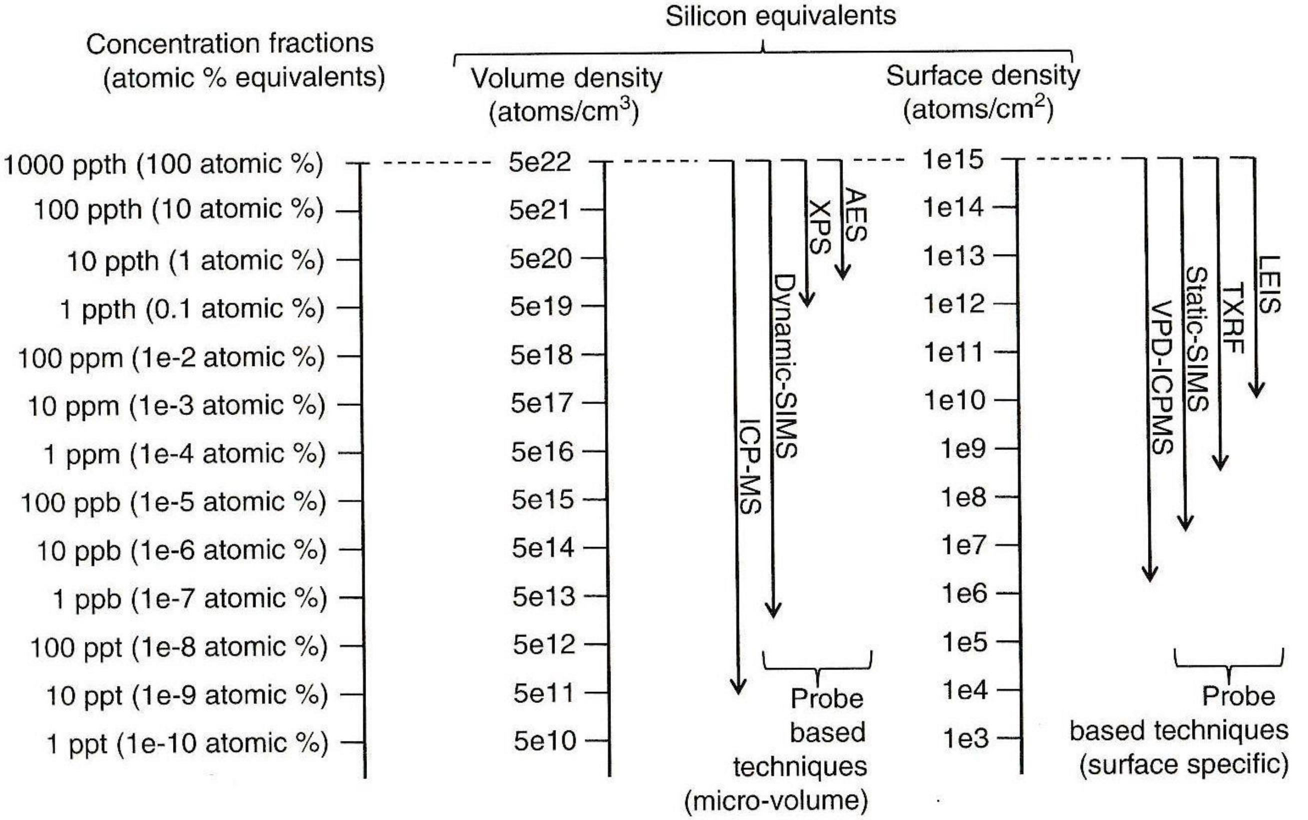
AES Auger electron spectroscopy

ICP-MS Inductively coupled Plasma-MS

LEIS Low-energy ion spectroscopy

TXRF Total reflectance X-ray fluorescence

XPS X-ray photoelectron spectroscopy



Paul van der Heide, Secondary ion mass spectrometry p.11

SIMS – Measurements, Quantification

Quantification of SIMS measurements are difficult (esp. ionization)

1. **Matrix effect**
2. surface coverage of reactive material
3. Background pressure in sample area
4. Orientation of crystallographic axes
5. Angle of incidence of primary beam
6. Angle of emission of detected secondary ions
7. Mass-dependent transmission of mass spectrometer
8. Energy bandpass of mass spectrometer
9. Dependence of detector efficiency on element

Benninghoven et al, Secondary Ion Mass Spectrometry, (1987), p.277

SIMS – Measurements, Quantification

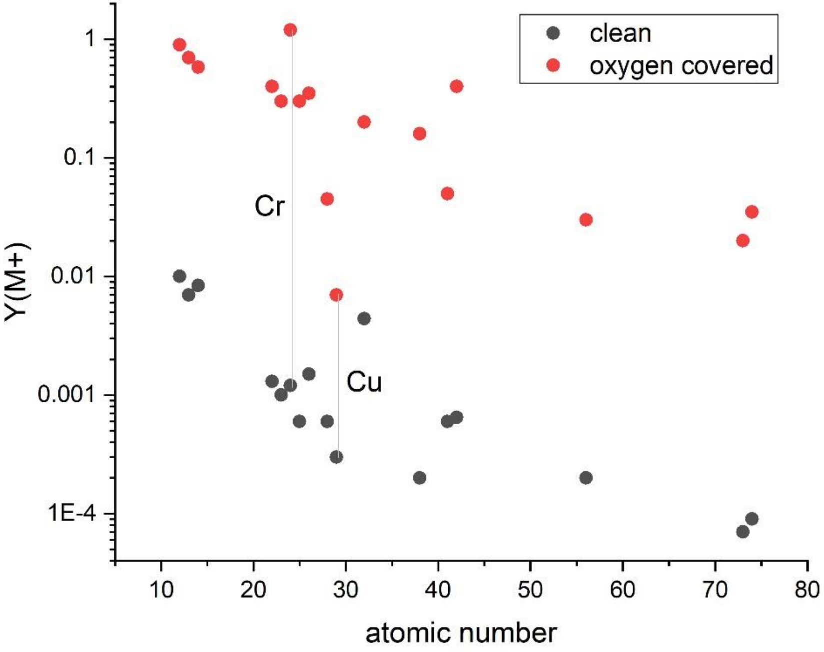
Matrix effect

Example oxide layer

Enhancement of ion yield

$$Y(O_x + Cu^+) = Y(Cu^+) \cdot 23$$
$$Y(O_x + Cr^+) = Y(Cr^+) \cdot 1000$$

Note: Sputter yield of oxides usually lower than metal



primary ion Ar+, 2.5 keV

Data taken from: Benninghoven et al, Surface science (1975) **53**

SIMS – Measurements, Quantification

Phenomenological Quantification, **R**elative **S**ensitivity **F**actor, RSF

$$X_M = RSF_M \cdot \frac{I_M}{I_R} \cdot X_R \quad , or\ analog \quad c_M = RSF_M \cdot \frac{I_M}{I_R} \cdot c_R$$

index M	Measured species
index R	Reference element

***RSF_M* must determine at same measurement conditions, same composition and microstructure of the sample.**

Implanted standards used for evaluation of RSF (see for instance Yu Kin Man)

https://pprco.tripod.com/SIMS/Theory.htm, 09.08.2024,
Prof YU Kin Man, Instrumental Methods of Analysis and Laboratory Secondary ion mass spectrometry

SIMS – Measurements, Quantification Tracer

If $X_R \cong 1$ constant, simplification

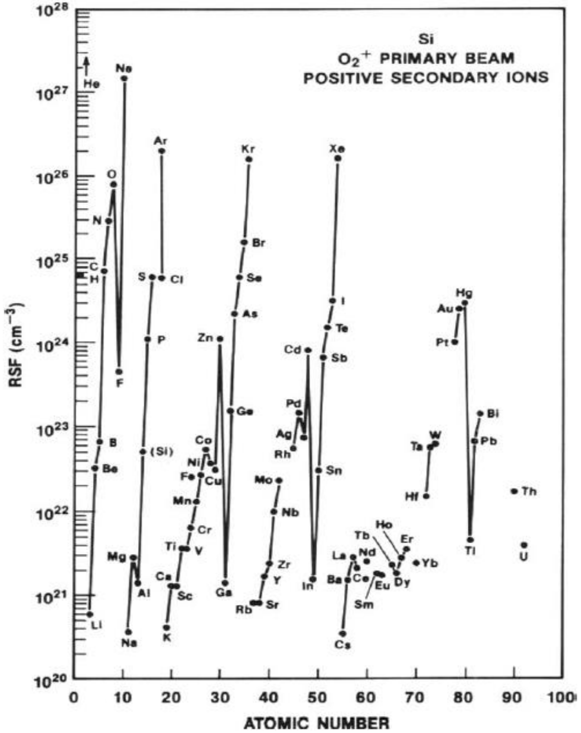
$$RSF\ (tracer\ M) = RSF_M \cdot c_R$$

$$c_M = RSF(tracer\ M) \cdot \frac{I_M}{I_R}$$

Note:

$RSM_E\ [-]$, $\quad RSF(tracer\ M)\left[{}^{atom}/_{cm^3}\right]$

Low RSF ≙ high sensitivity



Secondary Ion Mass Spectrometry, “A Practical Handbook for Depth Profiling and Bulk Impurity Analysis,” R. G. Wilson, F.A. Stevie and C.W. Magee (John Wiley and Sons, 1989)

SIMS – Mode of operation

Static SIMS

$E_p \sim 0.1 \ldots 10\ keV, I_p \sim 1\ pA, R \sim 1\ nm/h$

Surface analysis

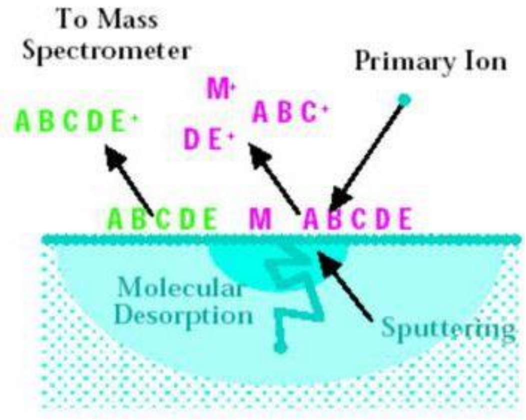
Single ions and molecules

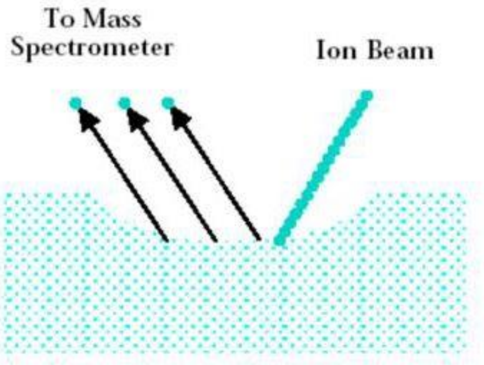
Dynamic SIMS

$E_p \sim 5 \ldots 30\ keV, I_p \sim 100\ nA, R \sim 1\ \mu m/h$

Continuous erosion

Depth profiling

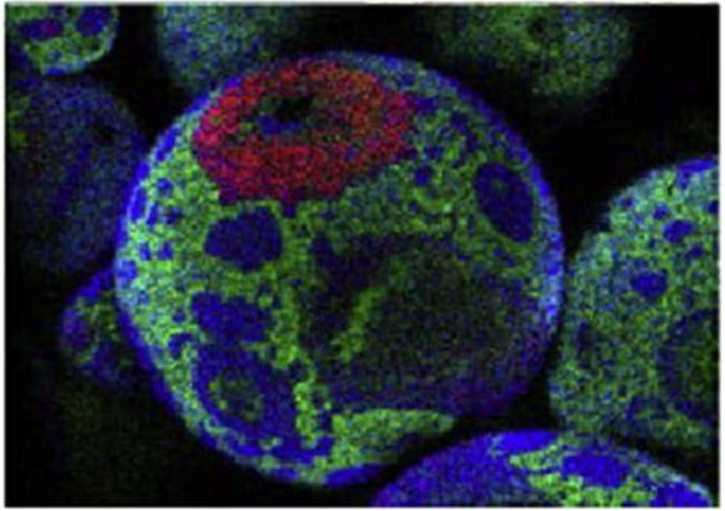




Prof YU Kin Man, Instrumental Methods of Analysis and Laboratory Secondary ion mass spectrometry

SIMS – Static SIMS

- Primary ion dose < $\mathbf{10^{12}}\ \boldsymbol{ions/cm^2}$
- Every primary ion hit a fresh area (statistically)
- Fragment ions or even intact molecules emitted from the top monolayer
- Molecular surface distribution imaged by scanning the primary ion beam
- Imaging and mass spectrum



static ToF-SIMS imaging, microsphere (149 µm) for drug delivery applications, overlay showing poly(lactic-co-glycolic) acid (green), polyvinyl alcohol (blue) and lysozyme (red).

Rafati, Journal of Controlled Release 162 (2012) 321–329

SIMS – SIMS imaging

Two types used

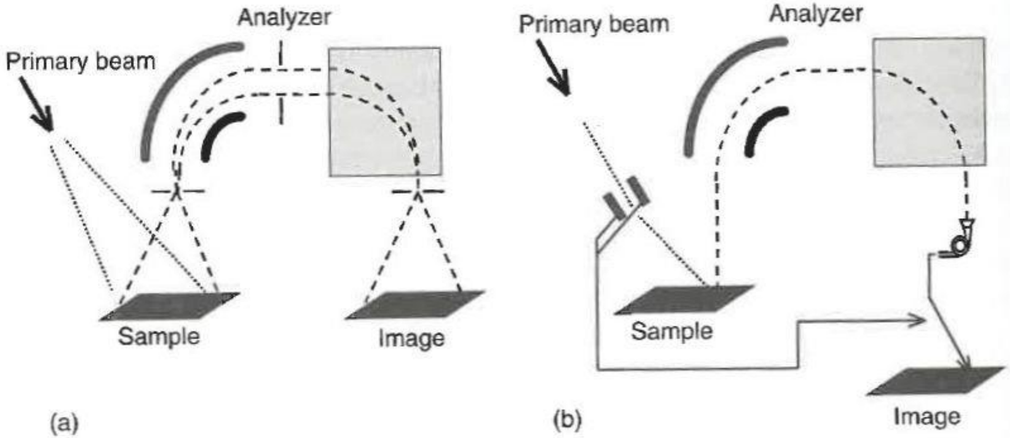
(a) microscope mode,
similar to optical microscope,
resolution independent of focus,
2D sensor necessary

(b) microprobe mode
improved spatial resolution,
no 2D sensor necessary,
resolution depend on focus,
3D images easy to realize

Assumptions:

- sample flat
- homogeneous sputter rate

Check topology before and after imaging



Paul van der Heide, Secondary ion mass spectrometry Figure 5.16

SIMS – Spatial resolution

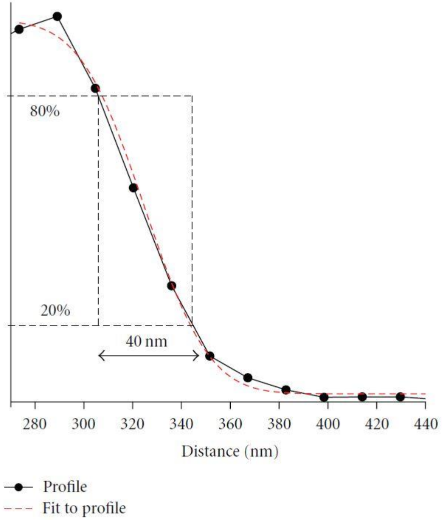
Imaging and line scan,

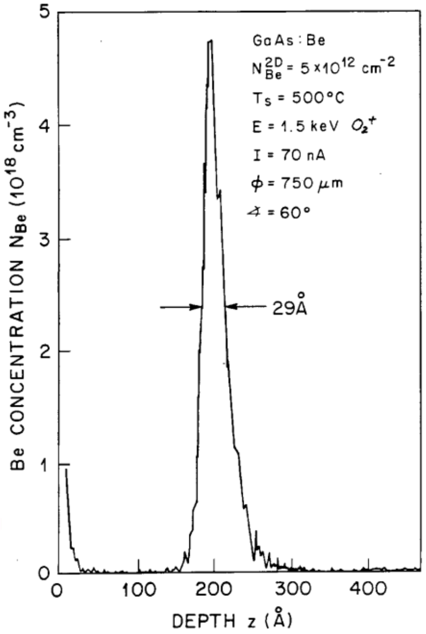
Important parameter:

Spatial (lateral) resolution Δx

(analogue depth resolution Δz)

- Minimum distance to separate two regions with different composition and/or sputter rate
- Typically taken from abrupt changing signal (different criteria)or
- FWHM in case of delta shaped signal.





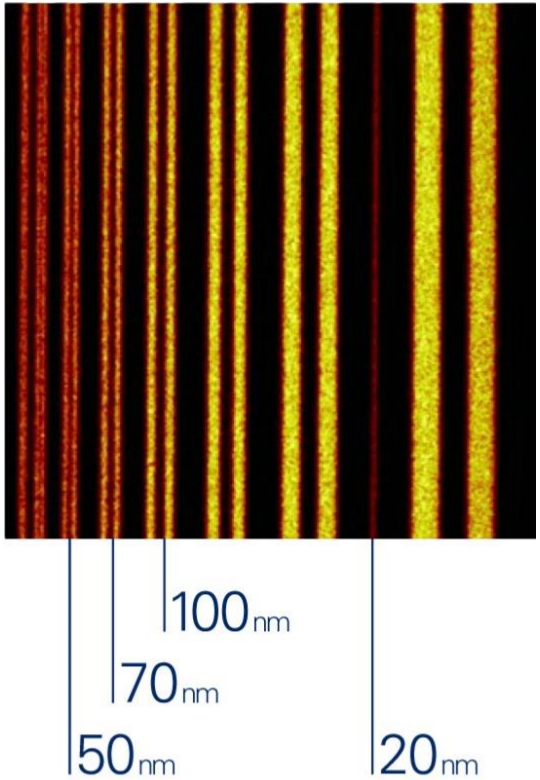
Whitby, Advances in Materials Science and Engineering Volume 2012, Article ID 180437, Fig.11, Prof YU Kin Man, Instrumental Methods of Analysis and Laboratory Secondary ion mass spectrometry

SIMS – SIMS imaging, Excamples

IONTOF M6
Nanoprobe 50

Aluminium distribution on test sample (L-200, provided by the German BAM), lateral resolution < 50 nm

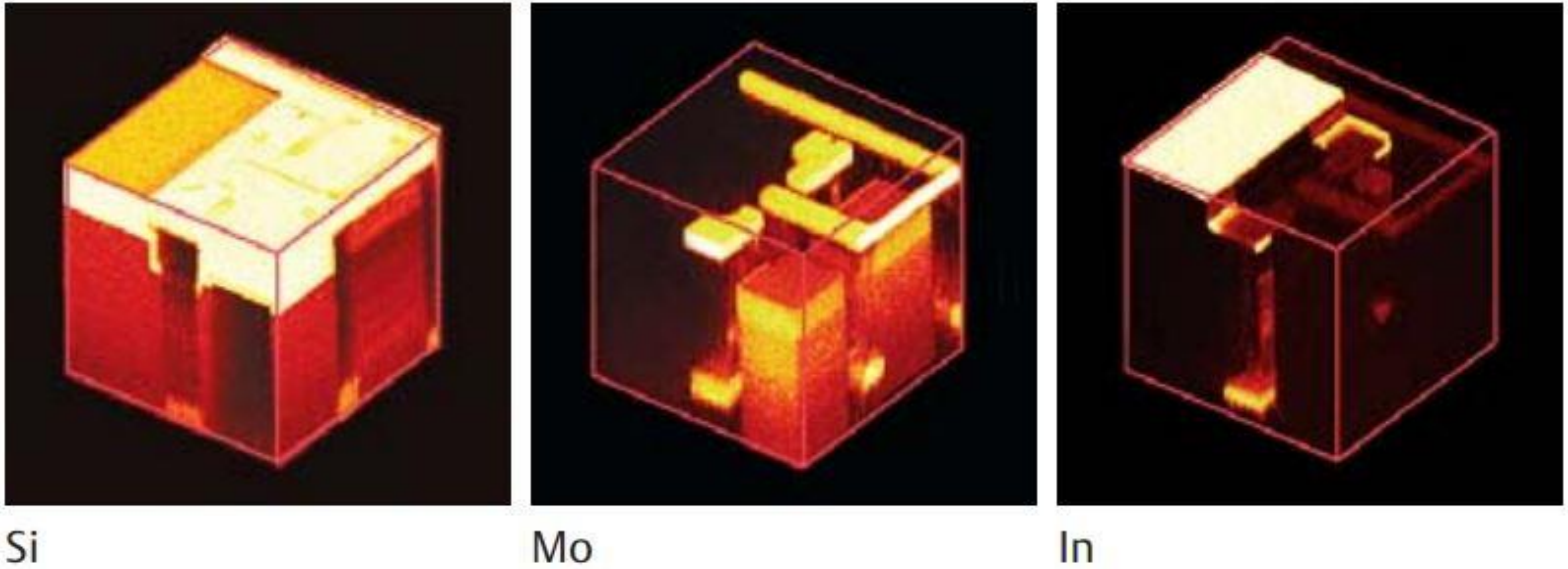
Primary ion: Bi3^{++},
Field of view: 8 x 8 µm^2,
Pixel size: 15 nm



https://www.iontof.com/m6-tof-sims-technical-details.html#anker-2, 17.09.2024

SIMS – SIMS imaging, Excamples

TFT-Pixel, analysed volume 100 · 100 · 1,7 µm³, Si, Mo and In signal



TOF.SIMS⁵ – Flyer, ION-TOF GmbH

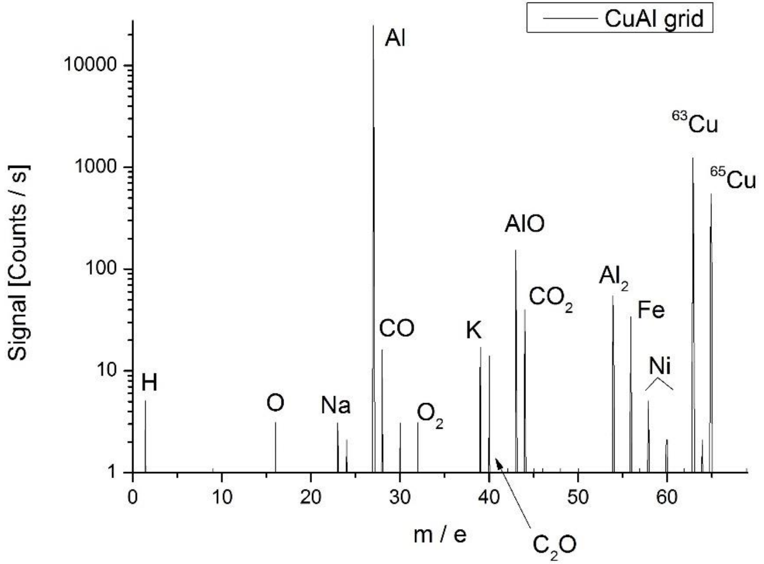
SIMS – Mass spectrum

$$I_S = f\left({}^{m}/_{q}\right), [\, counts/s \,]\ or\ [\, cps \,]$$

Just to remember:

- Detection of all species in sample
- Detection of primary beam
- Detection of (surface-) contaminations
- Detection of residual gas
- Detection of all isotopes
- Detection of molecules build up during sputtering
- Detection of multiple charged species

Spectrum analysis could be complex



Sample Al with Cu grid
CAMECA IMS 3/4 f
Primary ion: O^-, 15 keV, 100 nA

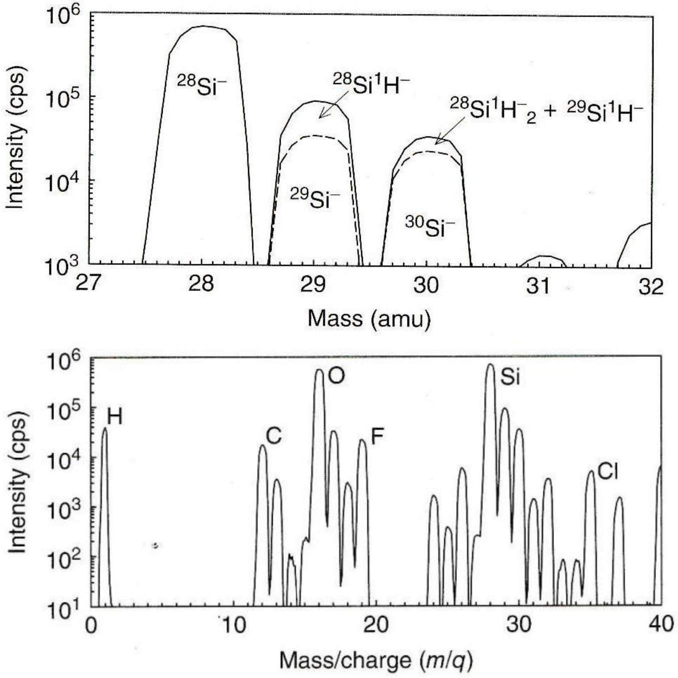
SIMS – Mass spectrum, Interference

(Isobaric) interference

Interference on (nominal) same ${}^{m}/_{q}$

Correct signals due to

- **Peak stripping**
    - Use known (natural) abundance
    - Find extend to measured peak
    - Subtract the calculated from measured
- Kinetic energy filtering
- High mass resolution



Paul van der Heide, Secondary ion mass spectrometry Figure 5.1 and 5.11

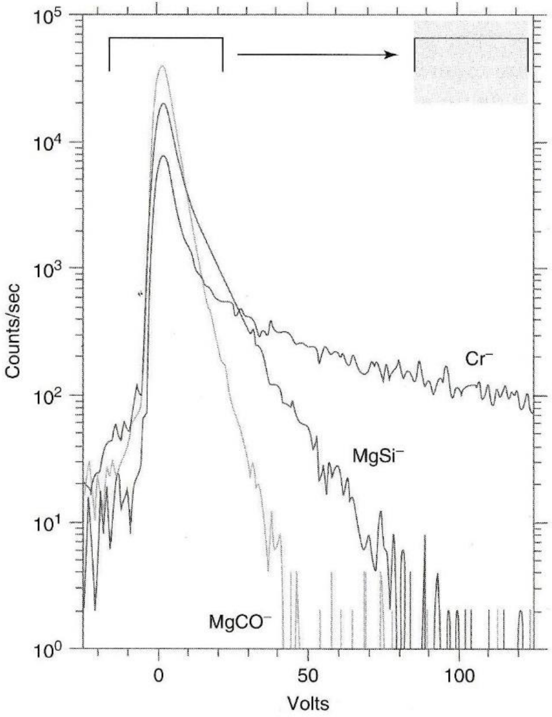
SIMS – Mass spectrum, Interference

Kinetic energy filtering

Moving measurement window to higher energy

Three possibility's

- Move the Energy slit
- Modify the ESA voltage
- Modify the secondary acceleration voltage (easiest)



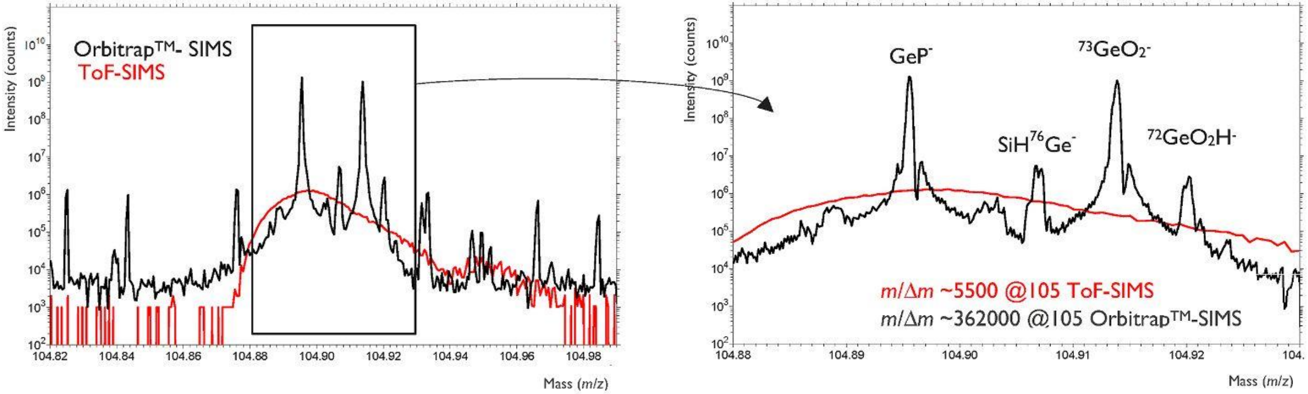
Paul van der Heide, Secondary ion mass spectrometry Figure 5.13

SIMS – Mass spectrum, High mass resolution

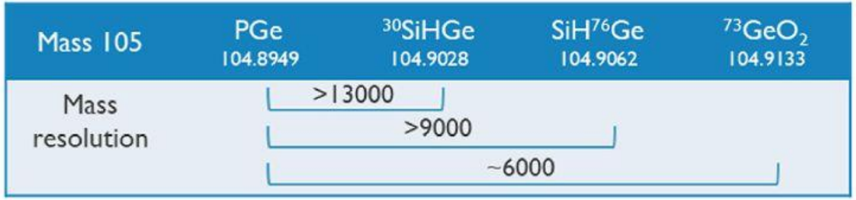
Mass resolution

Important for interpretation

Shape of peak as hint



Sample SiGe:P



Mass 105	PGe 104.8949	$^{30}SiHGe$ 104.9028	$SiH^{76}Ge$ 104.9062	$^{73}GeO_2$ 104.9133
Mass resolution	>13000			
	>9000			
	~6000			

measurement	device	Prim. ion	E_p	I_p
TOF-SIMS	NCS	Bi_1^+	30 keV	0.8 pA
Orbitrap	M6	Bi_3^+	2 keV	22 nA

Franquet et al, Vacuum 202 (2022) 111182, Fig.4

SIMS – Dynamic SIMS

Continuous sputtering (primary/additional beam)

Main application: in-depth distribution of species

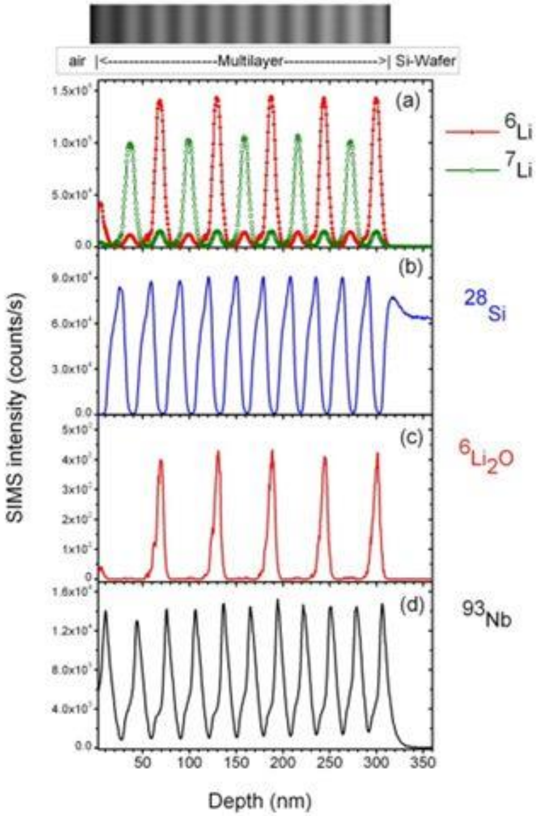
$$I_S = f({}^{m}/_{q}\,, t), [\,counts/s\,]\ or\ [\,cps\,]$$

With sputter rate R

➔ $I_S = f({}^{m}/_{q}\,, z)$, depth profile

Intensity typically averaged over certain area

Important parameter: Depth resolution Δz



Sample: Multilayer, (^{6}LiNbO$_3$|Si|^{nat}LiNbO$_3$|…)x5
CAMECA IMS 3/4 f, Primary ion: O_2^+, 5 keV, 20 nA

SIMS – Depth profiling, Sputter rate

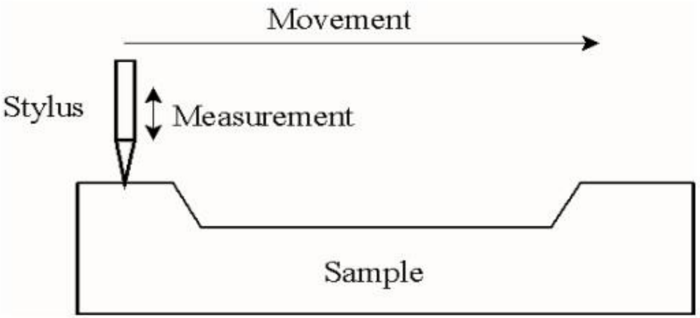
Determination possible by:

- Calculation (difficult)
- Internal marker
- Ex-situ depth measurement
- Ex-situ mass measurement
- In-situ mass measurement (rare)
- In-situ depth measurement (rare)

Interferometric

Laser Scanning Microscope

Profilometer



SIMS – Depth profiling, Sputter rate

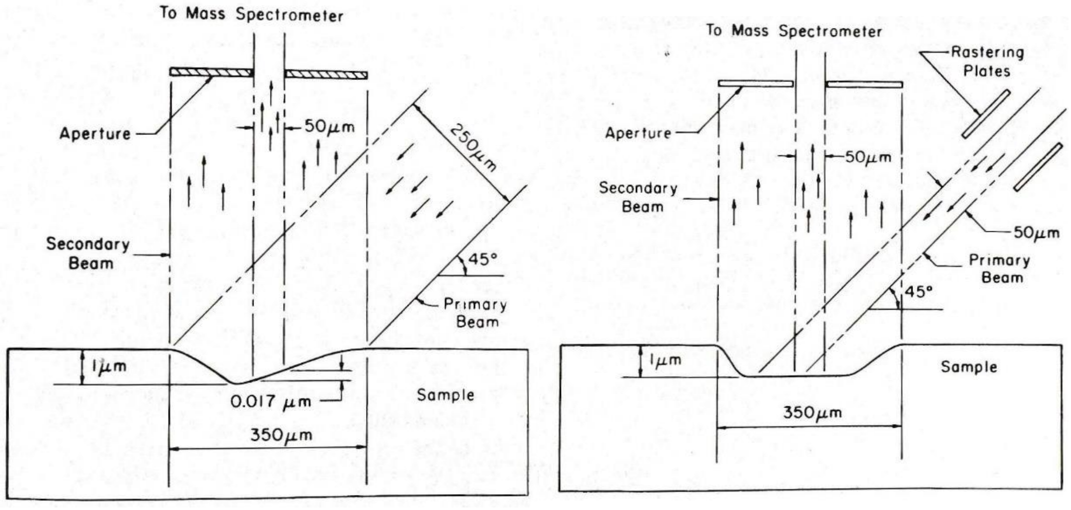
Influenced during measurement by:

- Sample structure (e.g. layered structure), correction necessary
- Variation in primary beam (measure time ~ h), monitor I_p
- Variation due to charging, correction difficult

SIMS – Depth profiling, Depth resolution

Influenced by:

- Krater (edge) effect
- Primary beam (mixing)
- Sample topology
- Sputter induced roughness
- Imperfect charge balancing (samples with isolating layers)

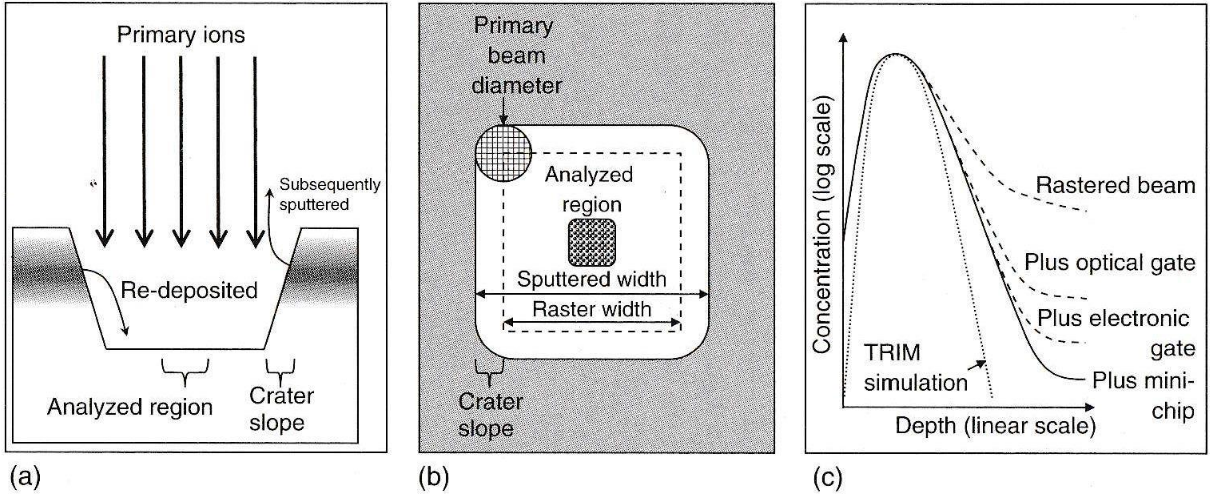


Benninghoven et al, Secondary Ion Mass Spectrometry, (1987), Fig. 5.16

SIMS – Depth profiling, Krater edge

Krater edge , two effects influence depth resolution

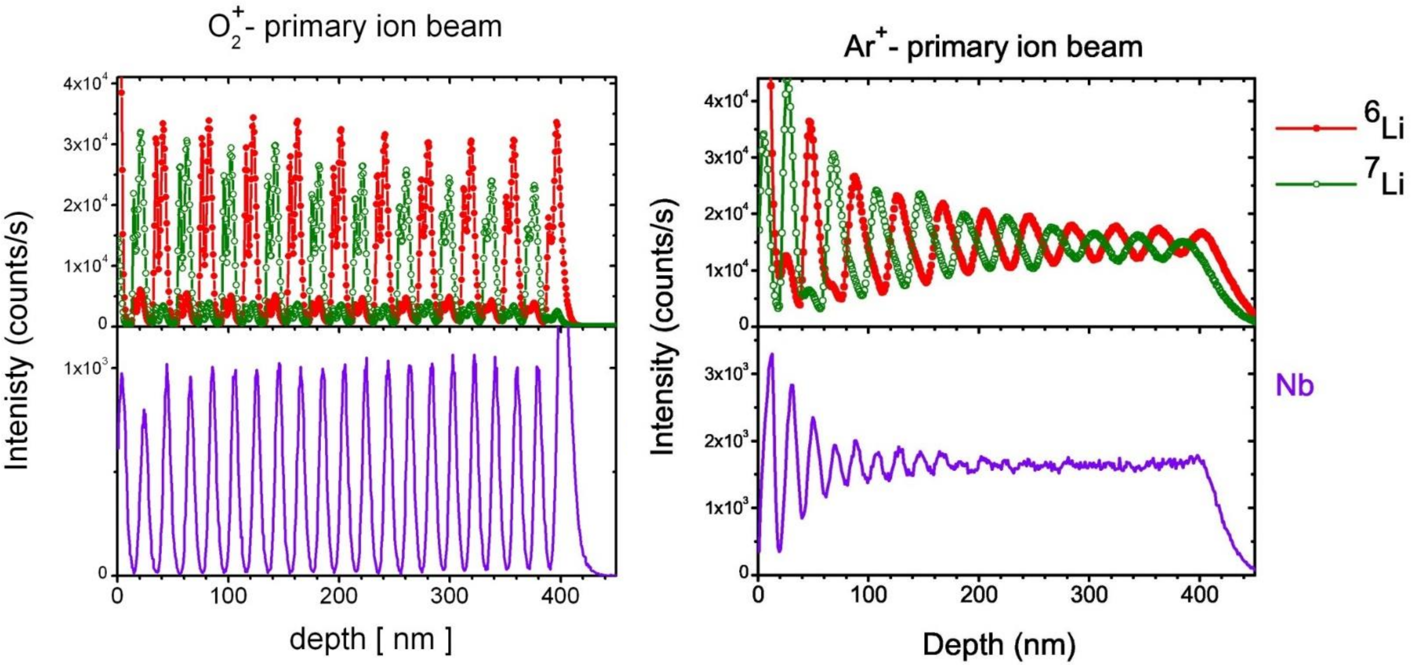
- Sputtering from edge
- Re-deposition



Paul van der Heide, Secondary ion mass spectrometry, (2014), Fig. 5.19

SIMS – Depth profiling, Mixing (example)

Influence of primary ion to depth resolution



Sample: Multilayer, ($^6LiNbO_3$|Cr|$^{nat}LiNbO_3$|…)x5, CAMECA IMS 3/4 f, 5 keV, 20 nA

SIMS – Isotope analysis, general

Measurement of Isotopes ${}^{A}_{Z}M$, Distribution of Isotopes

$$I_S\left({}^{A}_{Z}M^{q}\right) = I_p \cdot T_t \cdot Y\left({}^{A}_{Z}M\right) \cdot \alpha\left({}^{A}_{Z}M^{q}\right) \cdot X_{{}^{A}_{Z}M}$$

Different isotopes of same element, same charge.

$$Z_1 = Z_2 = Z, q_1 = q_2 = q, \alpha\left({}^{A_1}_{Z}M^{q}\right) = \alpha\left({}^{A_2}_{Z}M^{q}\right), I_p\ constant, T_t\ constant$$

$$\frac{I_S\left({}^{A_1}_{Z}M^{q}\right)}{I_S\left({}^{A_2}_{Z}M^{q}\right)} = \frac{\cancel{I_p \cdot T_t} \cdot \cancel{Y\left({}^{A_1}_{Z}M\right)} \cdot \cancel{\alpha\left({}^{A_1}_{Z}M^{q}\right)} \cdot X_{{}^{A_1}_{Z}M}}{\cancel{I_p \cdot T_t} \cdot \cancel{Y\left({}^{A_2}_{Z}M\right)} \cdot \cancel{\alpha\left({}^{A_2}_{Z}M^{q}\right)} \cdot X_{{}^{A_1}_{Z}M}} \cong \frac{X_{{}^{A_1}_{Z}M}}{X_{{}^{A_2}_{Z}M}}$$

SIMS – Isotope analysis, general

- Isotope ratios (earth, averaged values) known
- Small local deviations
  - Evaporation / condensation (light elements)
  - Chemical processes (light elements)
  - Radioactive processes (heavy elements)
  - Cosmic interactions (meteorites)
- In lab: isotope ratios adjustable (diffusion investigations)

SIMS – Important parameter 2

- Secondary ion intensity: I_S [counts], [counts/s]
- Mass resolution, $R_{mass} = \frac{\bar{M}}{\Delta M}$
- Depth resolution, Δz
- Spatial resolution, Δx
- Sensitivity $S_a(M) = I_p \cdot Y \cdot \alpha(M^q) \cdot T_t(M^q)$
- Detection limit $c_{min} = \frac{I_{min}(M^q)}{S_a(M)}$

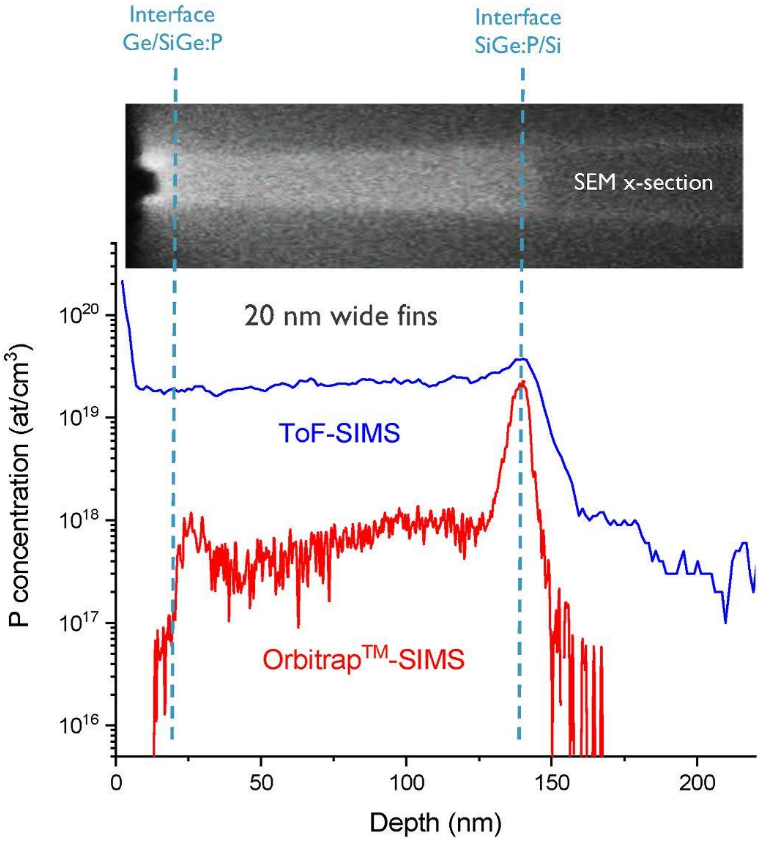
SIMS – Examples

Sample: Ge/SiGe:P/Si

Depth profile, different mass resolution

Interferences

Apparently enlarged phosphorus content in Ge layer and inside SiGe:P



Franquet et al, Vacuum 202 (2022) 111182, Fig.5

SIMS – References and further literature

A. Benninghoven, Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications, and Trends, by, F. G. Rüdenauer, and H. W. Werner, Wiley, New York, (1987);

A. Benninghoven, Surface Science 53, 596-625 (1975);

B.L. Benz, H. Weiß, and H. Liebl, Cs+ Ion Source for Secondary Ion Mass Spectromety, IPP 9/37 (1981);

J.P. Biersack, Nuclear Instruments and Methods 182/183, 199-206 (1981);

CAMECA, Dynamic secondary ion mass spectrometry, first edition, John Wiley & Sons Ltd (2019);

B.T. CHAIT and K.G. STANDING, International Journal of Mass Spectrometry and Ion Physics, 40, 185-193 (1981);

R.v. Criegern and I. Weitzel, SIMS Depth Profiling with Oblique Primary Beam Incidence, A. Benninghoven et al. (eds.), Secondary Ion Mass Spectrometry SIMS V, © Springer-Verlag Berlin Heidelberg (1986);

Tobias Steinbach, Ionenstrahlinduzierte Strukturmodifikationen in amorphem Germanium, (2012), Dissertation FSU Jena;

A. Franquet et al, Orbitrap™-SIMS analysis of advanced semiconductor inorganic structures, Vacuum 202 (2022) 111182;

C. Guillermier and C. P. Lechene, Rev. Sci. Instrum., Vol. 74, No. 7, July (2003);

T. Ishitani et al, *Jpn. J. Appl. Phys.* **11** 125 (1972), DOI 10.1143/JJAP.11.125;

SIMS – References and further literature

A.Yu. Konobeyev et al, Nuclear Energy and Tech 3, (2017), http://dx.doi.org/10.1016/j.nucet.2017.08.007;

H. Liebl; J. Appl. Phys. 38, 5277–5283 (1967), https://doi.org/10.1063/1.1709314;

LINDHARD et al, Mat. Fys. Medd . Dan. Vid. Selsk . 33, no.14 (1963);

MACFARLANE et al, International Journal of Mass Spectrometry and Ion Physics, 21 (1976) 8 I-92;

A. Makarov, Analytical Chemistry, Vol. 72, No. 6 (2000), DOI: 10.1021/ac991131p;

J. Malherbe et al, Anal. Chem. (2016), 88, 7130−7136, DOI: 10.1021/acs.analchem.6b01153;

W. Möller, HZDR, FUNDAMENTALS OF ION-SOLID INTERACTION - A Compact Introduction, HZDR-073 . ISSN 2191-8708, (2017);

MS2-2, https://www.ia.uni-bremen.de/Lehre/MS2-2.pdf, 12.09.2024;

Probion Analysis, Physical description of SIMS analysis, https://probion.fr/physical-description-of-sims-analysis-en, 09.08.2024;

B.I. Prenitzer et al, Microsc. Microanal. 9, 216–236, (2003), DOI: 10.1017/S143192760030034;

A. Rafati et al, Journal of Controlled Release 162 (2012) 321–329, doi:10.1016/j.jconrel.2012.05.008;

Schatz and Weidinger, Nukleare Festkörperphysik - Kernphysikalische Meßmethoden und ihre Anwendungen, Teubner-Studienbücher : Physik, ISBN 978-3-519-13079-6 (1992);

Secondary Ion Mass Spectrometry Theory Tutorial, https://pprco.tripod.com/SIMS/Theory.htm, 09.08.2024;

SIMS – References and further literature

H. E. Schiøtt, Projected ranges of light ions in heavy substances, Canadian Journal of Physics, 46(6) (1968) ;

R. Scrivens, CERN, Classification of Ion Sources, https://cds.cern.ch/record/1693319/files/p9.pdf, 09.08.2024;

Table of ionic sputtering yields and rates in FIB & SIMS - www.globalsino.com , 20.08.2024

Paul van der Heide, Secondary ion mass spectrometry, (2014), Wiley & Sons Ltd., ISBN: 978-1-118-48048-9

H. Wyrwich and F. Lenz, Z. Naturforschg. 13 a, 515—523 (1958);

H.W. Werner, Jpn. J. Appl. Phys. 13 367 (1974);

Whitby Advances in Materials Science and Engineering_(2012), doi:10.1155/2012/180437;

I. Yamada, Applied Surface Science 310 (2014) 77–88, http://dx.doi.org/10.1016/j.apsusc.2014.03.147;

Kin Man Yu, http://www.cityu.edu.hk/phy/appkchu/AP5301/AP5301_lecture8_SIMS.pdf, 09.08.2024;

Yuliya Stark, Abtragsverhalten von Einkristallen und Strukturierung von Siliziumnitrid-Membranen mittels Fokussiertem Ionenstrahl, Dissertation Universität Hamburg (2013);

P.C. Zalm, Journal of Vacuum Science & Technology B 2, 151 (1984); doi: 10.1116/1.582936;