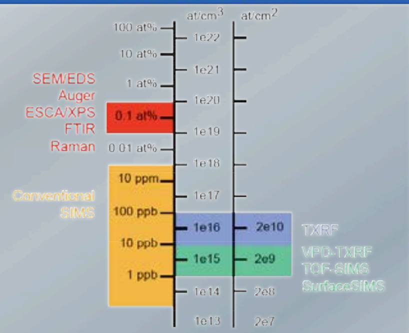
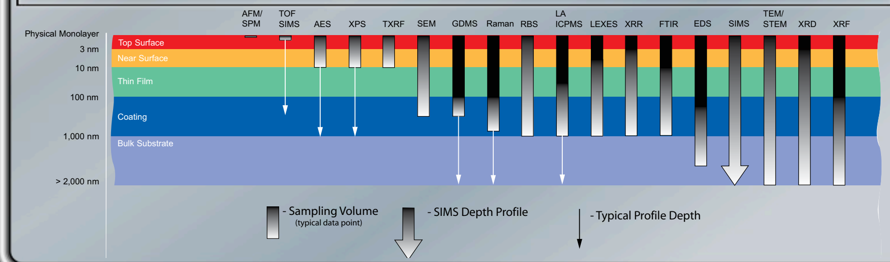
Secondary-Ion Mass Spectrometry

Technique	Resolution	Sample Size
VPD-TXRF	whole wafer	whole 300mm wafer
TXRF	10 mm	whole 300mm wafer
Lifetime	1 mm	whole 200mm wafer
ESCA/XPS	10 μm	whole 200mm wafer
SIMS	20 μm	1-2"
μ-ESCA/XPS	10 μm	whole 200mm wafer
FTIR	15 μm	whole 200mm wafer
Raman	1 μm	whole 200mm wafer
SEM/EDS	0.5 μm	whole 200mm wafer
TOF-SIMS	2000 Å	whole 200mm wafer
Auger	1000 Å	1"
FE Auger	150 Å	2"
AFM	50 Å	whole 300 wafer

Detection Sensitivity





Principle of SIMS

- composition depth profiling with *surface* analysis techniques?

→ *erosion* of specimen surface by energetic particle bombardment

- "sputtering"
- two possibilities for analysis:
  - freshly exposed surface (→ XPS, AES)
  - sputtered material
    ⇒ secondary ion mass spectroscopy (SIMS)
- depth profiling ↔ remove controlled thickness

History of SIMS

- early mass spectrometers: ion sources ions also generated ions from instrument construction materials
- later experiments: accelerated ions onto sample

→ first SIMS primary ion beam

- first SIMS instrument: early 1960s (under NASA contract)
- purpose: analyze moon rocks
- performed better than expected
- copies of the prototype were commercialized
- use of SIMS has grown steadily over the past decades

Principle of SIMS

→ bombarding with low-energy heavy ions

- $(O_2)^+$, Cs^+, Ar^+, …
- 0.5..20 keV

⇒ yield of sputtered atoms per ion ≈ 0.5..20

- depth profile

⇐ surface-sensitive techniques of analysis after each step

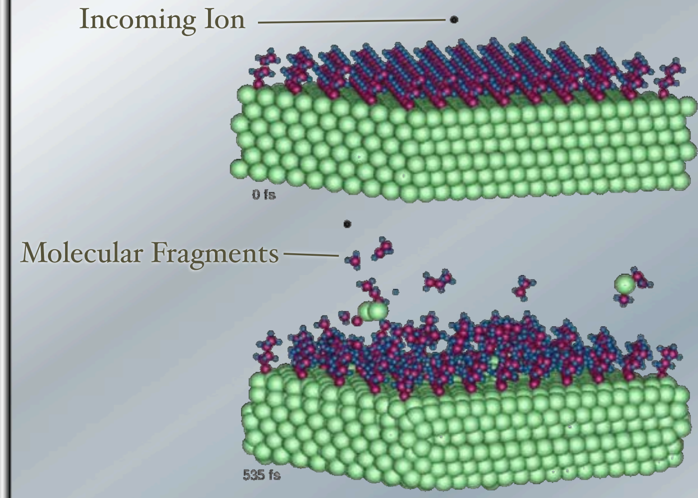
⇐ compositional analysis of the sputtered material

⇒ relative abundance of sputtered species provides direct measure of composition

Principle of SIMS

- additional way of determining specimen composition: measure characteristic *radiation* emitted from excited sputtered ions or atoms
- difference between bombardment with high-energy ions (RBS) and low-energy ions (sputtering, SIMS):
  - high-energy ions:
    - · energy transfer mainly by *electronic* energy loss
    - → PIXE (particle-induced X-ray emission)
  - low-energy ions:
    - · transfer mainly by *nuclear* energy loss
    - ← elastic collision with nuclei

Modeling Ion Desorption from Solid Sample



Energy cascade from incoming ion ejects neutral and charged atoms, molecule fragments and molecules

General Concepts of Sputtering

- erosion rate is characterized by the sputtering yield

$$Y := \frac{\text{mean number of emitted atoms}}{\text{incident particle}}$$

- depends on
  - structure and composition of target
  - parameters of incident ion beam
  - geometry (angle etc.)
- measured values of Y cover an interval of more than 7 orders of magnitude
- for medium-mass ion species and keV energies: $Y \approx 0.5..20$

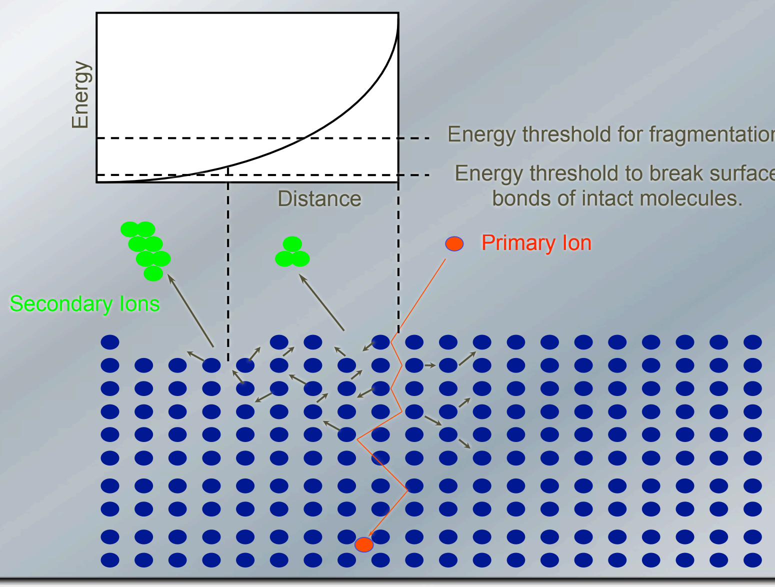
General Concepts of Sputtering

- compare sputtering yields of MeV light ions: $\approx 10^{-3}$

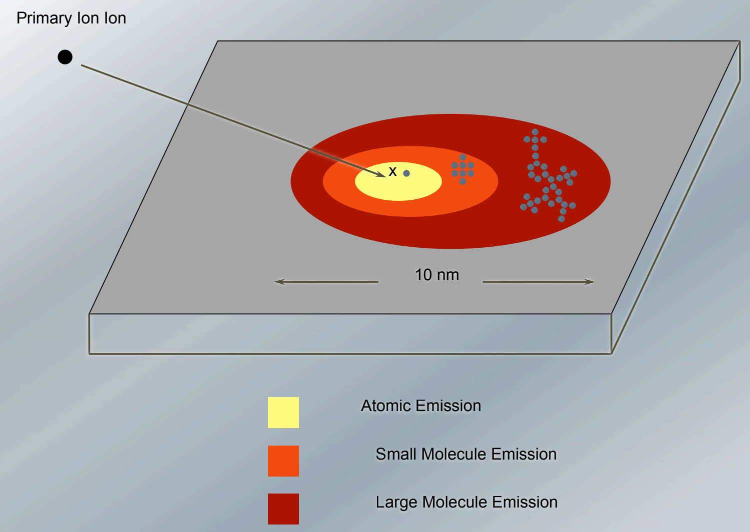
→ RBS typically only sputters off a fraction of a monolayer

- determination of *sputtering yield* Y:
  - *single-element* materials
    - accurate *theory* exists – assumptions:
    - nuclear energy loss mechanism
    - energy loss shared among large number of atoms
    - "collision cascade"
    - example: sputtering yield of Si
    - experimental values agree with calculations (solid line)
  - *else*: tabulated values or experimental calibration

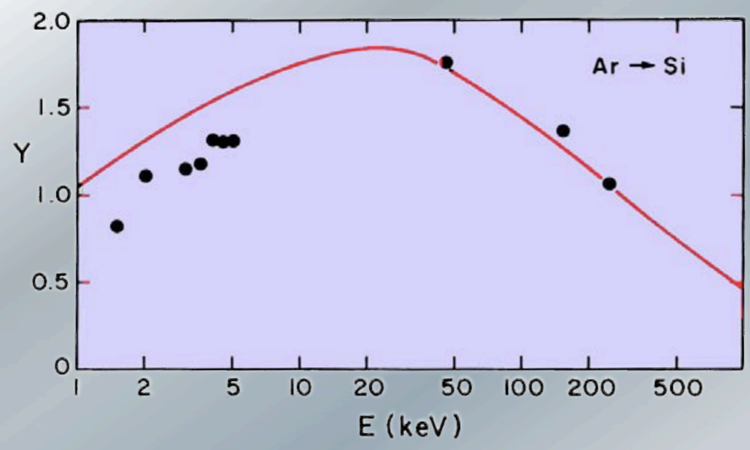
Energy Cascade for Ejection of Ions



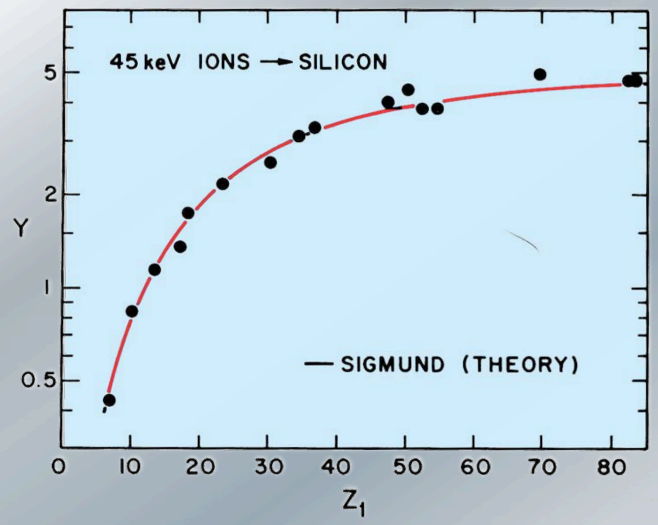
Ejection of Atom and Molecules



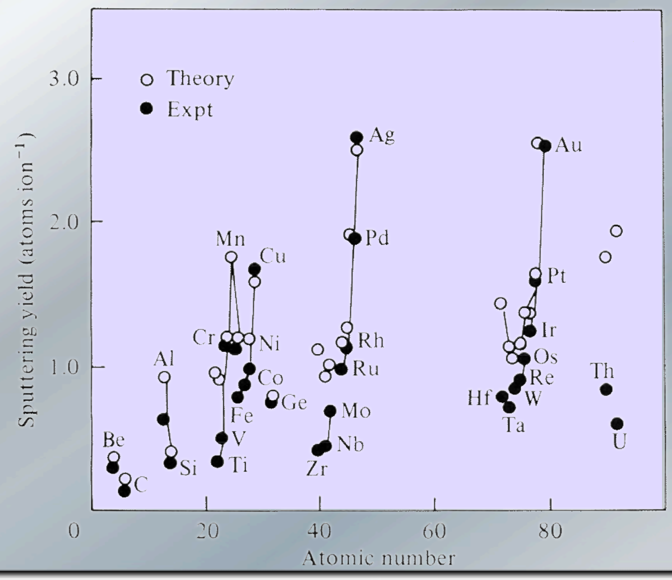
Sputtering Yield of Si: Dependence on Ar^+ Energy



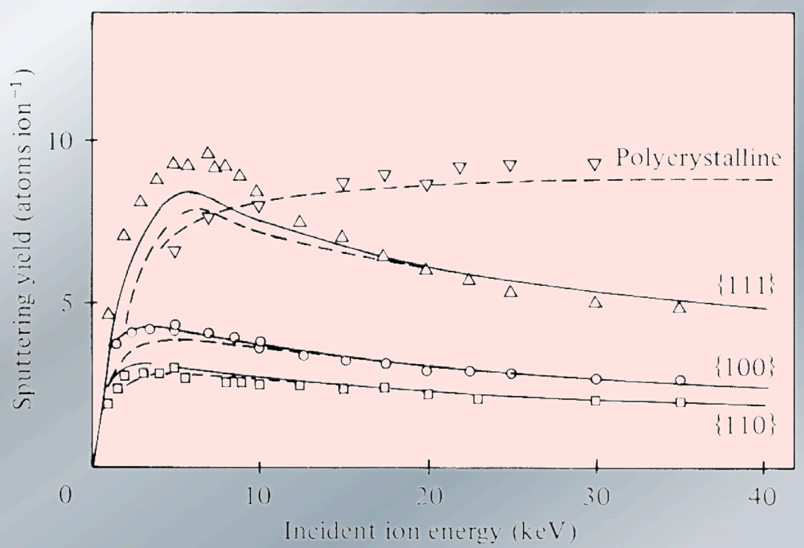
Sputtering Yield of Si: Dependence on Incident Ion Mass



Sputtering Yield: Dependence of Atomic Number



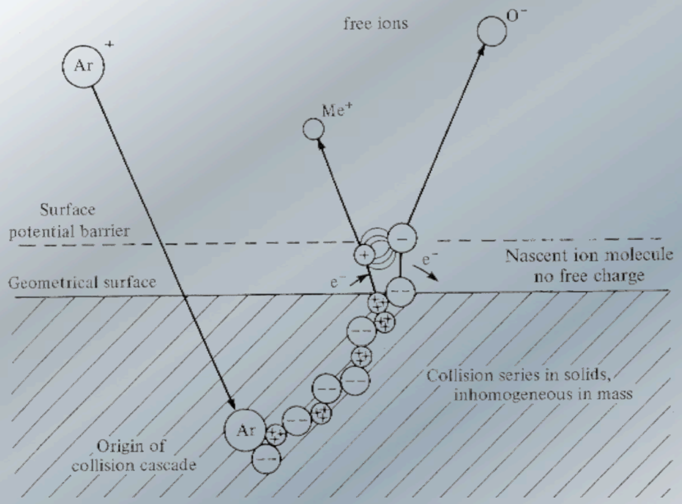
Sputtering Yield of Si: Dependence of Incident Direction



General Concepts of Sputtering

- physical understanding:
  - bombarding ion transfers energy to target atoms
  - these recoil with sufficient energy to generate further recoils
  - some backward-recoiled atoms ($\approx 1..2$ for a 20 keV Ar^+ ion) approach surface with enough energy to escape
  - these secondary recoils make up most of the sputtering yield
  - the most important parameter in this process is the energy deposited at the surface
  - the sputtering yield should be proportional to number of displaced or recoil atoms

General Concepts of Sputtering



- Only a small fraction is ionized for SIMS analysis
- SIMS reveals **elemental** (H included) and **isotopic** surface composition

General Concepts of Sputtering

- physical understanding (continued):
  - linear cascade regime (for medium-mass ions as Ar^+):
    - number of recoils proportional to the energy deposited per unit depth

    ⇒ sputtering yield:

$$Y = \Lambda \cdot F_D[E_0]$$

Λ: all material properties (surface binding energies etc.);
$F_D[E_0]$: density of deposited energy at the surface.

  - $F_D[E_0]$ depends on
    - incident ion (type, energy, direction)
    - target parameters (Z_2, M_2, and atomic density N)

General Concepts of Sputtering

- deposited energy at the surface can be expressed as

$$F_D[E_0] = \alpha N S_n[E_0]$$

$S_{n[E]}$: nuclear stopping cross-section;
$N \cdot S_n[E]$: nuclear energy loss, $= dE/dx$;
α: correction factor.

- correction factor α:
  - accounts for
    - angle of incidence
    - contributions from large-angle scattering events

General Concepts of Sputtering

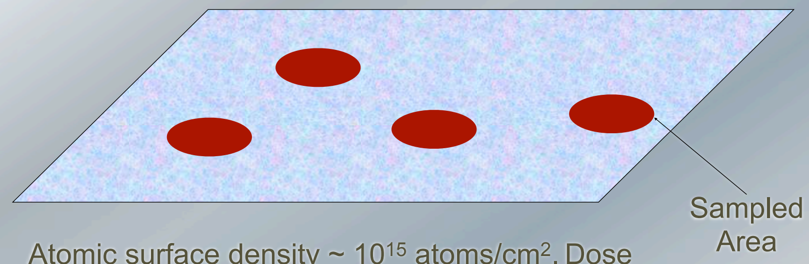
- nuclear stopping cross-section $S_n E$:
  - in the keV sputtering regime particle velocity is much less than Bohr velocity
  - → theory must account for screening of nuclear charge by electrons
  - then derive collision cross-section based on screened potential
  - → nuclear stopping cross-section

Experimental Aspects of SIMS

- common technique:
  collection and analysis of *ionized* species
  - "secondary ions"
  - → secondary ion mass spectroscopy (SIMS)
- SIMS: the most *sensitive* of all surface analysis techniques

Static SIMS

When 'dose' of primary ions is low: each ion strikes a *new* area of the surface = Static SIMS.

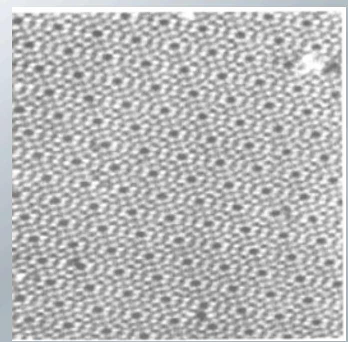


Atomic surface density ~ 10^{15} atoms/cm^2. Dose equivalent to ~ 10^{12} - 10^{13} atoms/cm^2. ToF-SIMS analysis optimized in this regime.

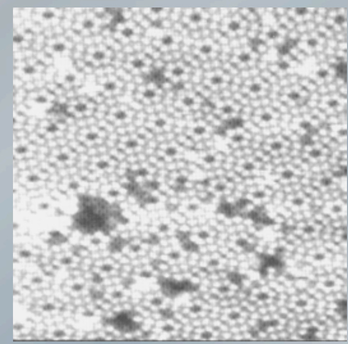
Classification of SIMS

- Static SIMS
  - very low beam current (1 nA/cm^2) hence only remove fraction of monolayer (<0.1 nm/h)
  - less sensitivity
  - good for imaging and surface analysis
- Dynamic SIMS
  - high primary beam current (10 mA/cm^2) and fast removal of surface (100 μm/h)
  - remove more materials in a given time hence better detection limit
    - significantly damage the surface
  - good for depth profiling (with caution)
- nowadays: dual beam profiling for the best of both world

Surface after Static SIMS Acquisition



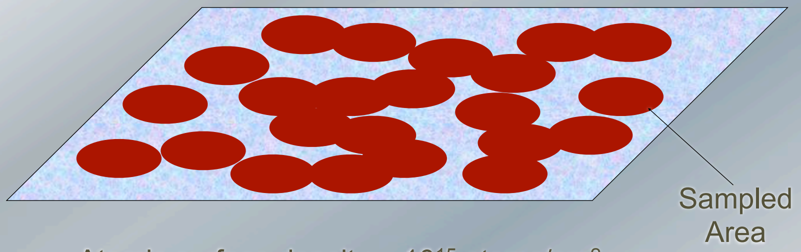
Si surface.



Si surface exposed to 3×10^{12} ions/cm^2.

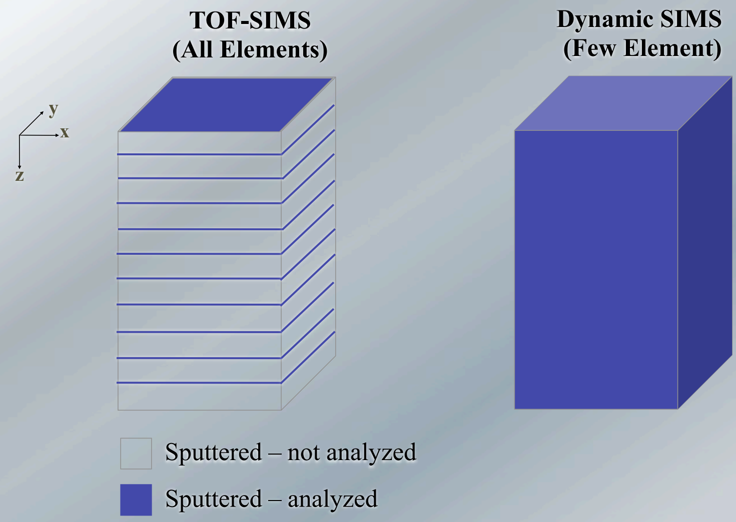
Dynamic SIMS

Primary ion 'dose' is increased: there is significant chance of striking a previously sampled area = loss of high molecular weight information (damage accumulation).



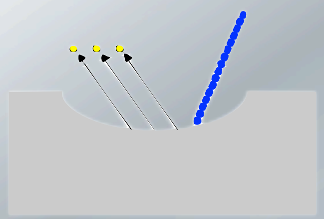
Atomic surface density ~ 10^{15} atoms/cm^2.
Dose equivalent to ~ 10^{14} atoms/cm^2.

Dynamic vs. Static SIMS



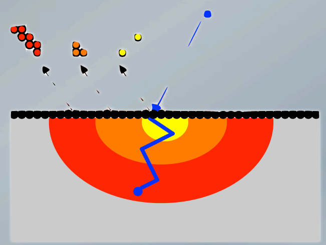
Dynamic vs. Static SIMS

Dynamic SIMS



- Material removal.
- Elemental detection.
- Profiling (concentration as a function of depth).

Static SIMS

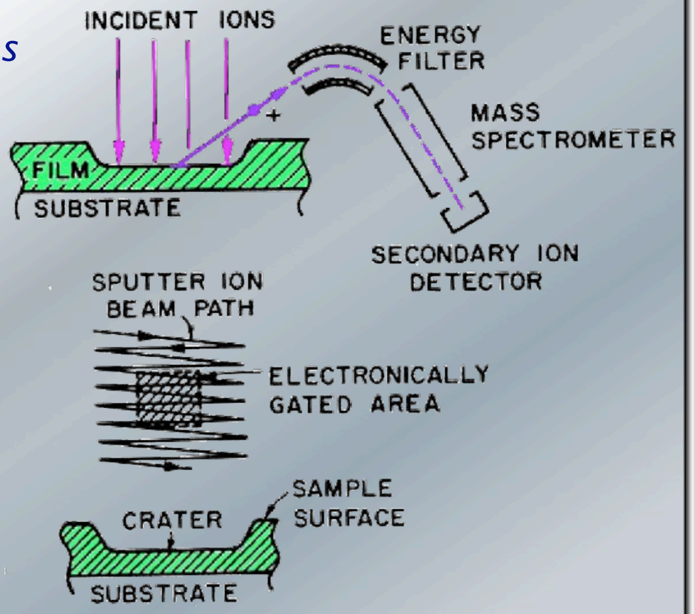


- Surface analysis.
- Molecular and elemental detection.
- Analysis complete before significant fraction of molecules destroyed.

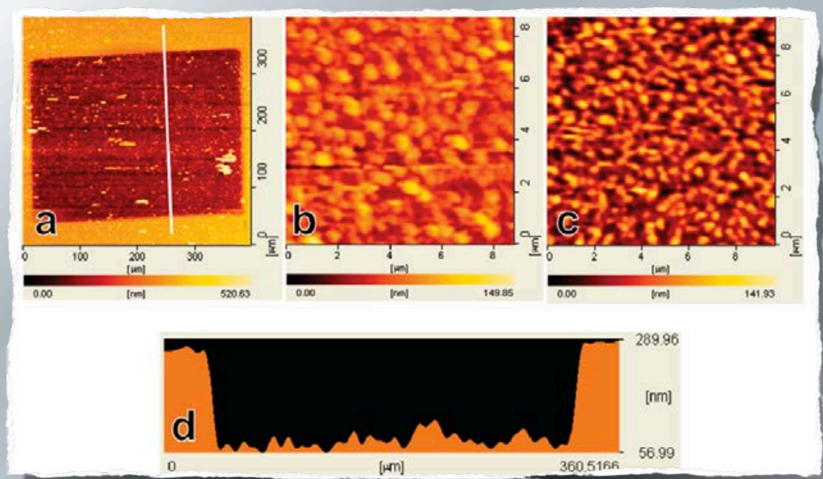
SIMS Apparatus

- incident ion beam ⇒ sputtered ions
- mass spectrometer
  - electrostatic energy filter
  - ion detector
- beam sweeping
  - large area of the sample
  - signal detected from thin central portion of the sweep
  - → avoid crater edge effects

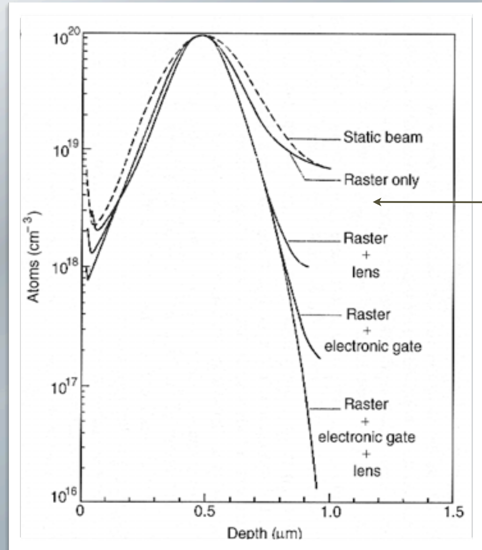
SIMS Apparatus



Edge Effect

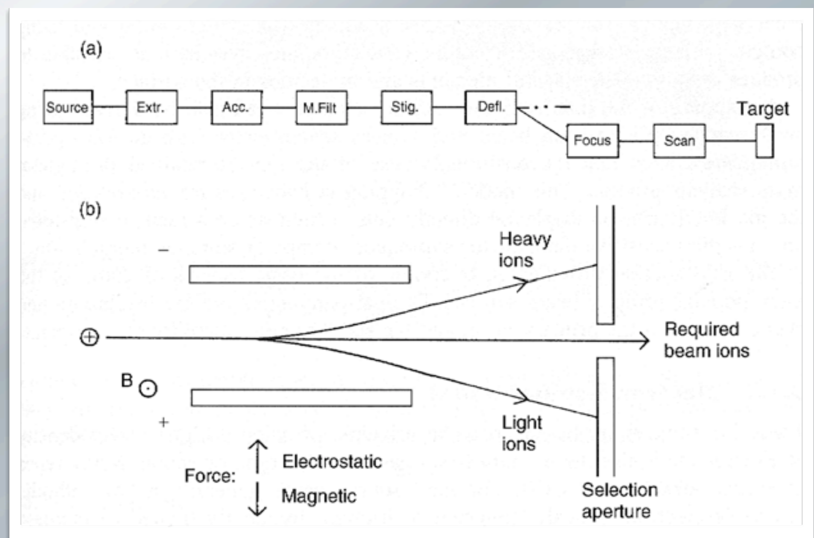


Avoiding "Edge Effect": Gating

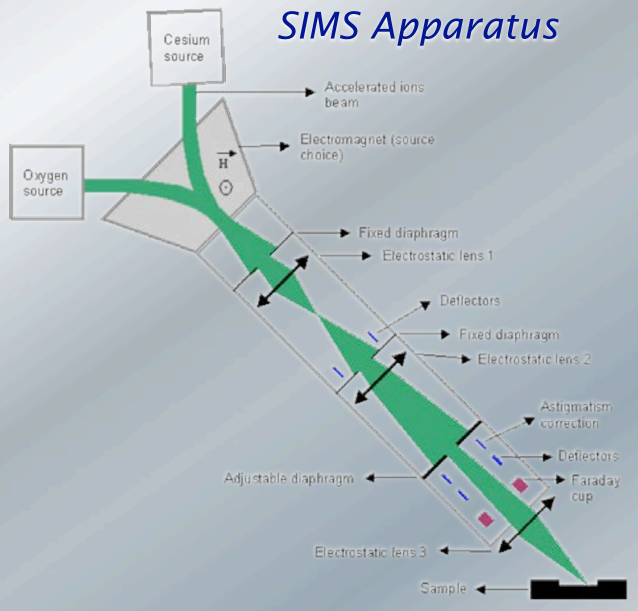


we are somewhere around here currently

SIMS Apparatus: Ion Sources

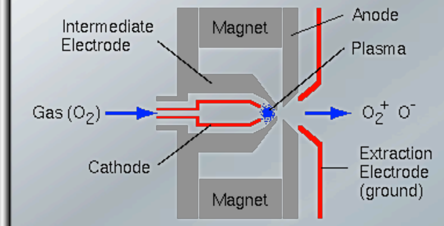


SIMS Apparatus



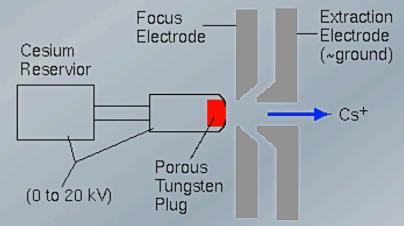
SIMS Apparatus: Ion Sources

Duoplasmatron



10^4~10^7 A/m²Sr

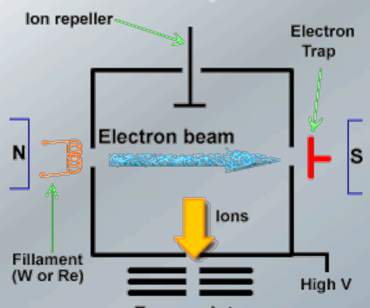
Surface Ionization



>10^6 A/m²Sr

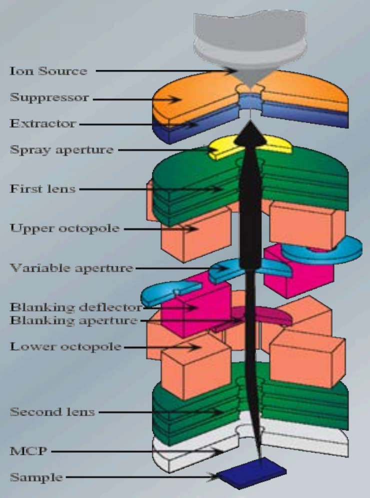
SIMS Apparatus: Ion Sources

Electron-Impact (EI)



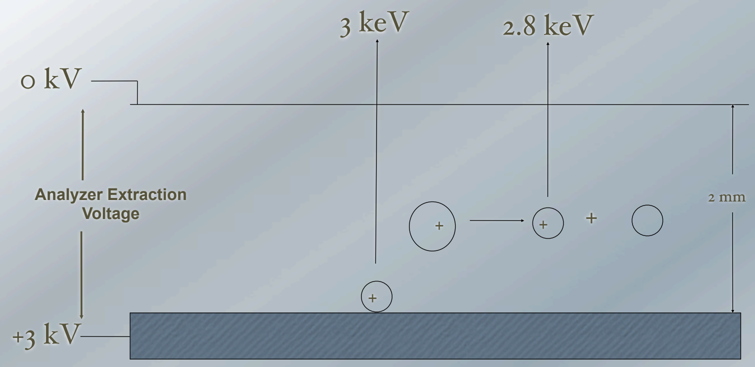
10^5 A/m²Sr

Field Emission (LMIS)



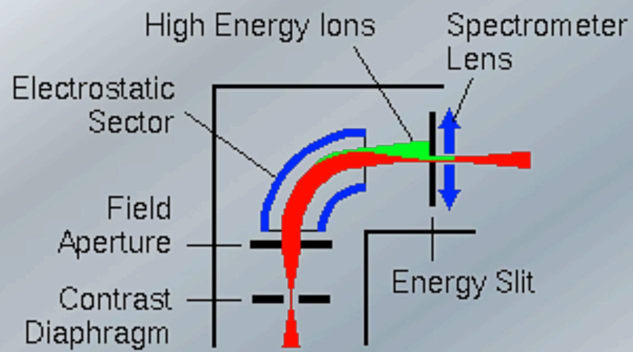
10^{10} A/m²Sr

Metastable Background in SIMS

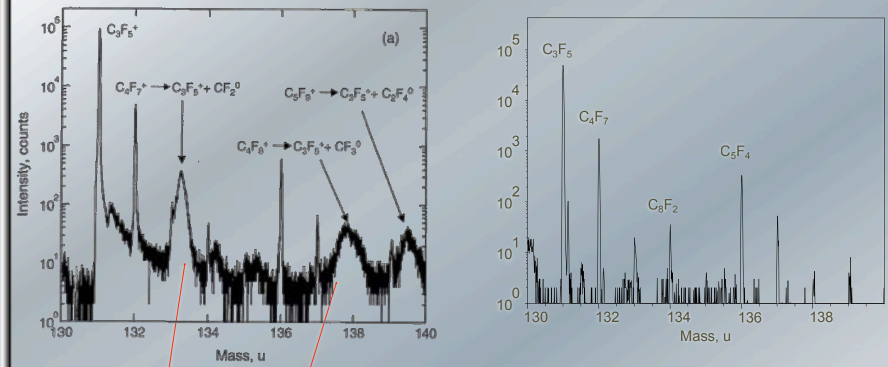


- Uni-molecular decay of “excited” or “hot” secondary ions in extraction field produce metastable background in organic TOF-SIMS
- Metastable ions have the “wrong” energy causing a broad background

SIMS Apparatus: Ion Energy Analyzers



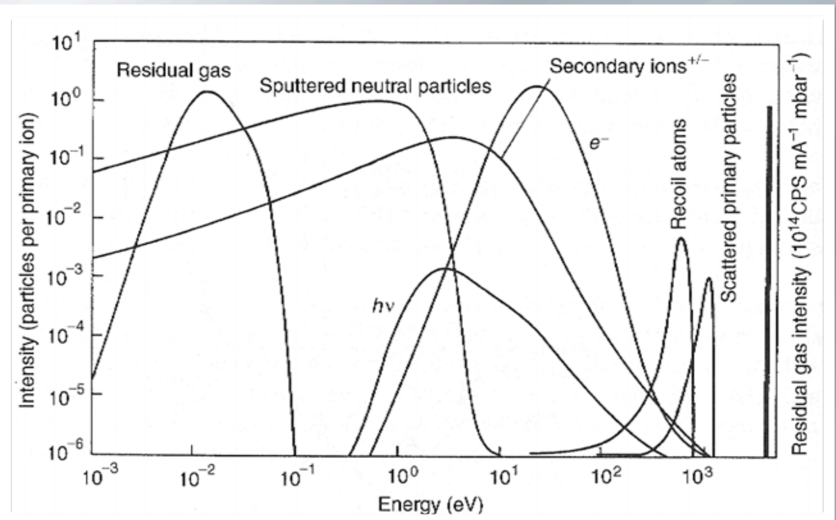
Teflon Spectra with and w/o Energy Filtering



High Metastable Ion Background with Reflectron

Very Low Metastable Ion Background with TRIFT

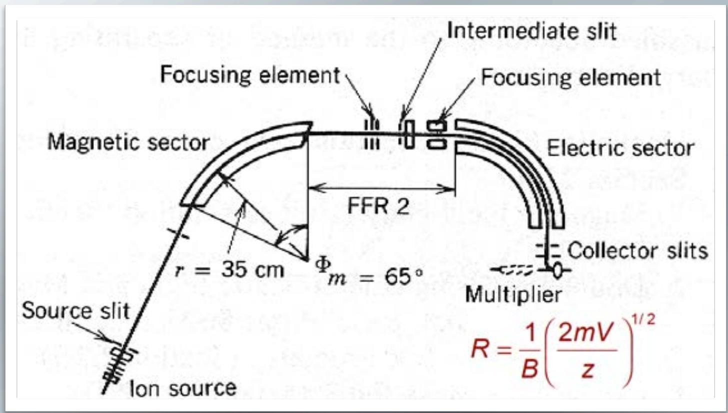
Energy Distribution of Emitted Particles



SIMS Apparatus: Mass Filter

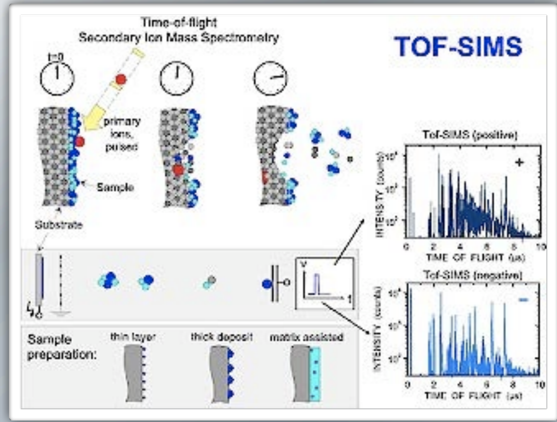
- Magnetic Field Deflection (direction focusing)
  - Magnetic Field Only (unit resolution)
  - Double Focusing (electrostatic field and magnetic field, high resoultion)
- Quadrupole
  - Quadrupole Mass Filter
  - Quadrupole Ion Storage (ion trap)
- Time of Flight
  - Reflectron
  - Multi-Sector
- Fourier Transform

Magnetic Field Deflection



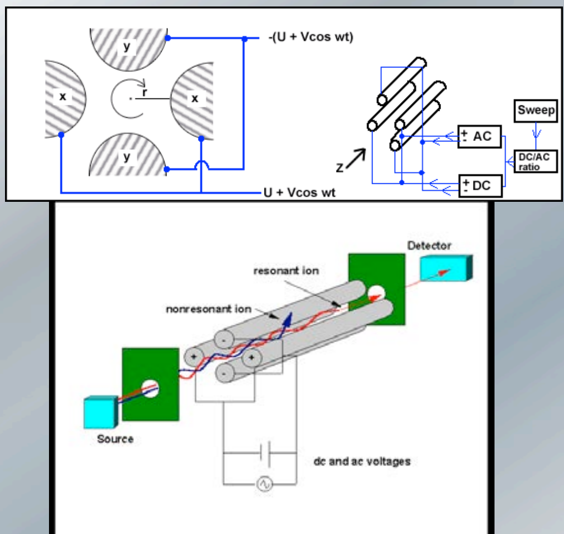
- possible to have multi-channel detector to maintain high transmission
- large cumbersome device and difficult to use with UHV

Time-of-Flight Secondary Ion Mass Spectrometry



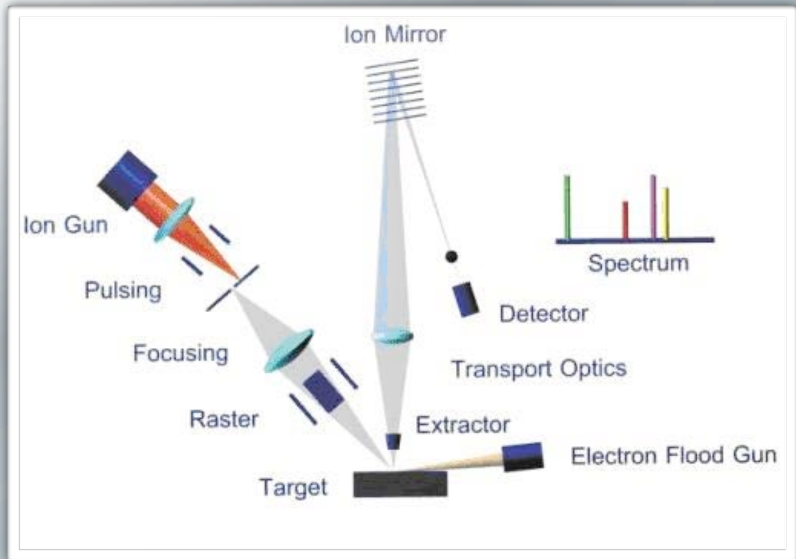
- great transmission, but low duty-cycle
- great for static SIMS

Quadrupole Mass Filter

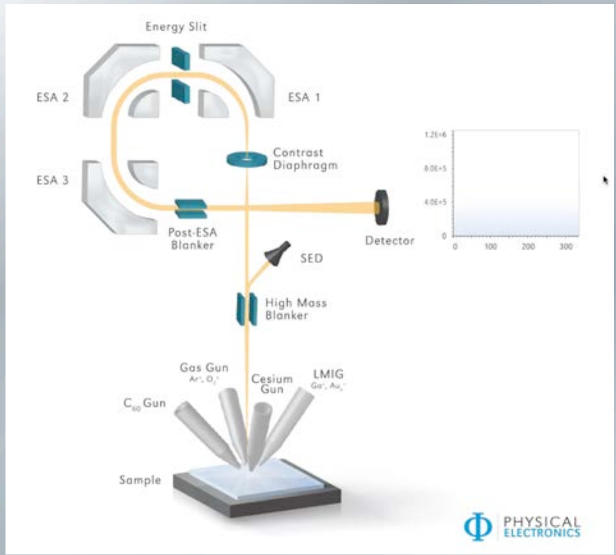


single channel detection with low transmission

Time-of-Flight Analyzer: Reflectron



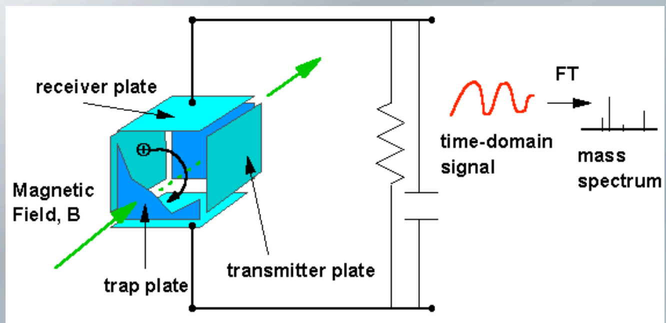
Time-of-Flight Analyzer: Multi-Sector Analyzer



Comparison of Mass Analyzer

	Quadrupole	Magnetic Sector	Time of Flight
Resolution	10^2-10^3	~10^4	>10^3
Mass range	<1000	>10^4	unlimited
Transmission	1%-10%	10%-50%	50%-100%
Detection	sequential	sequential	parallel
Relative sensitivity	1	10	10000

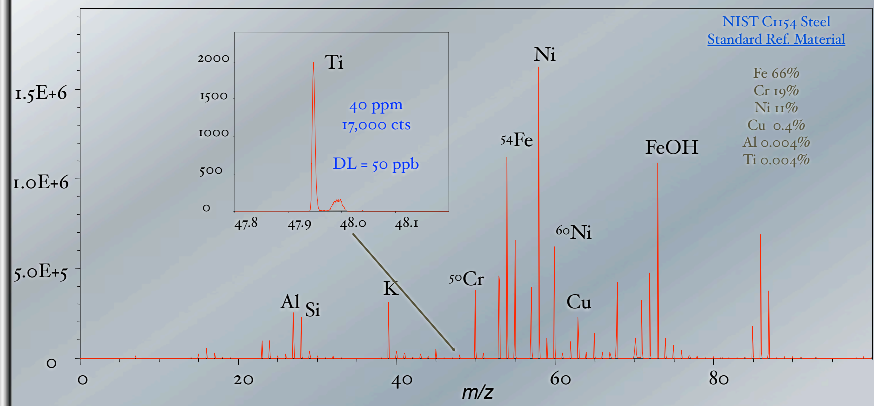
Fourier Transform Mass Spectrometry



good transmission but not usually used with SIMS

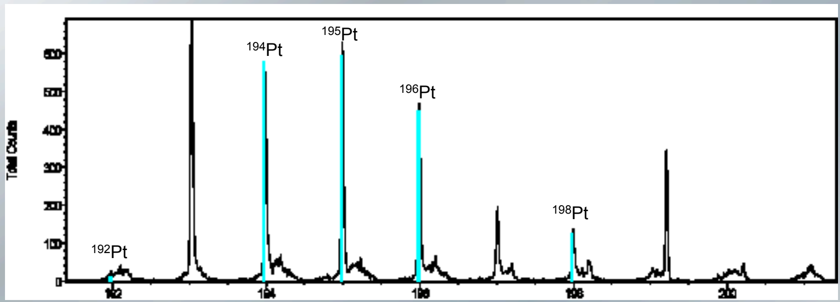
Sensitivity of SIMS

Blanking matrix signal from the mass spectrum increases detection sensitivity.



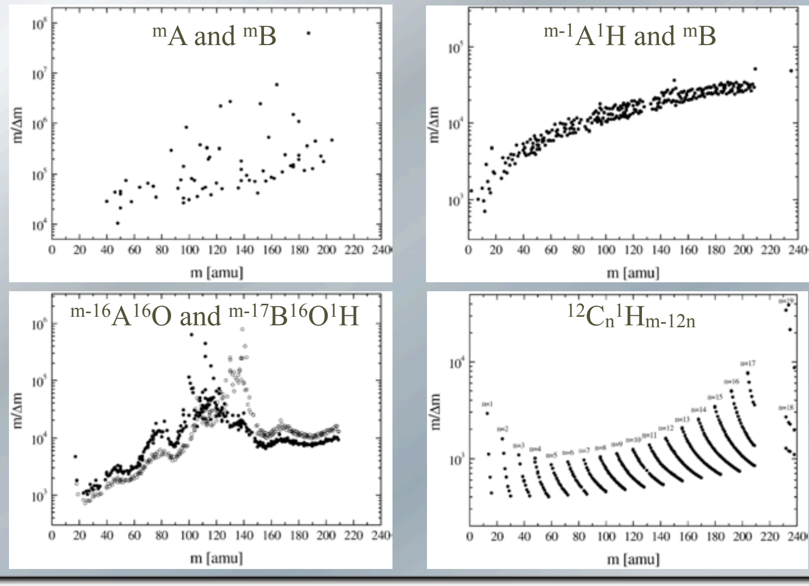
Ga+ beam current = 20 nA; 5 min. acquisition. (^{56}**Fe blanked**.)

Isotopic Identification

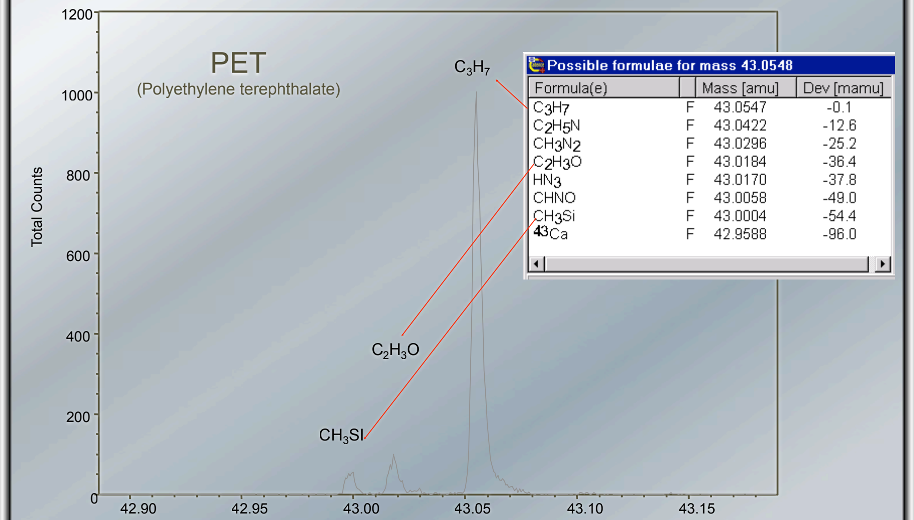


The markers of the *Isotope Tool* indicate the natural abundance of the Pt isotopes.

Required Resolution

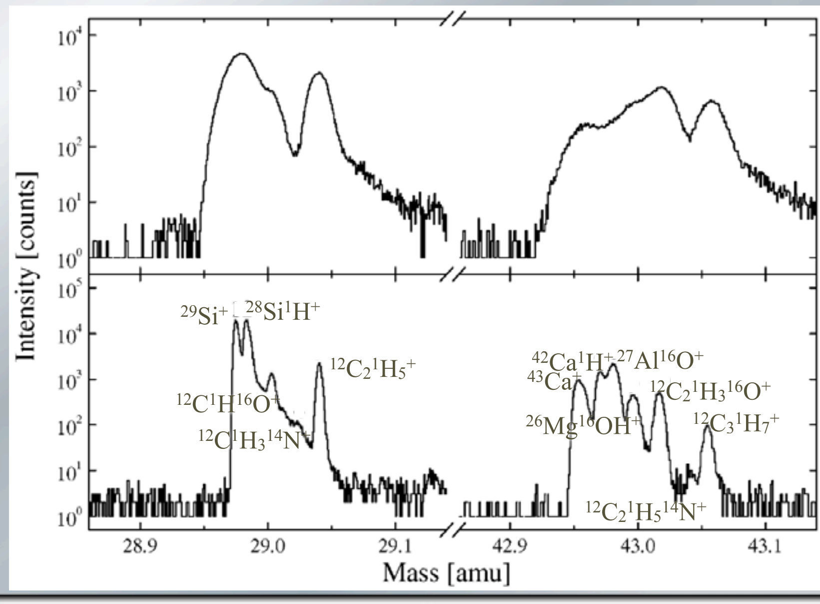


Mass Resolution of SIMS

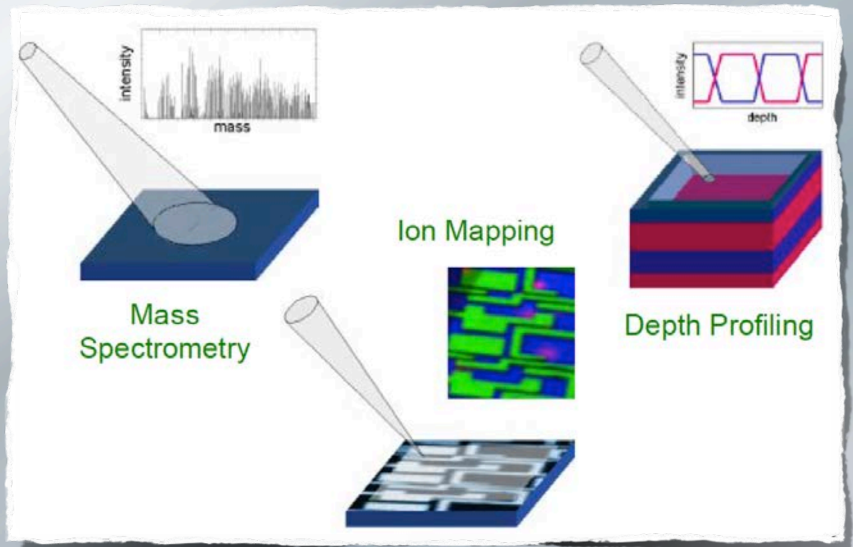


Formula(e)		Mass [amu]	Dev [mamu]
C_3H_7	F	43.0547	-0.1
C_2H_5N	F	43.0422	-12.6
CH_3N_2	F	43.0296	-25.2
C_2H_3O	F	43.0184	-36.4
HN_3	F	43.0170	-37.8
CHNO	F	43.0058	-49.0
CH_3Si	F	43.0004	-54.4
^{43}Ca	F	42.9588	-96.0

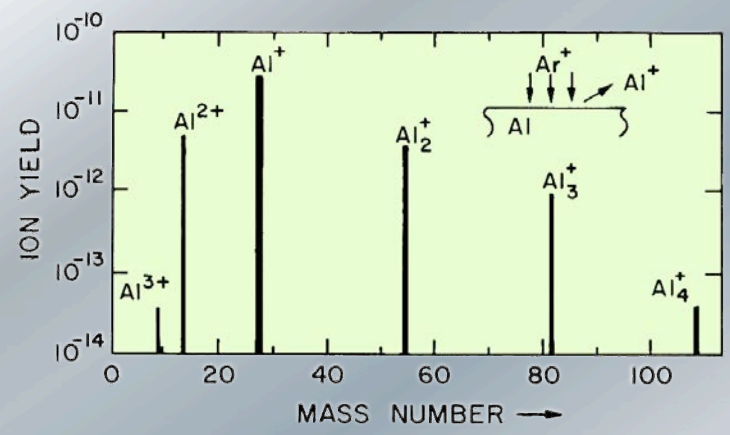
Effect of Resolution



Operation Modes of SIMS



Example of SIMS Spectra

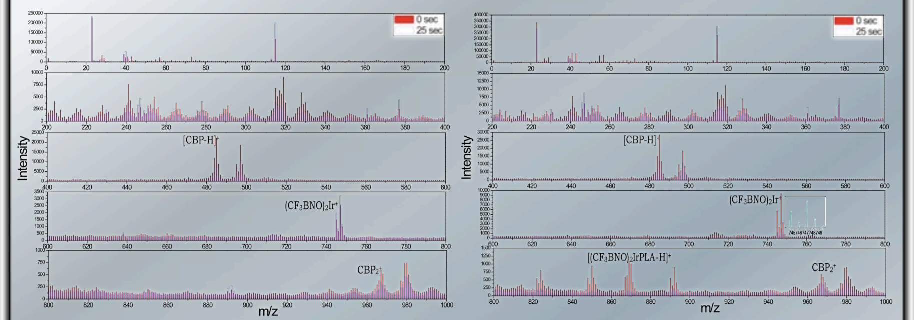


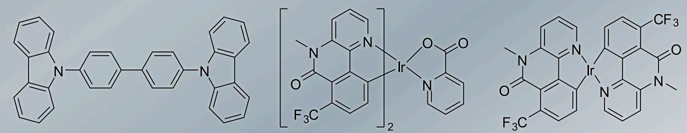
SIMS Spectra

- sputtered species are emitted as neutrals in various excited states
  - ions
  - positive and negative
  - singly and multiply charged
  - clusters of particles
- example: secondary ion cluster spectrum of Al
  - obtained by Ar^+ bombardment
  - ordinate is log scale!
  - predominant species: Al^+
  - but also: Al^{2+}, Al^{3+}, $(Al_2)^+$, $(Al_3)^+$, $(Al_4)^+$

ToF-SIMS of Organic EL

Spin-Coating | Thermo-Evaporation





CBP, m.w. 484 | $(CF_3BNO)_2IrPLA$, m.w. 869 | $(CF_3BNO)_2Ir$, m.w. 747

SIMS Spectra

- in most cases, singly ionized atoms dominate the spectrum
- ratio ionized to neutral species from same sample can vary by orders of magnitude – depending nature of the surface
- sputtered particles emerge with a distribution of energies

⇐ fluctuations in individual events that make up sputtering process

- total yield of sputtered can be expressed by integrating over the yields at all different energies E from 0 to the maximum possible energy E_{max}:

$$Y = \int_0^{E_{\text{max}}} Y[E]\,\mathrm{d}E$$

SIMS Spectra

- yield of positively ionized secondary ions, $Y^+[E]$, is related to sputtering yield $Y[E]$ by

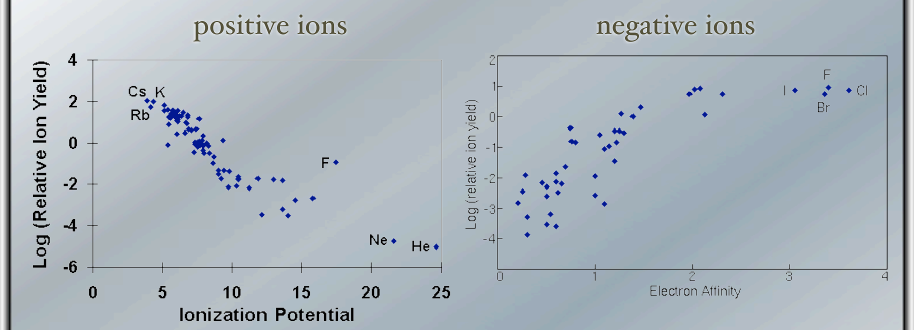
$$Y^+ = \alpha^+[E] \cdot Y[E]$$

$\alpha^+[E]$: ionization probability.

- this implies

$$Y^+ = \int_0^{E_{\text{max}}} \alpha^+[E] \cdot Y[E]\,\mathrm{d}E$$

Secondary Ion Yield: Elemental Effects



Example of SIMS Spectra

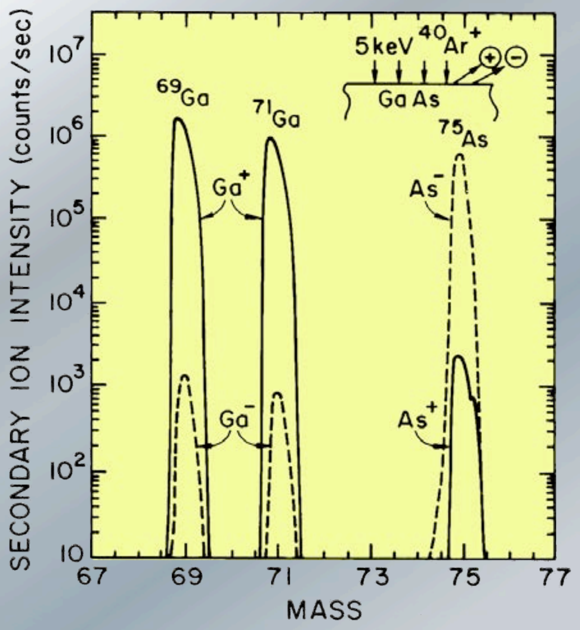
- GaAs
  - bombarded with 5 keV Ar^+ ions
  - positive ion yields: "———"
  - negative ion yields: "- - - - -"

  → sputtering yields of Ga and As are nearly identical

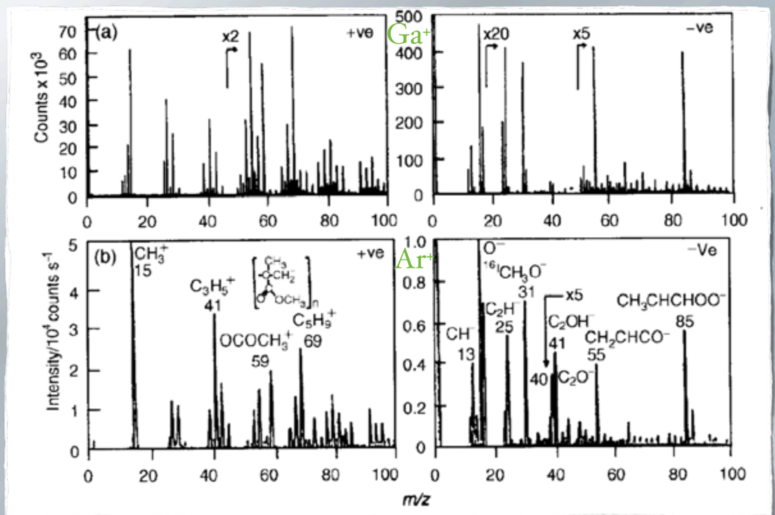
  → ionization yield can vary by three orders of magnitude between species with nearly identical sputtering yields

⇒ major problem in quantification of SIMS: determination of $\alpha^+[E]$

Example of SIMS Spectra



PMMA SIMS



Quantification of SIMS

- consider mono-isotopic element of mass A and concentration C_A in the target
- measured signal I^+ (counts/s)

$$I_A^+ = C_A \cdot i_\mathrm{p} \cdot \beta \cdot T \cdot \alpha^+[E,\theta] \cdot Y[E,\theta] \cdot \Delta\Omega \cdot \Delta E$$

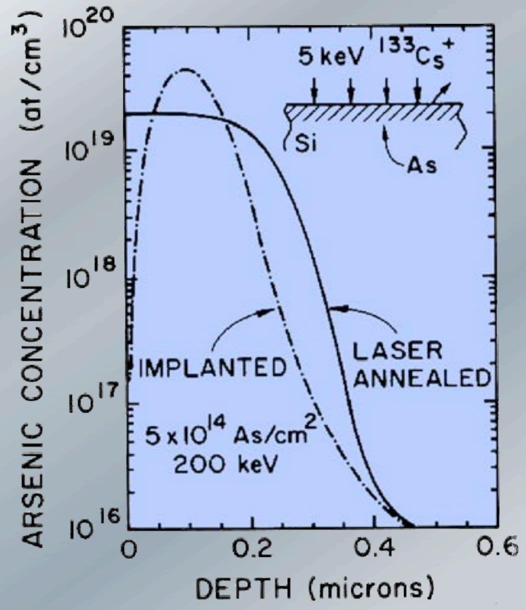
i_p: primary beam current (ions/s);
θ: angle of the detector system;
E: pass energy of the detector system;
$\Delta\Omega$: solid angle of the energy filter;
ΔE: width of the energy filter;
β: detector sensitivity;
T: transmission of the system for the ion species being measured.

α^+ and Y depend on sample composition and ion beam!!

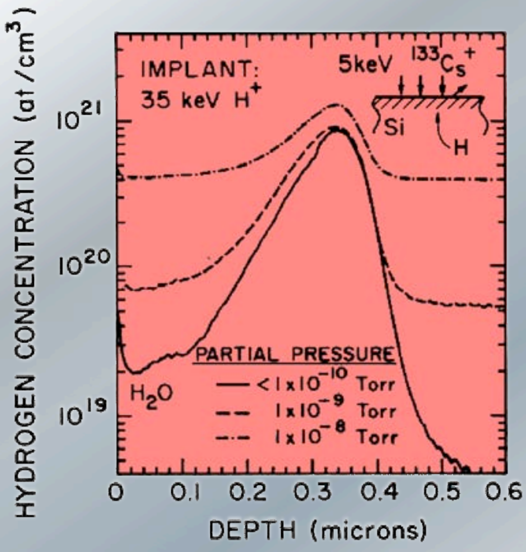
Quantification of SIMS

- composition dependence can frequently be neglected for concentration profiles of low-level constituent
- matrix of otherwise constant composition
- example: SIMS concentration depth profile of As in Si
  - doping
  - ion-implanted
  - re-distributed by pulsed laser melting of the outer Si layer
  - maximum concentration below 10^{-3}
  - ⇒ presence of As has minimal effect on α
  - measured concentration below $10^{16}\,\mathrm{cm}^{-3}$

SIMS Example



SIMS Example



Hydrogen Detection

- further advantage of SIMS: can analyze H (hydrogen)
- example: SIMS concentration-depth profile of H in Si
- Si implanted with H
- dose: $1 \cdot 10^{-6}$ ions cm^2
- energy: 35 keV
- sputtering: 5 keV Cs^+ ions
- effect of H_2O partial pressure in the chamber on H profile

← surface contamination with H_2O affects H implantation

Quantification of SIMS

- SIMS relies on ions leaving the surface of the material under study
- however: secondary-ion yields are sensitive to presence of electropositive or electronegative ions at the target surface
- consider a positive ion leaving a surface:
- electrons at the surface may fill electron vacancy

⇒ neutralization

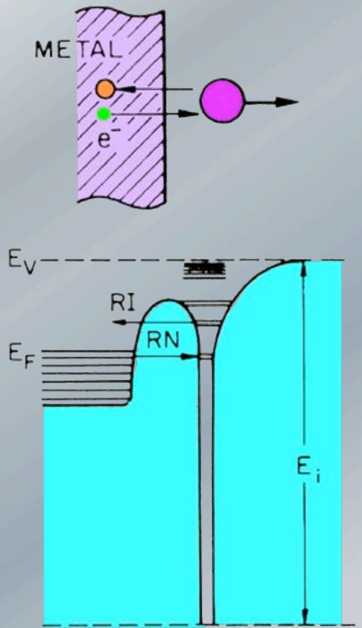
⇒ will not be detected

⇒ avoid

Neutralization

- model for microscopic process of neutralization: resonant tunneling
  - involved electrons of the same energy level as the vacancy
  - probability of neutralization depends on the electron bandstructure of the material and on the energy level of the electron vacancy
- for high yields of ions: reduce neutralization probability
- possible method: build up thin oxide layer
  - results in large forbidden band gap at the surface
  - decreases concentration of electrons available for neutralization of a positive ion

Neutralization

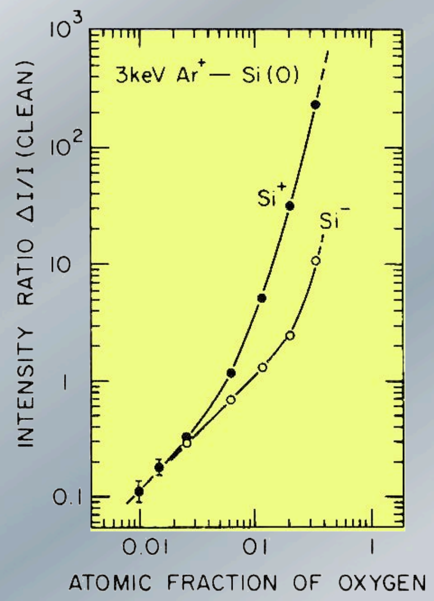


Examples Demonstrating Neutralization by Tunneling

- secondary ion yield for metals with and without oxygen coverage
- in practice:
  - surface "flooded" with oxygen
  - or bombarded with oxygen beam
- intensity ratios $\Delta I/I_C$ for Si^+ and Si^- ion yields from oxygen-implanted Si
  - ion emission from clean Si: I_C
  - ion emission from oxygen-doped Si: I

  ⇒ oxygen-induced intensity $\Delta I = I - I_C$

Example



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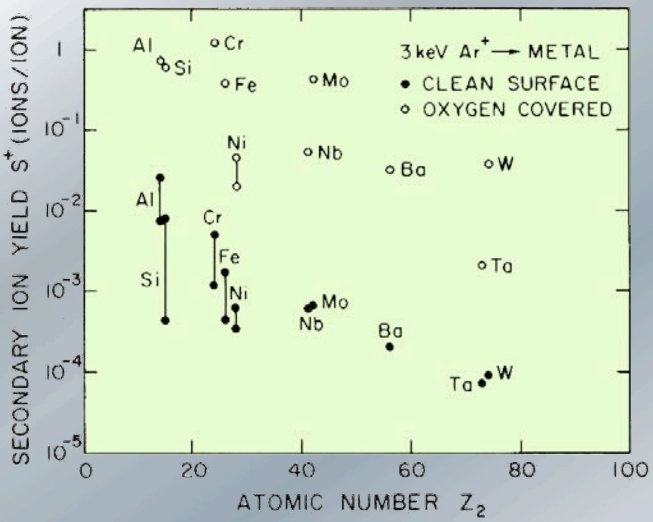
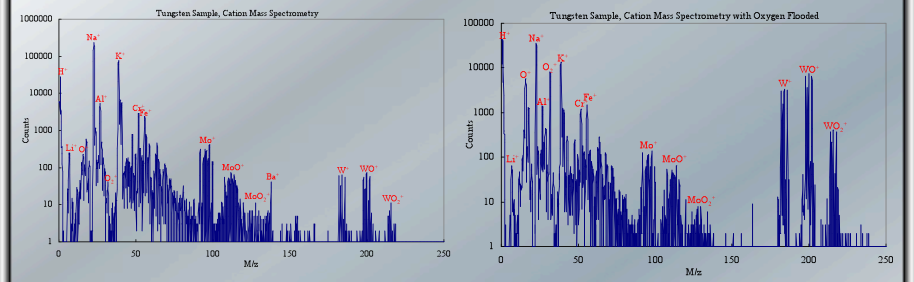
  - ion emission from clean Si: I_C
  - ion emission from oxygen-doped Si: I
  - ⇒ oxygen-induced intensity $\Delta I = I - I_C$
  - plot: relative oxygen-induced intensity ΔI versus atomic fraction of oxygen
  - demonstrates enhancement in yield over three orders of magnitude!

Examples Demonstrating Neutralization by Tunneling



Oxygen-Flooding on Metallic Sample

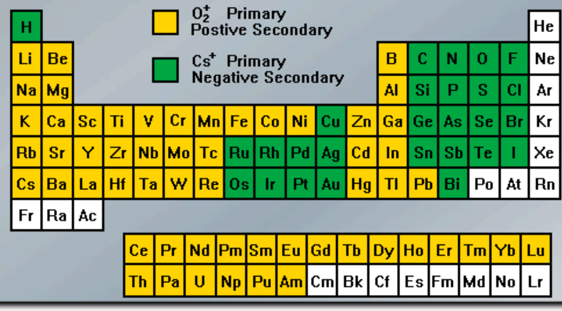


lower M^+ intensity, but enhanced MO_x^+ intensity

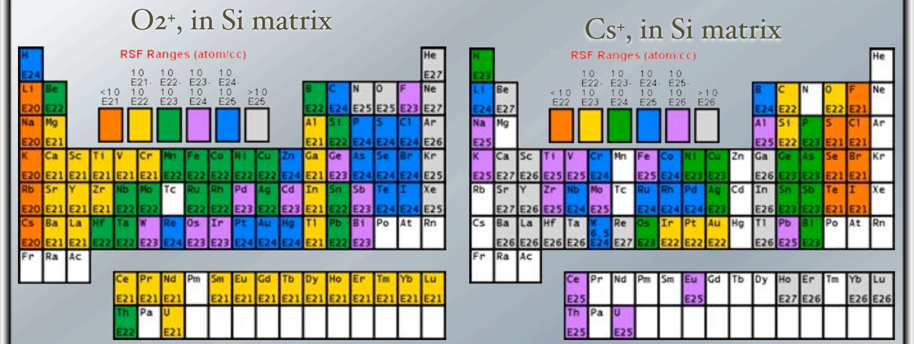
Reactive Primary Ion

Oxygen enhancement occurs as a result of metal-oxygen bonds in an oxygen rich zone. When these bonds break in the ion emission process, the oxygen becomes negatively charged because its high electron affinity favors electron capture and its high ionization potential inhibits positive charging. The metal is left with the positive charge. Oxygen beam sputtering increases the concentration of oxygen in the surface layer.

The enhanced negative ion yields produced with cesium bombardment can be explained by work functions that are reduced by implantation of cesium into the sample surface. More secondary electrons are excited over the surface potential barrier. Increased availability of electrons leads to increased negative ion formation.



Relative Sensitivity Factors



Principle of Depth Profile

- composition depth profiling with *surface* analysis techniques?

➡ *erosion* of specimen surface by energetic particle bombardment

- “sputtering”
- two possibilities for analysis:
  - freshly exposed surface (=> XPS, AES)
  - sputtered material (=> SIMS)
- depth profiling -> remove controlled thickness

Scanning Ion Microscopy

- similar to scanning electron microscopy (SEM)
- scan an ion beam over the specimen
- analyze sputtered ions at each scan point
- quantify yield of a particular element
- represent yield by intensity of corresponding pixel in the image

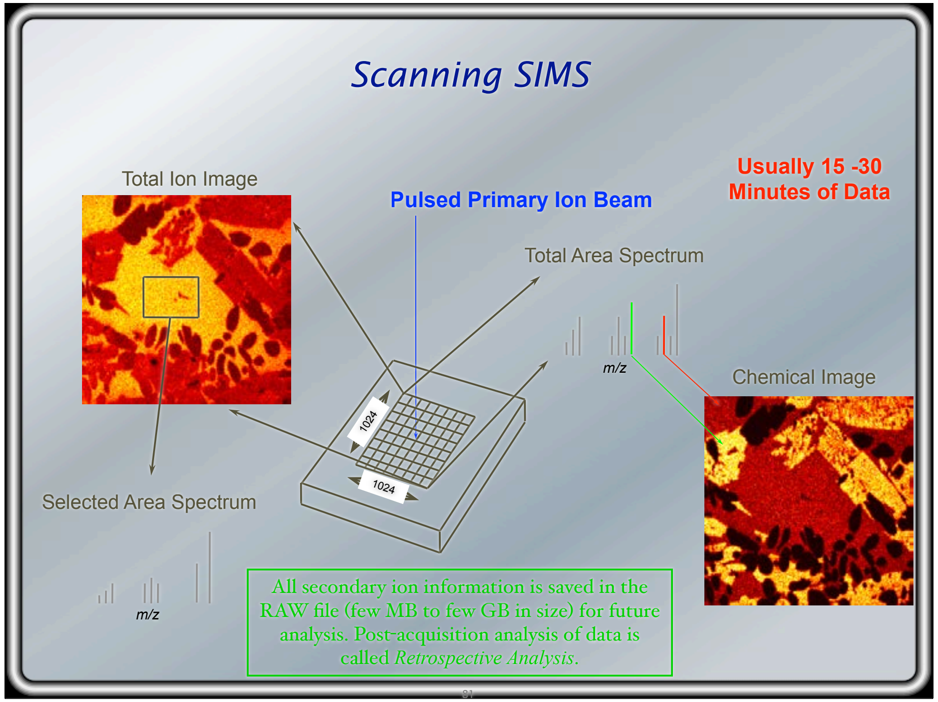
→ elemental map

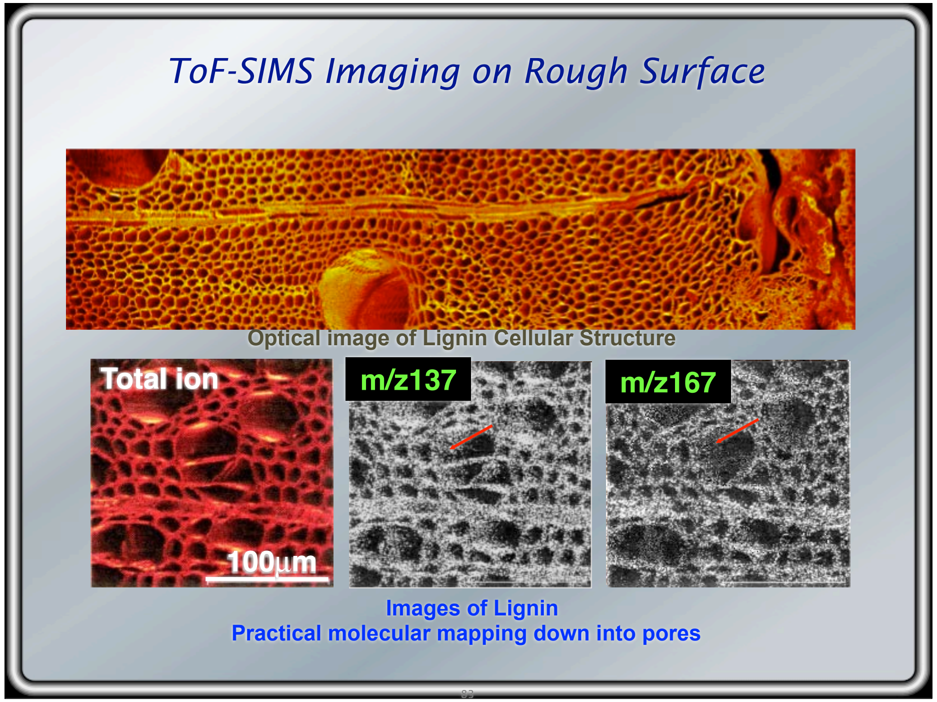
- at the same time: topography

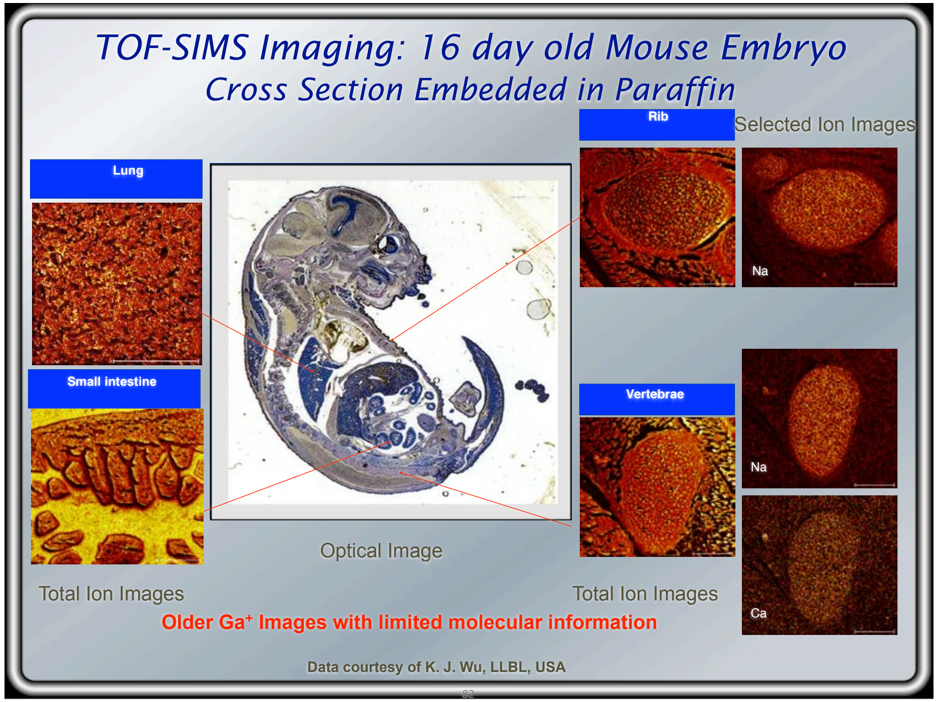
→ combination of signals, → synergy

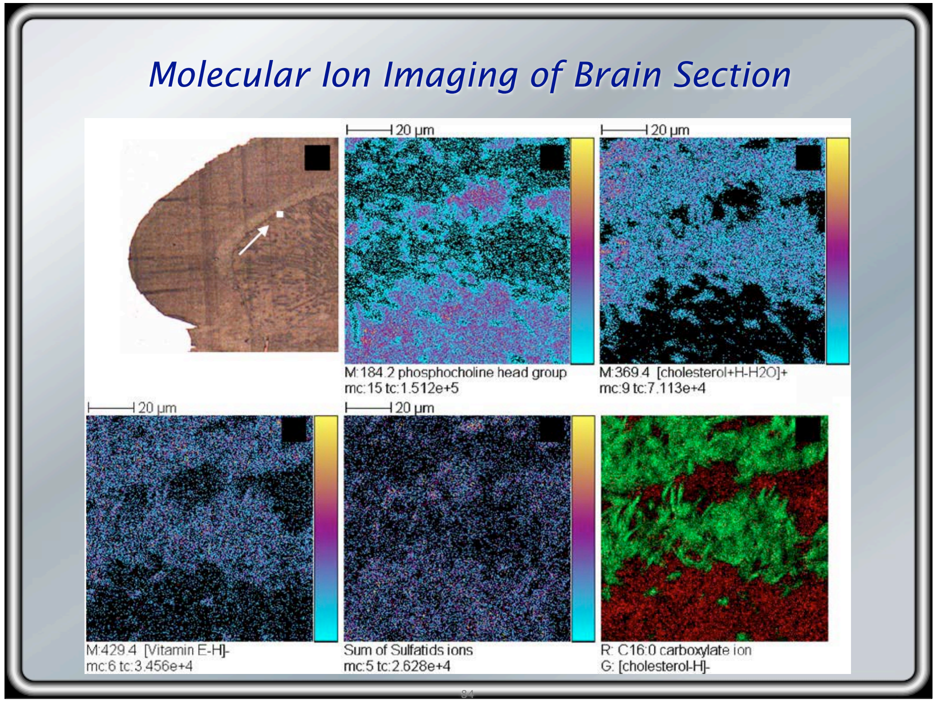
Pre-requisition for SIMS Imaging

- Static SIMS
- Parallel detection of multiple masses (high transmittance)
  - difficult with quadrupole
  - up to 7 masses with magnetic sector
- High angular solid angle and depth-of-focus
  - Extremely short working distance (500nm on Cameca)
    - co-axial primary beam and secondary ions with opposite charge
    - require O_2^- beam
  - Reflectron can only compensate time or space so that only high mass resolution or high solid angle
    - normally 4°
  - Multi-Sector is limited by pulse duration hence less efficiency or sensitivity
    - up to 180°

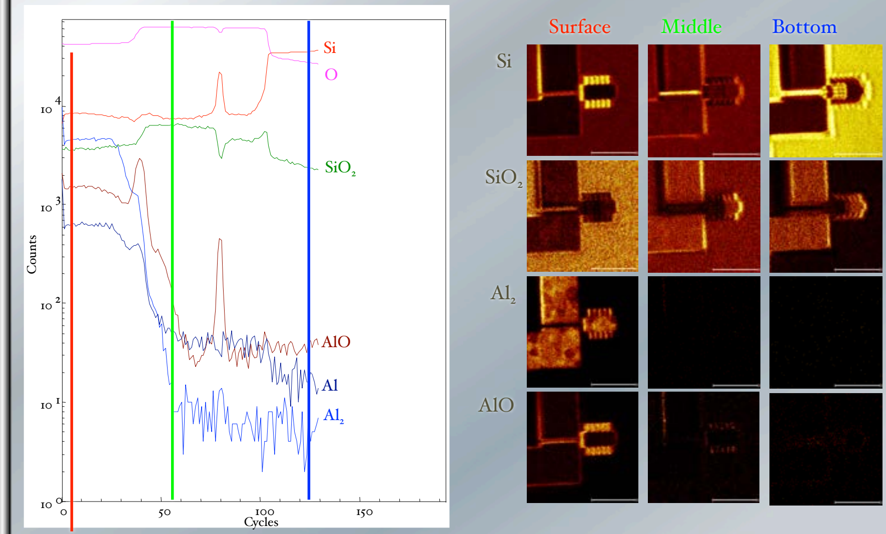

Scanning SIMS
Total Ion Image
Pulsed Primary Ion Beam
Usually 15 -30 Minutes of Data
Total Area Spectrum
m/z
Chemical Image
1024
1024
Selected Area Spectrum
m/z
All secondary ion information is saved in the RAW file (few MB to few GB in size) for future analysis. Post-acquisition analysis of data is called Retrospective Analysis.


ToF-SIMS Imaging on Rough Surface
Optical image of Lignin Cellular Structure
Total ion
m/z137
m/z167
100µm
Images of Lignin
Practical molecular mapping down into pores

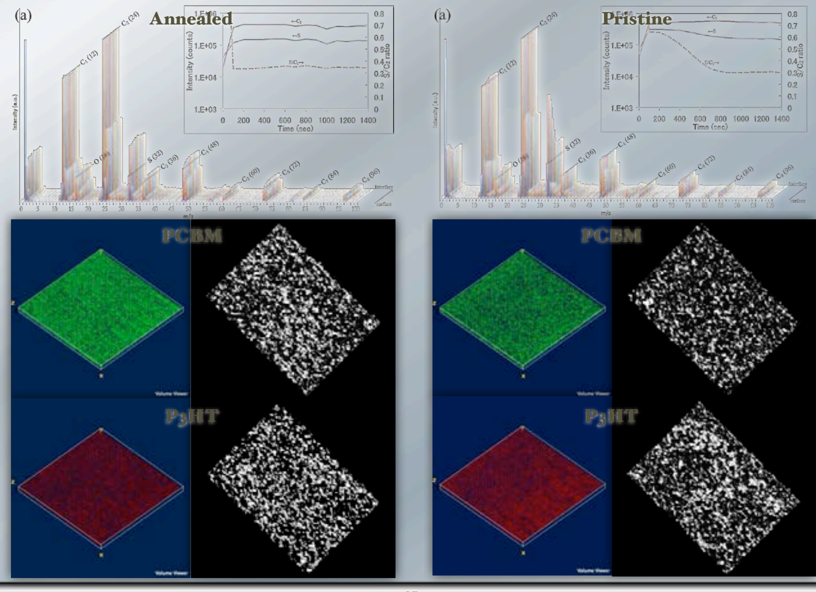

TOF-SIMS Imaging: 16 day old Mouse Embryo
Cross Section Embedded in Paraffin
Rib
Selected Ion Images
Lung
Na
Small intestine
Vertebrae
Na
Ca
Optical Image
Total Ion Images
Total Ion Images
Older Ga+ Images with limited molecular information
Data courtesy of K. J. Wu, LLBL, USA


Molecular Ion Imaging of Brain Section
20 µm
20 µm
M:184.2 phosphocholine head group
mc:15 tc:1.512e+5
M:369.4 [cholesterol+H-H2O]+
mc:9 tc:7.113e+4
20 µm
20 µm
M:429.4 [Vitamin E-H]-
mc:6 tc:3.456e+4
Sum of Sulfatids ions
mc:5 tc:2.628e+4
R: C16:0 carboxylate ion
G: [cholesterol-H]-

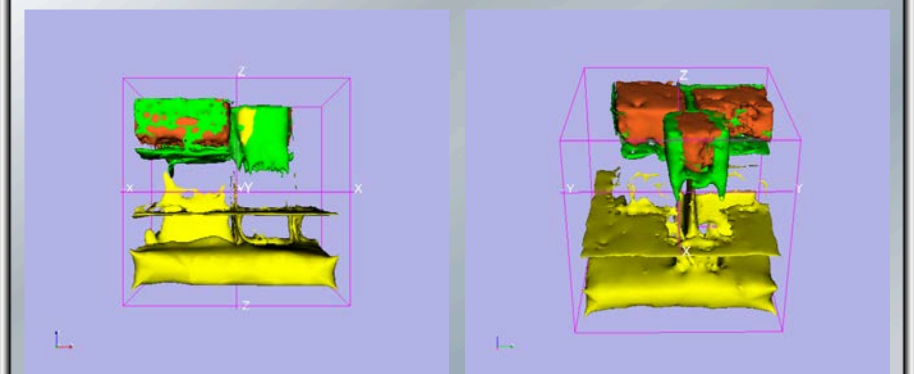
3D Imaging of CMOS Device



3D Imaging of P3HT:PCBM using Scanning ToF-SIMS

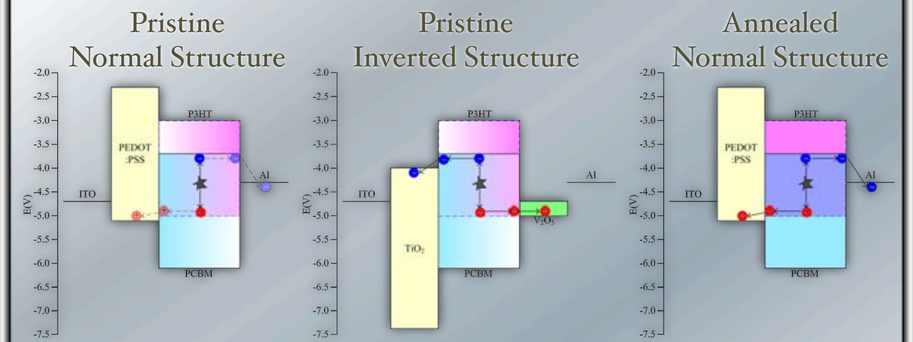


3D Imaging of CMOS Device



Al_2 (Orange) AlO (Green) Si (Yellow)

Effect of Molecular Depth Distribution on Solar Cells of Different Architecture



PCE=1.13%

PCE=2.71%

PCE=3.92%