Secondary Ion Mass Spectroscopy

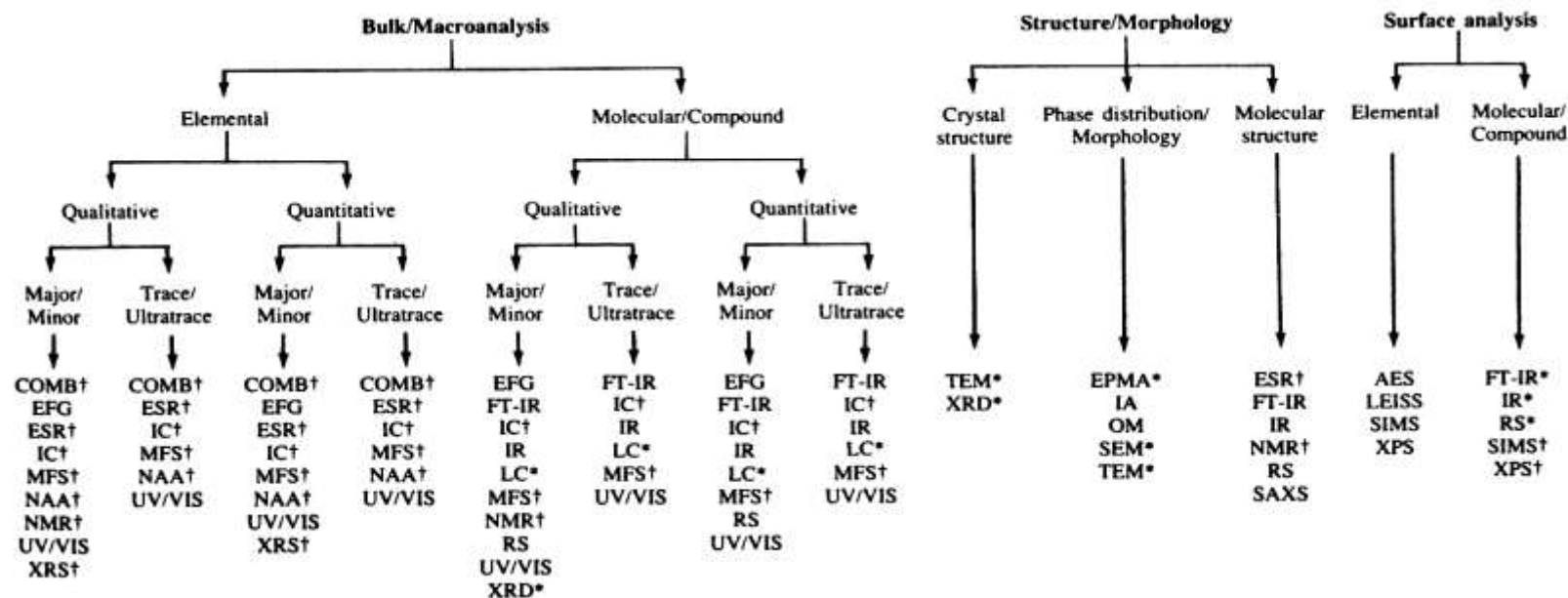## (SIMS)

Analyzing Inorganic Solids

Bulk/Elemental

Qualitative | Quantitative

Major/Minor | Trace/Ultratrace | Major/Minor | Trace/Ultratrace

IC†	ESR†	AAS	AAS
ICP-AES	FT-IR**	IC†	COMB†
NAA	IC†	ICP-AES	ESR†
OES	ICP-AES	IGF†	FT-IR**
SSMS	IR**	NAA	IC†
XRS	NAA	OES	ICP-AES
	OES	SSMS	IGF†
	SSMS	XRS	IR**
			NAA
			OES
			SSMS

Microanalysis/Structure

Crystal structure/Phase ID | Phase distribution/Morphology | Elemental | Defects

ESR*	EPMA	AES	SEM*
TEM	IA	EPMA	TEM
XRD	OM	SEM	XRD
	SEM	TEM	
	TEM		

Surface analysis

Elemental | Molecular/Compound

AES	FT-IR*
LEISS	RS*
RBS	SIMS*
SIMS	XPS
XPS	

* = under special conditions ** = semiconductors only + = limited number of elements or groups

AAS	Atomic absorption spectrometry	ICP-AES	Inductively coupled plasma atomic emission spectroscopy	RBS	Rutherford backscattering spectrometry
AES	Auger electron spectroscopy	IGF	Inert gas fusion	RS	Raman spectroscopy
COMB	High-temperature combustion	IR	Infrared spectroscopy	SAXS	Small-angle x-ray scattering
EFG	Elemental and functional group analysis	ISE	Ion selective electrode	SEM	Scanning electron microscopy
		LC	Liquid chromatography	SIMS	Secondary ion mass spectroscopy
EPMA	Electron probe x-ray microanalysis	LEISS	Low-energy ion-scattering spectroscopy	SSMS	Spark source mass spectrometry
ESR	Electron spin resonance			TEM	Transmission electron microscopy
FT-IR	Fourier transform infrared spectroscopy	MFS	Molecular fluorescence spectroscopy	UV/VIS	Ultraviolet/visible absorption spectroscopy
GC/MS	Gas chromatography/mass spectrometry	NAA	Neutron activation analysis	XPS	X-ray photoelectron spectroscopy
GMS	Gas mass spectrometry	NMR	Nuclear magnetic resonance	XRD	X-ray diffraction
IA	Image analysis	OES	Optical emission spectroscopy	XRS	X-ray spectrometry
IC	Ion chromatography	OM	Optical metallography		

Analyzing Organic Solids

Bulk/Macroanalysis

- Elemental
  - Qualitative
    - Major/Minor
      - COMB†
      - EFG
      - ESR†
      - IC†
      - MFS†
      - NAA†
      - NMR†
      - UV/VIS
      - XRS†
    - Trace/Ultratrace
      - COMB†
      - EFG
      - ESR†
      - IC†
      - MFS†
      - NAA†
      - UV/VIS
  - Quantitative
    - Major/Minor
      - COMB†
      - EFG
      - ESR†
      - IC†
      - MFS†
      - NAA†
      - UV/VIS
      - XRS†
    - Trace/Ultratrace
      - COMB†
      - ESR†
      - IC†
      - MFS†
      - NAA†
      - UV/VIS
- Molecular/Compound
  - Qualitative
    - Major/Minor
      - EFG
      - FT-IR
      - IC†
      - IR
      - LC*
      - MFS†
      - NMR†
      - RS
      - UV/VIS
      - XRD*
    - Trace/Ultratrace
      - FT-IR
      - IC†
      - IR
      - LC*
      - MFS†
      - UV/VIS
  - Quantitative
    - Major/Minor
      - EFG
      - FT-IR
      - IC†
      - IR
      - LC*
      - MFS†
      - RS
      - UV/VIS
    - Trace/Ultratrace
      - FT-IR
      - IC†
      - IR
      - LC*
      - MFS†
      - UV/VIS

Structure/Morphology

- Crystal structure
  - TEM*
  - XRD*
- Phase distribution/Morphology
  - EPMA*
  - IA
  - OM
  - SEM*
  - TEM*
- Molecular structure
  - ESR†
  - FT-IR
  - IR
  - NMR†
  - RS
  - SAXS

Surface analysis

- Elemental
  - AES
  - LEISS
  - SIMS
  - XPS
- Molecular/Compound
  - FT-IR*
  - IR*
  - RS*
  - SIMS†
  - XPS†

* = under special conditions   ** = semiconductors only   + = limited number of elements or groups

AAS	Atomic absorption spectrometry
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GC/MS	Gas chromatography/mass spectrometry
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MFS	Molecular fluorescence spectroscopy
NAA	Neutron activation analysis
NMR	Nuclear magnetic resonance
OES	Optical emission spectroscopy
OM	Optical metallography
RBS	Rutherford backscattering spectrometry
RS	Raman spectroscopy
SAXS	Small-angle x-ray scattering
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectroscopy
SSMS	Spark source mass spectrometry
TEM	Transmission electron microscopy
UV/VIS	Ultraviolet/visible absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRS	X-ray spectrometry

Surface Analysis

excitation   emission

Methods according to excitation and emission processes on a solid surface.

TABLE I   Abbreviations of the most important methods for surface analysis and imaging, classified according to the kind of exciting and emitting particles (pure imaging methods in brackets)

excitation by	detection of			
	electrons	ions	X-rays	light
electrons	(SEM, TEM, STEM) AES/SAM, EELS LEED/HEED/RHEED	ESID	EMPA/EDX	(CL)
ions		SIMS/IMMA ISS RIBS	PIXE	
X-rays	ESCA/XPS		XFA XRD	
light	ESCA/UPS (PHEEM)	LAMMA	–	OES LASERprobe Ramanprobe

TABLE II   Meaning of the abbreviations of Table I

Imaging methods

SEM	= Scanning electron microscopy
TEM	= Transmission electron microscopy
STEM	= Scanning transmission electron microscopy
CL	= Cathodoluminescence
PHEEM	= Photoemission electron microscopy

Analysing methods

EELS	= Electron energy loss spectroscopy
LEED	= Low energy electron diffraction
HEED	= High energy electron diffraction
RHEED	= Reflection high energy electron diffraction
ESID	= Electron-stimulated ion desorption
IMMA	= Ion microprobe mass analysis
RIBS	= Rutherford/Ion backscattering spectroscopy
LAMMA	= Laser microprobe mass analysis
PIXE	= Particle induced x-ray emission
XFA	= X-ray fluorescence analysis
XRD	= X-ray diffraction
OES	= Optical emission spectroscopy
UPS	= Ultraviolet photoelectron spectroscopy

AES	= Auger electron spectroscopy
SAM	= Scanning Auger microprobe
ESCA	= Electron spectroscopy for chemical analysis
XPS	= X-ray photoelectron spectroscopy
SIMS	= Secondary ion mass spectrometry
ISS	= Ion scattering spectroscopy
EMPA	= Electron microprobe analysis
EDX	= Energy-dispersive x-ray analysis
WDX	= Wavelength-dispersive x-ray analysis

Surface Analysis

TABLE IV Comparison and capability of the four methods for surface analysis to be discussed (Z=atomic number)

Method:	AES	ESCA	SIMS	ISS
excitation emission	electrons electrons (E)	$h\nu$ electrons (E)	ions ions (m/e)	ions ions (E/E_O)
information depth (monolayers)	2 – 10	2 – 20	1 – 3	1
detection limit [ppm] [g/cm^2]	1000 10^{-10}	1000 10^{-10}	.01 – 10 10^{-13}	1000 10^{-10}
sensitivity differences for the range of elements (factor)	10	10	10^5	10^2
range of elements detection of isotopes binding energies depth profiles	Z > 2 no for special cases yes, if sputtering	Z > 1 no yes yes, if sputtering	all yes (no) yes	Z > 2 yes no yes
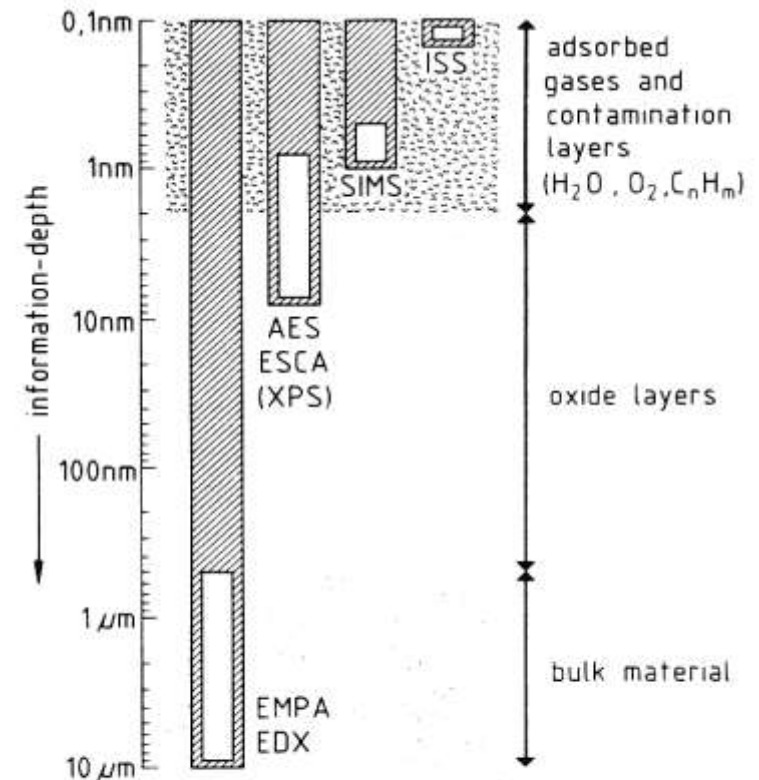
Information depth of some methods for surface analysis in comparison with the electron microprobe analysis. The non-hatched areas mark the variation of the information depths, which are dependent on some instrumental parameters and on the material itself.

Surface Analysis

Table 1. Surface Analysis Acronyms

AEM	Analytical electron microscopy	PIXE	Particle induced X-ray emission
AES	Auger electron spectroscopy	PL	Photoluminescence spectroscopy
AM	Acoustic microscopy	RIS	Resonance ionization spectroscopy
AMS	Accelerator mass spectroscopy	RBS	Rutherford backscattering spectroscopy
AP	Atom probe	SAM	Scanning Auger microprobe
BEEM	Ballistic electron emission microscopy	SEM	Scanning electron microscopy
CPA	Charged particle activation analysis	SIMS	Secondary ion mass spectroscopy
DCT	Double crystal X-ray topography	SNMS	Sputtered neutral mass spectroscopy
EMP	Electron microprobe	STM	Scanning tunneling microscopy
FIM	Field ion microscope	TEM	Transmission electron misroscopy
FTIR	Fourier transform infrared	XPS	X-ray photoelectron spectroscopy
HREM	High resolution electron microscopy	XRD	X-ray diffraction
LANG	Scanning Lang X-ray topography	XRF	X-ray fluoresence
NAA	Neutron activation analysis	μFTIR	Microspot FTIR
OM	Optical microscopy	μRAMAN	Raman microprobe

Surface Analysis

Methods of surface analysis

	Auger electron spectroscopy (AES)	X-ray photoelectron spectroscopy (XPS)	Static SIMS	Dynamic SIMS	Ion scattering spectroscopy (ISS)	Rutherford backscattering (RBS)
Incident particle	Electrons (1–20) keV	X-rays (1254 eV and 1487 eV)	Ions (Ar, Xe^+, Ga^+)(100 eV –30 keV)	Ions (Ar^+, Cs^+ O_2^+ O^- Ga^+)	Ions (He^+, Ne^+ Ar^+, Li^+, Na^+, K^+) (100 eV–5 keV)	Ions (H^+ He^+) (1–3 MeV)
Emitted particle	Auger electrons (20–2000) eV	Photoelectrons (20–2000) eV	Sputtered ions	Sputtered ions	Scattered primary ions	Scattered primary ions
Element range	> Li ($Z = 3$)	> Li ($Z = 3$)	> H ($Z = 1$)	> H ($Z = 1$)	> H ($Z = 1$)	> H ($Z = 1$)
Detection limit	10^{-3}	10^{-3}	10^{-6}–10^{-9}	10^{-6}–10^{-9}	10^{-1}–10^{-4}	10^{-1}–10^{-4}
Depth of analysis	2 nm	2 nm	1 nm	1 nm	< 1 nm	20 nm
Lateral resolution	> 200 Å	> 150 μm	(500 Å–10 mm)	(500 Å–50 μm)	> 10 μm	> 2 μm

Surface Analysis

	Acronym	Detection limits	Largest sample size, φ (cm)	Analysis time, sec	Depth of resolution, Å	Detectable elements	Approximate equipment cost (U.S. $)
Surface analysis instruments: Determining what the surface is							
Scanning Auger microscopy/spectroscopy	SAM AES	0.1 to 1.0 at-%	20	10 to 100	50*	Lithium to uranium (conductive only)	$150,000 to $500,000
Electron spectroscopy for chemical analysis	ESCA (XPS)	0.1 to 1.0 at-%	20	10 to 100	50*	Lithium to uranium (chemical groups)	$200,000 to $500,000
Secondary ion mass spectroscopy	SIMS	0.001 to 1.0 at-%	20	100	40*	Hydrogen to uranium	$200,000 to $700,000
Time-of-flight secondary ion mass spectroscopy	TOF-SIMS	<1 ppm	20	10	40	Hydrogen to uranium (large org. molecules)	$450,000 to $750,000
Energy dispersive x-ray spectroscopy (SEM acc.)	EDX	0.5 at-%	2	100	50,000	Sodium to uranium	$30,000 to $80,000
Rutherford backscattering spectroscopy	RBS	1 to 10 at-%	7	900	20,000	Lithium to uranium	$425,000 to $700,000
Ion scattering spectroscopy	ISS	1.0 at-%	20	50	10	Lithium to uranium	$150,000 to $350,000
Fourier-transform infrared spectroscopy	FTIR	1.0 at-%	7	10 to 500	10,000	Organic functional groups	$50,000 to $100,000
X-ray fluorescence spectroscopy	XRF	0.1 to 100 ppm	20	500	$2 \times 10^{8\dagger}$	Magnesium to uranium	$100,000 to $200,000
Laser ionization mass spectroscopy	LIMS	1 to 100 ppm	20	10	20,000	Hydrogen to uranium (large org. molecules)	$375,000 to $500,000
Surface analysis by laser ionization	SALI	10^{-6} of monolayer	2	50	20,000	Hydrogen to uranium	$600,000 to $800,000

* Techniques can etch in increments of 10 Å up to a few μm.   † Depth of analysis depends on the matrix.

Sources: Surface Science Laboratories, Charles Evans Associates, Perkin-Elmer Corp., *R&D Magazine*

Surface Analysis

Analytical parameter	AES	ESCA	SIMS	SEM/ EDX/WDX	RBS	LIMS
Probe particle	electrons	X-rays	ions	electrons	ions	photons (laser)
Detected entity	electrons	electrons	ions	electrons/X-rays	ions	ions
Detectable elements	all > helium	all but hydrogen	all	all > beryllium	all > helium	all
Routine small area analysis (dia.)	sub μm	150-300** μm	sub μm to several μm	1-3 μm (EDX/WDX) 0.01μm (SEM)	~1 mm	~1 μm
Surface sensitivity	~10-40 Å	~40 Å	~3-10 Å	>10,000 Å (EDX/WDX)	Depth resolution is 25 -200 Å	LD-adsorbed material LI~1000 Å
Routine detection limits* (atom%)	0.3-1	0.1-1	10^{-7}-10^{-1}	1 (EDX) 10^{-4} (WDX)	0.01-10	10^{-4}-10^{-2}
Routine survey analysis time (data acquisition)	5 min	5 min	5 min	2 min (EDX) 30 min (WDX)	15 min	<sec

Table caption (heading): **Table 1. Typical Parameters for the Common Surface Analysis Techniques**

* Detection limits are expressed as a range because different elements have different sensitivities. Minimum figures are difficult to achieve in routine work.
** Many older ESCA systems are limited to areas several millimeters on a side.

Surface Analysis
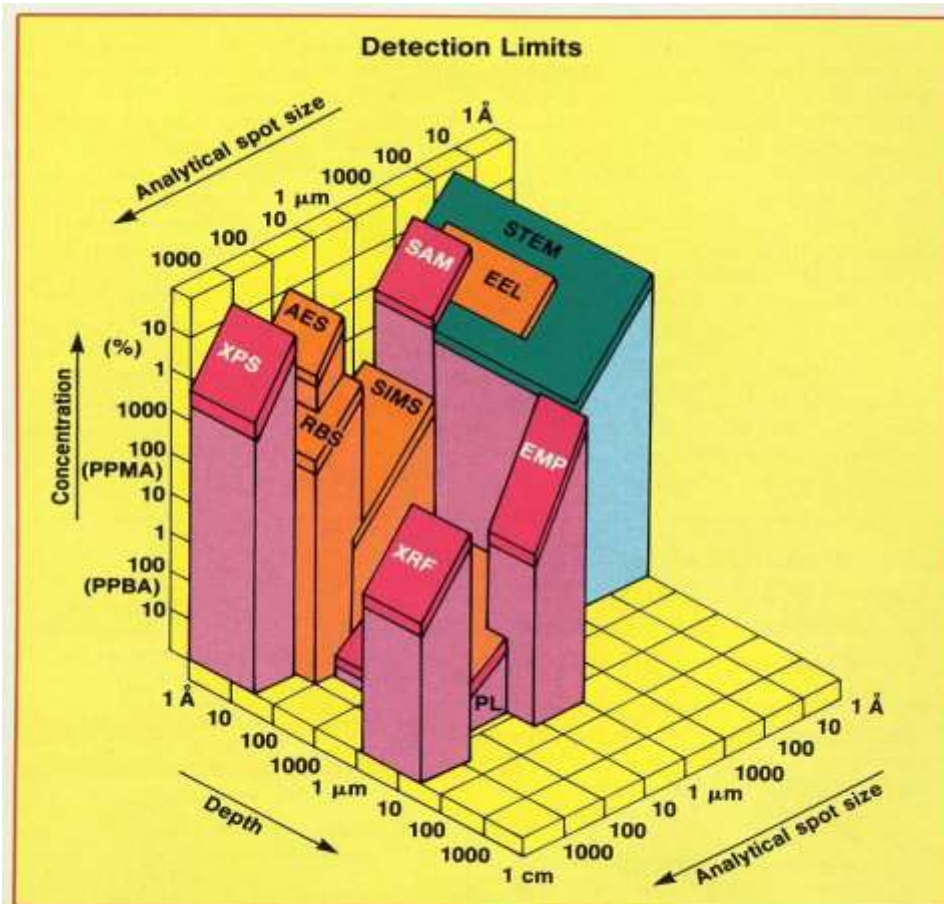
The detection limit of characterization techniques is dependent on both the surface character of the measurement and diameter of the probing radiation.

Surface Analysis

Analytical Characteristics of ESCA

Energy Range
  Kinetic Energies: 100–1500 eV
  Escape Depth: 20 Å
  Peak Location: ±0.1 eV
Chemical Information
  Oxidation State
  Organic Structure
  Bonding Information
Elemental Sensitivity
  Elements: $Z > 2$
  Specificity: very good
  Sensitivity Variations: 50X
Quantitative Analysis
  Absolute: ±30%
  Relative: ±5%
  Detection Limit: 0.1% monolayer
  Matrix Effects: some
Other Aspects
  Vacuum: $10^{-5} - 10^{-10}$ torr
  Depth Profiling Capability: yes, slow
  x-y Resolution; none
  Speed: slow; typical run is 30 min
  Sample Destruction: none in 95% of the samples

Analytical Characteristics of AES

Energy Range
  Kinetic Energies: 50–2500 eV
  Escape Depth: 20 Å
  Peak Locations: ±1 eV
Chemical Information: Marginal
Elemental Sensitivity
  Elements: $Z > 2$
  Specificity: good
  Sensitivity Variations: 50X
Quantitative Analysis
  Absolute: ±30%
  Relative: ±5%
  Detection Limit: 0.05% monolayer
  Matrix Effects: some
Other Aspects
  Vacuum: $10^{-8} - 10^{-19}$ torr
  Depth Profiling Capability: yes, rapid, multiplex
  x-y Resolution: 0.5 μ
  Elemental Mapping as a Microprobe
  Speed: fast, most spectra take minutes; elemental mapping in minutes
  Sample destruction; frequent; particularly bad for organics

Analytical Characteristics of SIMS

Spectral Range: 0–500 amu
Analysis Depth: 40Å (dynamic); monolayer (static)
Chemical Information: mass spectrum from surface layer
Elemental Sensitivity
  Elements: All
  Specificity: good (some overlap)
  Sensitivity Variations: 10^5
Quantitative Analysis
  Absolute: not possible
  Relative: ±50%
  Detection Limit: 10^{-4}% monolayer
  Matrix Effects: severe
Vacuum: 10^{-5} torr of ionizing gas
Depth Profiling Capability: yes, rapid, "dynamic" SIMS
x-y Resolution: 1 μ with ion microprobe;
  x-y rastering for "static" SIMS
Elemental Mapping: as a microprobe
Speed: fast, most spectra take minutes
Sample Destruction: yes, sputtering of surface

Principle of SIMS

- The **ion gun** directs a primary beam of energetic ion at a specimen, resulting in ejection of secondary ions from the sample surface.

- The secondary ions are analyzed with a **mass spectrometer**.

Diagrammatic representation of the basic SIMS experiment.
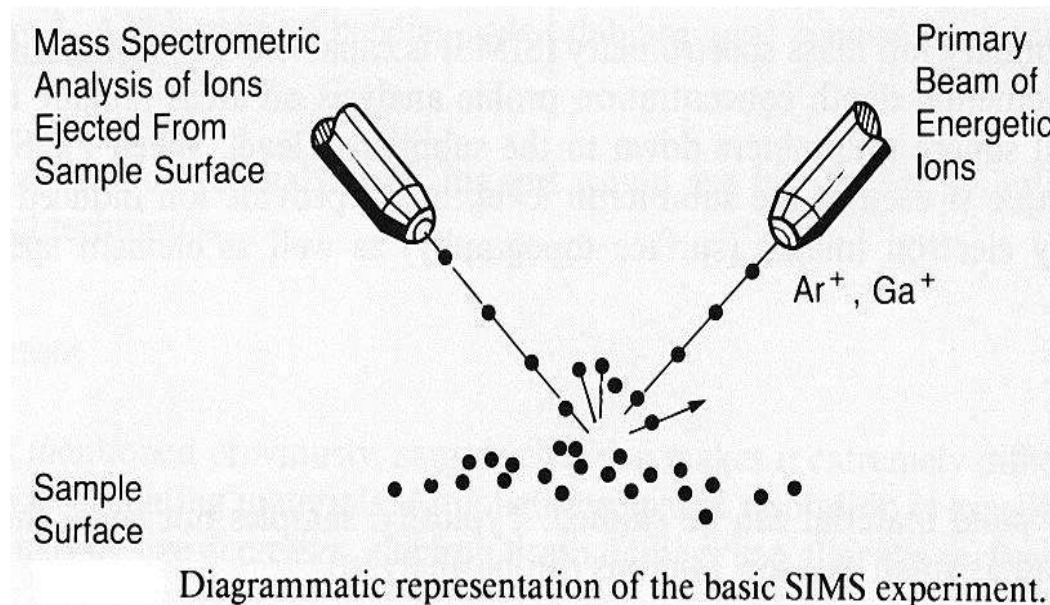
Ejected Fragments

- The ejected fragments are low energy, 5-50 eV.

- The ejected fragments consist of positively and negatively charged ions, neutral atoms, and molecular fragments.

Primary beam

Secondary electrons ●

Sputtered neutrals
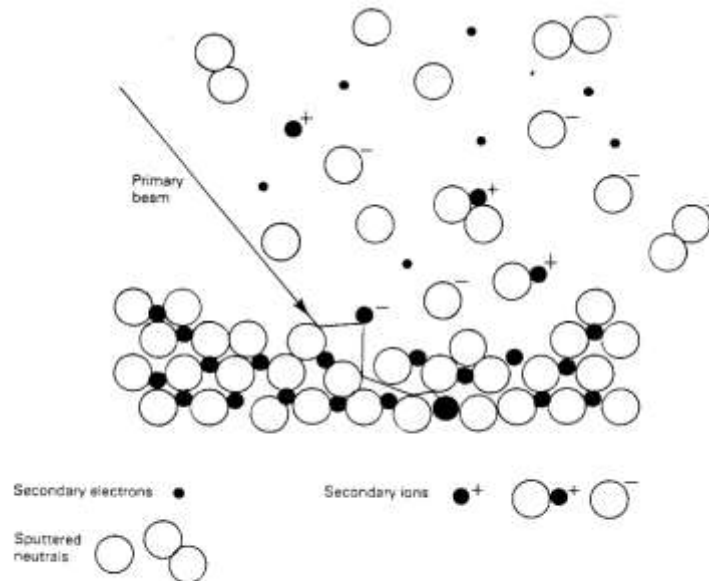
Secondary ions

The basic ion impact and ejection processes that occur when a primary beam of ions interacts with a surface.

Secondary Ion Yields
Primary Beam Effects

- Other factors affect the secondary ionization efficiencies in SIMS measurements. Oxygen bombardment increases the yield of positive ions and cesium bombardment increases the yield of negative ions. The increases can range up to four orders of magnitude.

- 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.

Secondary Ion Yields
Primary Beam Effects

- The variability in ionization efficiencies leads to different analysis conditions for different elements as indicated on the periodic table.

Ion Guns

Ion guns used in surface analysis

Type of source	Gas species	Minimum spot size	Applications
Cold cathode discharge ion source	Argon, other inert gases, O_2^+, N_2^+	10 mm	Surface cleaning and depth profiling in AES and XPS (1–10 keV)
Twin-anode electrostatic ion source	Argon, other inert gases, O_2^+, N_2^+	10 mm	Surface cleaning and depth profiling in AES and XPS (1–10 keV)
Kaufmann ion source	Inert gases	1 mm	Broad-area surface cleaning 500 eV–3 keV
Hot filament ion source	Inert gases	10 μm	Surface cleaning and depth profiling in AES and XPS (1–10 keV) Primary source for static SIMS (1–5 keV)
Duoplasmatron ion source	O_2^+, N_2^+ inert gases	1 μm	Surface cleaning and depth profiling in AES and XPS (1–10 keV) Primary ion source for dynamic SIMS (O_2^+, Ar^+, 1–20 keV)
Surface ionisation ion source	Cs^+, other alkali metals	1 μm	Source for ion accelerators used in RBS primary ion source for dynamic SIMS (Cs^+, 1–10 keV)
Liquid metal ion source	Ga^+, In^+, Cs^+ other metals and alloys	500 Å	Primary ion source for imaging SIMS (Ga^+, Cs^+, 1–30 keV)

Douplasmatron Ion Source

- Inert gases are used to form ions (He^+, Ar^+, Xe^+, etc.).

- Probe diameters between 5 μm and 1 mm.

- Ion current densities greater than 10 mA/cm².
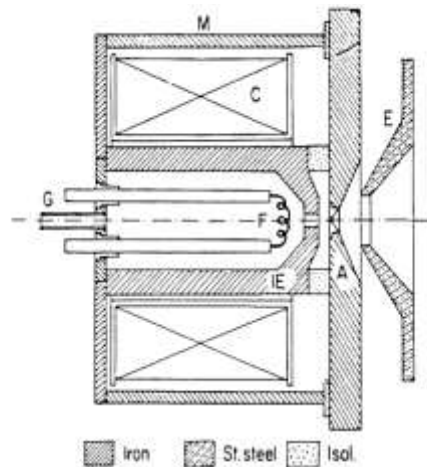
The schematic diagram of a duoplasmatron ion gun: A, anode; C, magnet coil; E, extraction electrode; F, filament cathode; G, gas feed; IE, intermediate electrode; M, magnetic yoke

Liquid Metal Ion Source

- **Low melting point metals are used to form ions (Cs^+, Ga^+).**

- **Sub micron probe diameters.**

- **Ion current densities greater than 1 A/cm^2.**

- **Beam can be focused and rastered.**

  - **Secondary electron images like in a SEM**

  - **Elemental or molecular maps similar to EDX**

A schematic diagram illustrating the construction of a liquid-metal ion source.
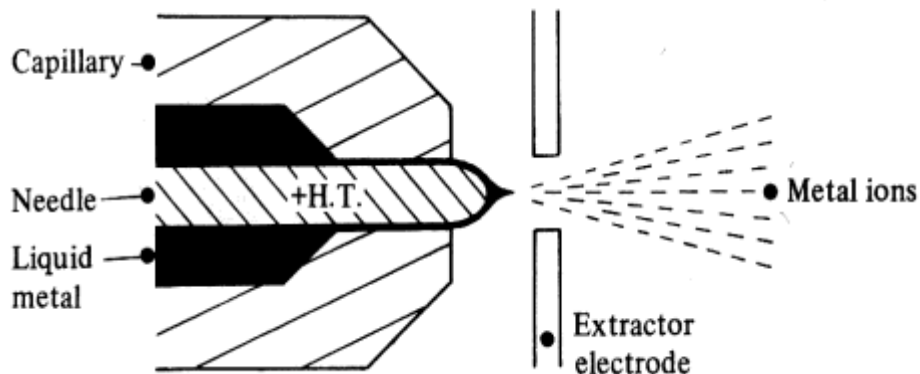
Mass Spectrometers

- Quadrupole

- Magnetic Sector
  - Single Focusing
  - Double focusing

- Time of Flight

Quadrapole Mass Spectrometer

- Comprises of four rods to which DC and RF fields are applied.

- The resulting electric field allows ions of a given mass entering the analyzer to follow a stable oscillatory trajectory between the rods and reach the detector.

- All other ions entering the analyzer are forced to follow unstable trajectories of increasing amplitude. They collide with the rods or housing and do not reach the detector.

ION SOURCE

DETECTOR

$U+V\cos\omega t$
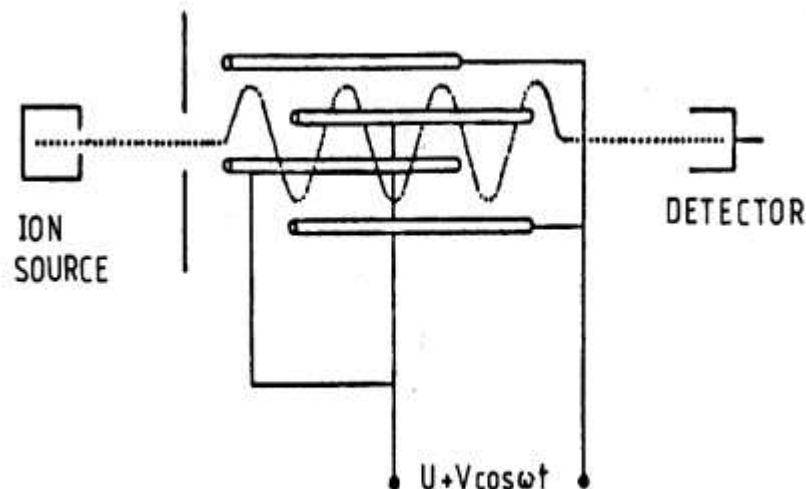
Schematic diagram of the quadrupole mass detector.

Quadrapole Mass Spectrometer
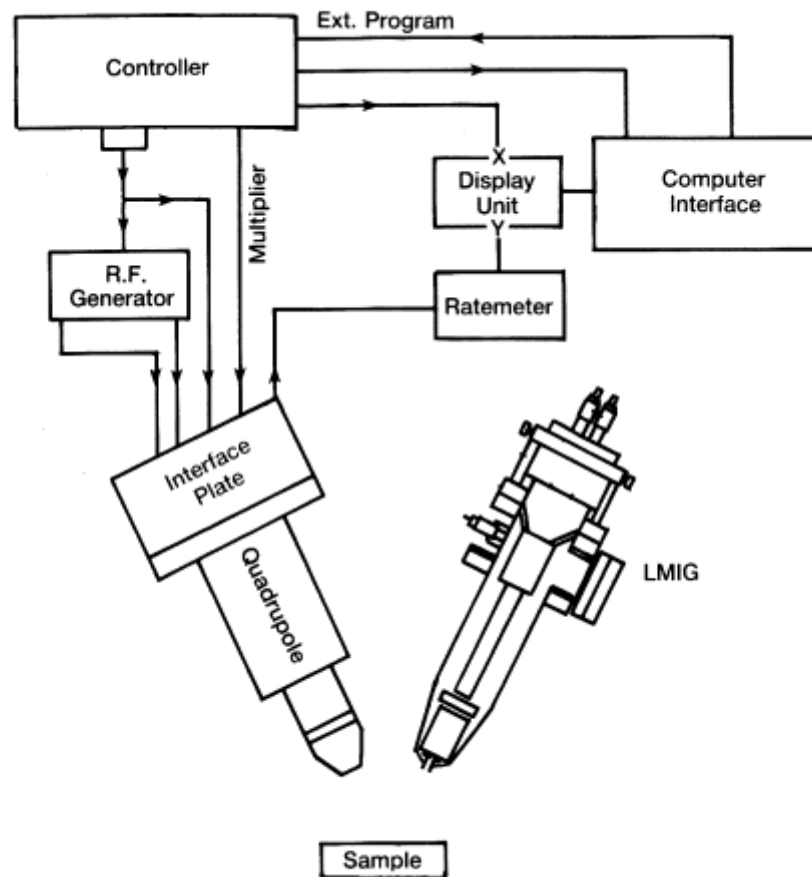
Simplified block diagram of a quadrupole based LMIG-SIMS system.

Quadrapole Mass Spectrometer

Single Focusing Magnetic Sector Mass Spectrometer

- **Ions are diverted into circular paths by a magnetic field.**

- **The magnetic field separates the components of the total ion beam according to momentum.**

- **The individual ion beams are separated spatially and each has a unuiqe radius of curvature.**

- **Only ions with the proper trajectory will exit the slit and arrive at the detector.**
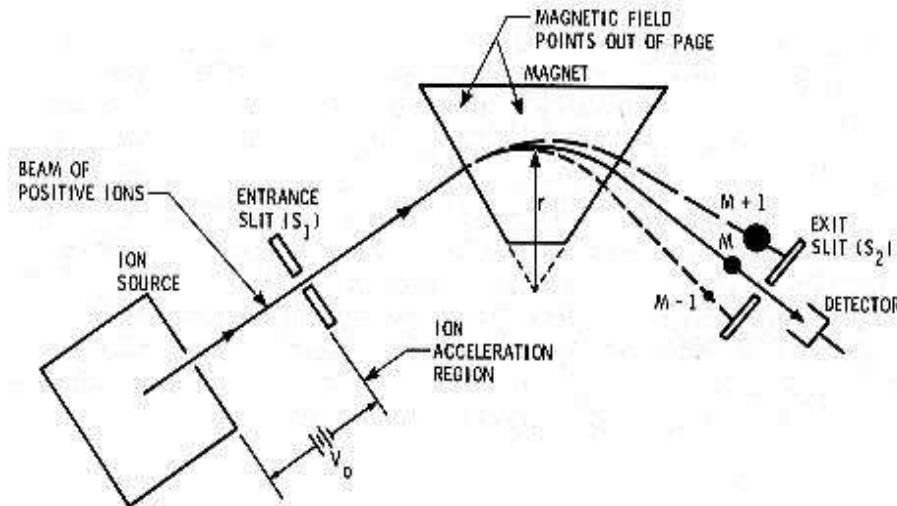
Magnetic sector analyzer.

Single Focusing Magnetic Sector Mass Spectrometer

- In a single focusing magnetic sector instrument there is a lack of uniformity of ion energies.

- The spread in ionic energies produces a spread in their radii of curvature in the magnetic field.

- The result is peak broadening and low to moderate mass resolution.

Double Focusing Magnetic Sector Mass Spectrometer

- Double focusing magnetic sector instruments use magnetic and electrostatic fields to disperse ions according to their momentum and translational energy.

- As ions pass through the electrostatic sector, they are dispersed according to their translational energy.

- Only those ions with the correct translational energy pass through a slit leading into the magnetic sector.

- Then the magnetic sector disperses the ions according to their momentum.
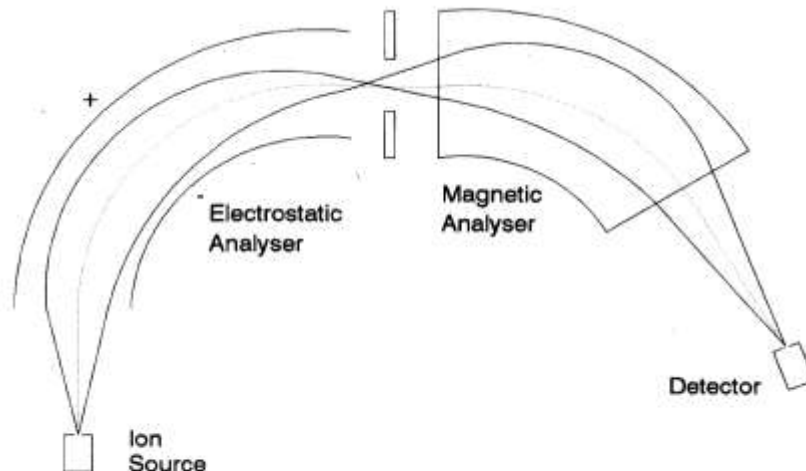
The double focusing analyser which combines a magnetic sector analyser with an electrostatic analyser.

Double Focusing Magnetic Sector Mass Spectrometer
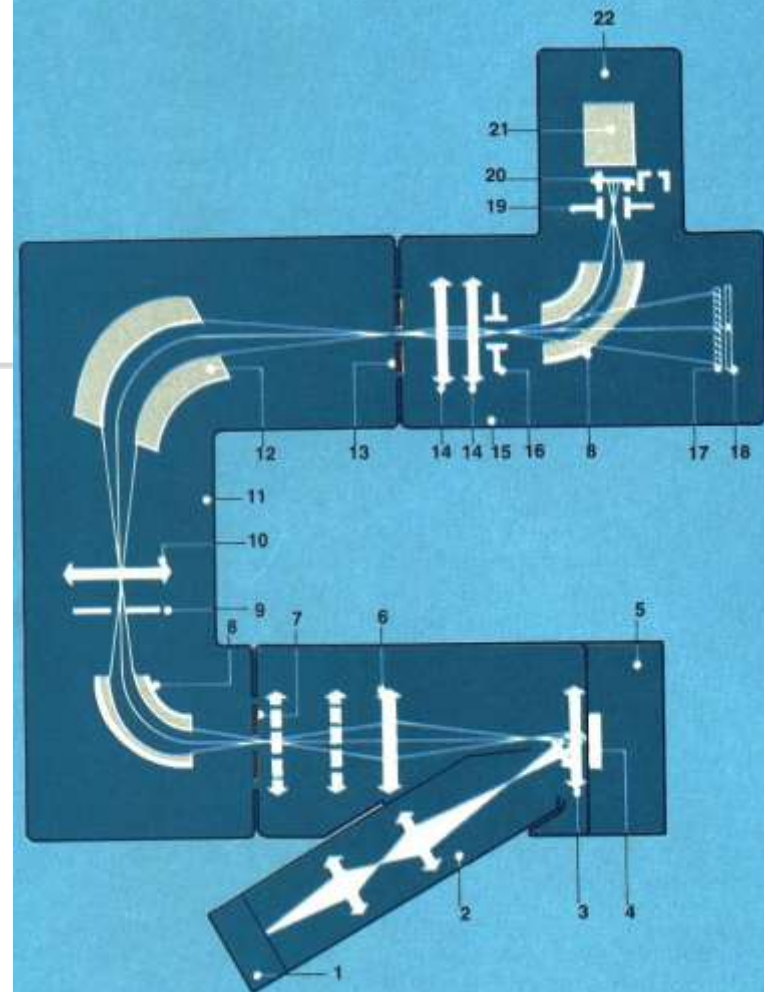
4. The IMS 4F permits elemental and isotopic analysis of very small volumes situated at the surface of solid samples.

1. Ion gun
2. Primary column
3. Immersion lens
4. Specimen
5. Specimen chamber
6. Transfer optics
7. Entrance slit
8. Electrostatic analyzer
9. Energy slit
10. Image transfer lens
11. Spectrometer
12. Electromagnet
13. Final slit
14. Projection lenses
15. Projection, display and detection system
16. Deflector
17. Channel-plate
18. Fluorescent screen
19. Deflector
20. Remote controlled Faraday cup
21. Electron multiplier
22. Detection system

Double Focusing Magnetic Sector Mass Spectrometer
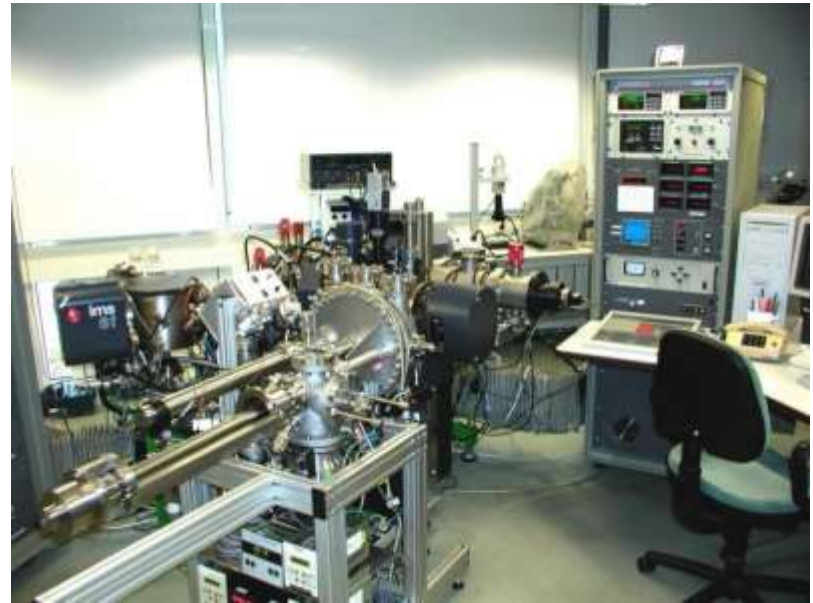
Time of Flight Mass Spectrometer

- **The time of flight mass spectrometer distinguishes between ions of different mass by detecting the time taken to travel a fixed distance when accelerated by a given field.**

- **A pulsed beam of ions is incident on the sample, the ions ejected from the pulse are then accelerated, allowed to travel down a drift tube, and the different times taken for them to reach the detector produces a spectrum.**
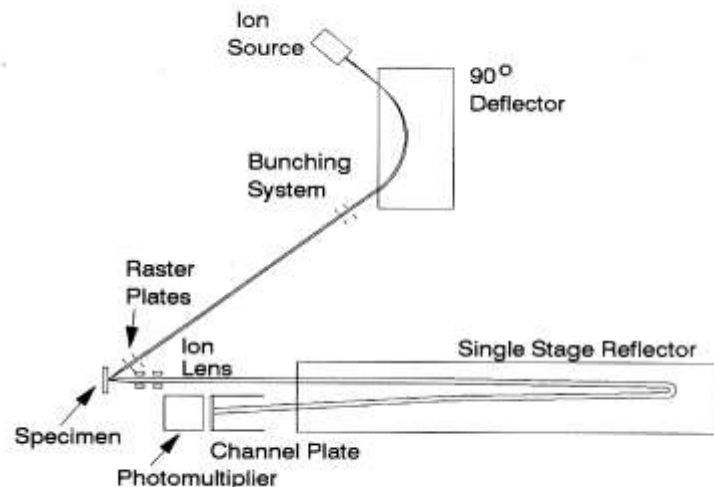
Schematic diagram of the time-of-flight SIMS instrument

Time of Flight Mass Spectrometer

This direct imaging TOF-SIMS instrument offers high mass resolution, high lateral resolution, and rapid image acquisition in the ion microscope mode.

Using time-of-flight to get better resolution

Cs⁺ ion source

Electrostatic analyzers

Electrodynamic buncher

Transfer lens

Sample

Secondary electron detector

Immersion lens

Electron flood gun

Liquid metal ion gun

Position sensitive detector
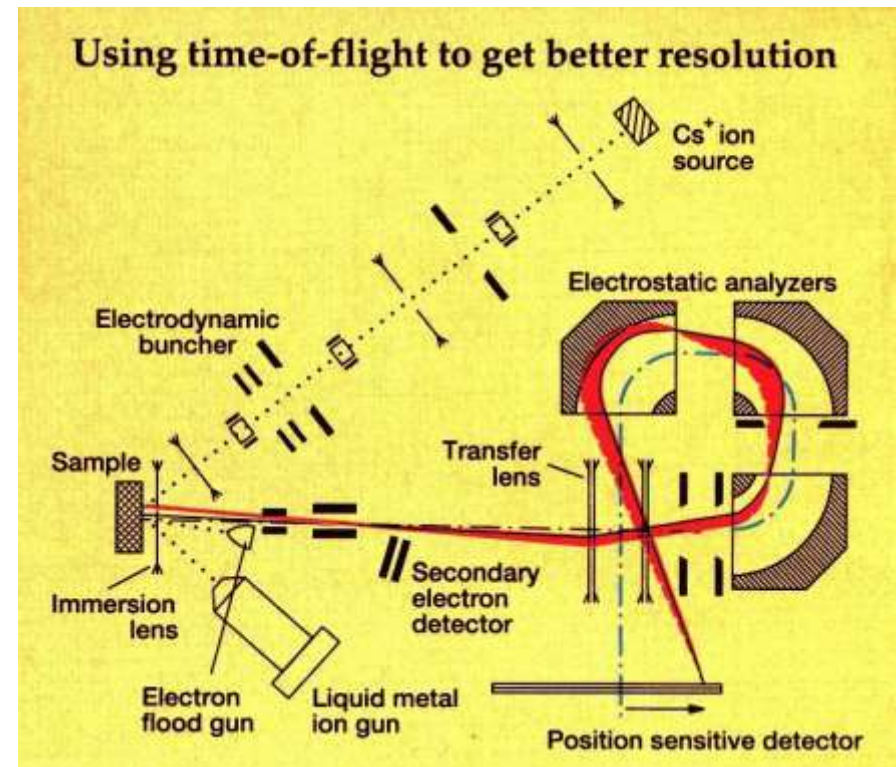
Time of Flight Mass Spectrometer
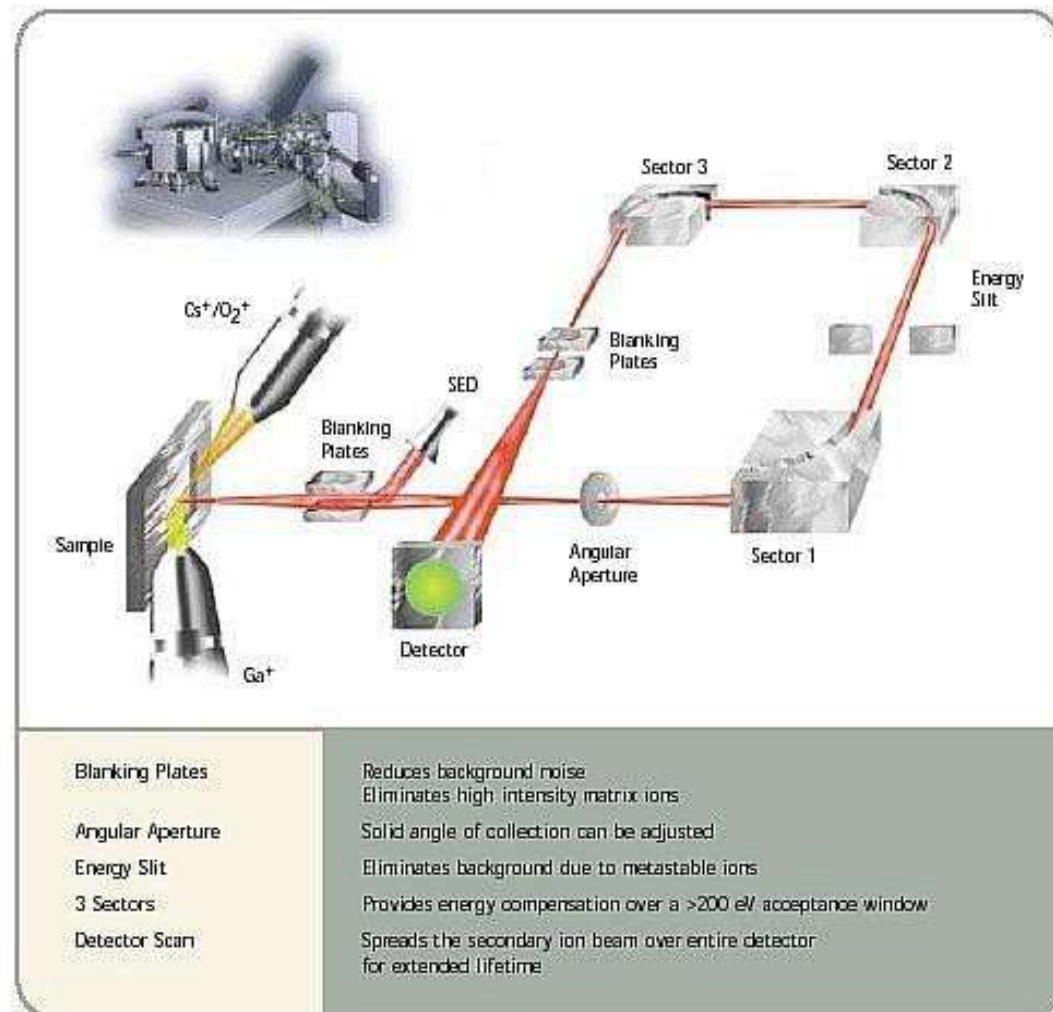
Time of Flight Mass Spectrometer

Resolution

- The most important parameter of a mass analyzer is its resolution.

- Mass peaks of ions have no natural line width so that the breath of a peak is representative of mass analyzer performance.

- Resolution = $m/\Delta m$

   where m is the mass of the lighter peak.

Mass Interferences

- Mass interferences occur whenever another ion has the same nominal mass as the analyte ion. Such interferences are called isobaric.

- During the analysis of iron in silicon for example, $28Si_2+$ interferes because it has the same mass (m/z 56) as $56Fe+$.

- Oxides are common interferences since oxygen-metal bonds are particularly stable. Thus, $40CaO+$ can also interfere with $56Fe+$ measurements.

- Low intensity hydrides of many elements appear one mass unit higher than the elements themselves. A good example is silicon-30 hydride ($30SiH+$) which interferes with trace phosphorous analysis.

- Primary ions often combine with sample elements to produce interferences. For example $133Cs32S_2-$ is isobaric with Au- (m/z 197) during the measurement of gold in pyrite (FeS_2).

High Mass Resolution

- Mass spectrometers with sufficient mass resolution can separate atomic ions from molecular ion interferences.

- Mass resolution is usually specified in terms of *m/delta m* where *m* is the nominal mass of the two ions and *delta m* is their difference. For example, 56Fe and 28Si2 (m/z 55.9349 and 55.9539) require *m/delta m* 5,600 for separation while Au and 133Cs32S2 (m/z 196.9666 and 196.8496) require *m/delta m* 1700.

- Each different kind of SIMS mass analyzers has a range of possible mass resolutions. For example, a (well tuned) double focusing magnetic sector instrument can have mass resolution in the range *m/delta m* 500 to 10,000. Loss of secondary ion intensity accompanies operation at the high end of the mass resolution range.

Mass Range and Resolution

Analyzer	Range (amu)	Resolution
SF Magnetic Sector	2500	2500
DF Magnetic Sector	2500	100000
Time of Flight	10000	10000
Quadrupole	1000	1000

Sample Charging

- The SIMS primary ion beam, secondary ions, and secondary electrons produce a net electric current at the sample surface. If the sample material conducts, the current flows through the sample into the instrument.

- However, insulating samples undergo charge buildup. Sample charging diffuses the primary beam and diverts it from the analytical area, often eliminating the secondary ion signal entirely.

- Sample charging also changes the energy distribution of the secondary ions, which effects their transmission and detection by the mass spectrometer.

- When the sample is a thin dielectric on a conducting substrate, a strong electric field develops. Mobile ions such as sodium and lithium migrate in the electric field and depth profiles no longer reflect the original compositions of the layers.

- Several techniques are available to manage sample charging, and they are often used in combination.

Sample Charging

- **Electron Bombardment**

  Electrons compensate for positive charge buildup that results from positive primary ions and/or negative secondary ions and electrons. Low energy electron beams work better because higher energies produce more than one secondary electron for every incoming electron. Low energy electron beams are more easily implemented in quadrupole SIMS instruments, making quadrupoles the system of choice for insulating materials. In contrast to quadrupoles, magnetic sector instruments maintain the sample at high positive potential for positive ion spectroscopy, making it difficult to bring in a low energy electron beam. High energy electron beams, though less effective, are widely used.

- **Adjacent Conductors**

  Conducting grids placed over the sample reduce the effects of charging on ion optics and bring a source of electrons near to positively charged areas of the sample. When struck by a primary ion, the conductors emit secondary electrons that migrate to the charging area. Similarly, samples are often coated with conducting materials such as gold or carbon. Before starting the analysis, the coating must be sputtered away, but only in the analytical area.

- **Negative Primary Ion Beams**

  The most common negative primary ion beam is O, available from the same duoplasmatron sources that more commonly produce $O2+$. Primary O beams find wide use for insulating geological samples.

- **Automatic Voltage Offset**

  A continuously variable voltage offset can be applied to the accelerating voltage for samples that are only slightly charging. Automatic voltage offset procedures (called autovolt) are often incorporated into instrument control software. After every cycle in a depth profile analysis, the software invokes an energy distribution measurement and adjusts the voltage offset as needed to keep the peak of the distribution constant.

Types of SIMS Analysis

- **Static SIMS**

  Ion dosage and energy are kept low so that undamaged surface molecular fragments can be detected. Chemical structure of surfaces can be determined.

- **Dynamic SIMS**

  Ion dosage and sputter rates are high resulting more fragmentation.

  Positive charge builds up on the sample surface and may need to be neutralized with an electron flood.

Table 5. Difficulties Caused by Sample Charging

Distortion of Spectra
Shifts of Peak Location
Movement on Surface
Extent of Problem
    Insulators >> Semiconductors > Conductors
Compensation
    Surface Conductivity
    Stray Electrons
    Calibration
    Flood-Gun

Spectra

- When bombarded by electrons in the electron impact method of ionization, every substance ionizes and fragments uniquely.

- The uniqueness of the molecular fragmentation aids in structural identification.

- The mass spectrum becomes a finger print for each compound because no two molecules are fragmented and ionized in exactly the same manner on electron bombardment.

- This permits identification of different molecules in complex mixtures.

Spectra

- TOF-SIMS mass spectrum of an organic contaminant, Irganox 1010 a common polymer additive, on a Si wafer. The peak at m/z 219 is a unique fragment from the Irganox molecule.
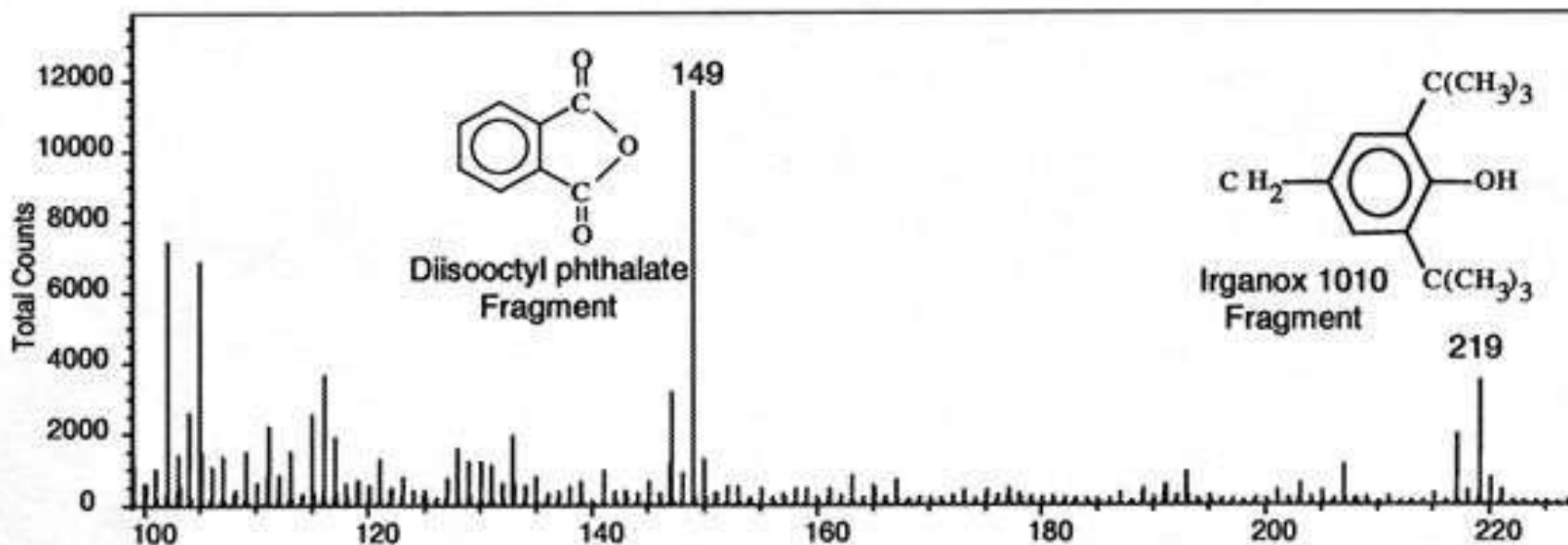
Spectra
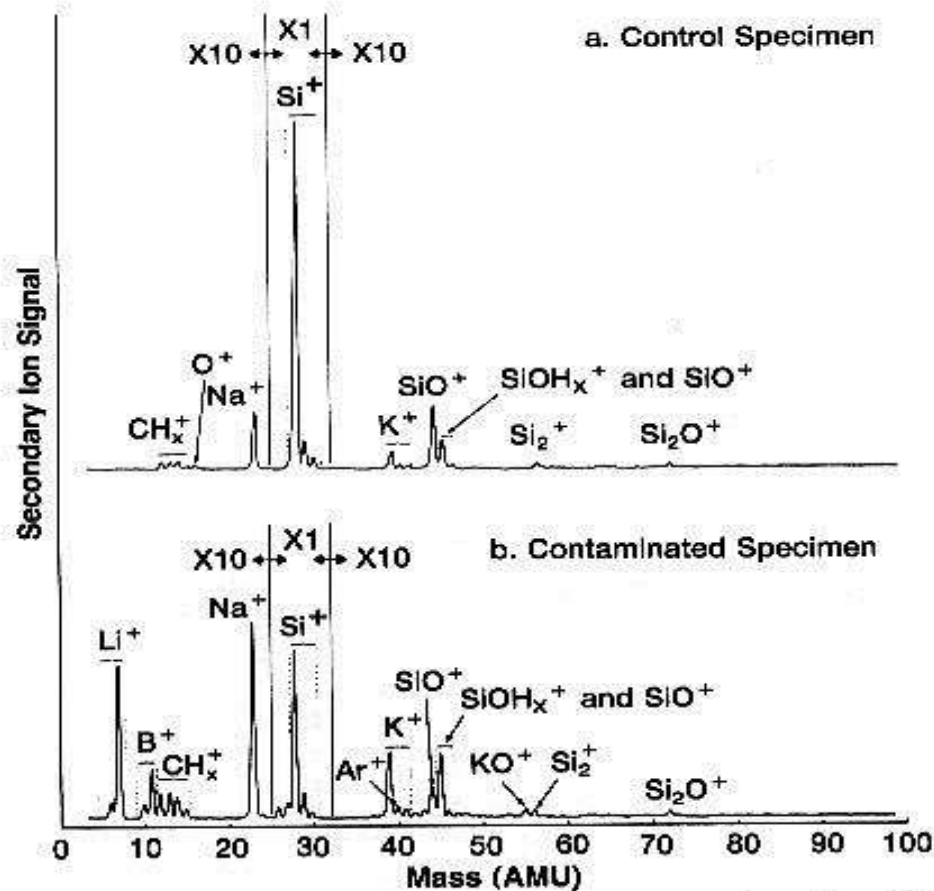
SIMS spectra of deposited SiO_2 layers for (a) control sample and (b) contaminated sample.

Depth Profiling


Depth profile of P implanted in Si.

Depth Profiling

Matrix element profile through a GaAs/GaAlAs/GaAs interface.
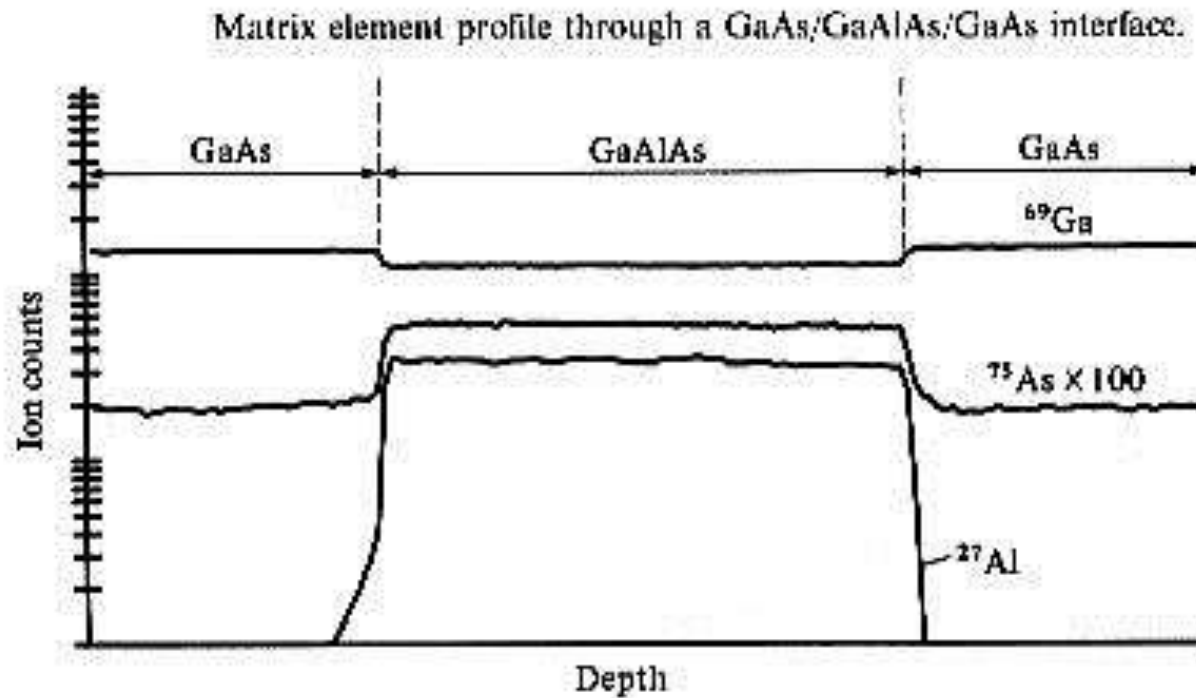
Depth Profiling

- TOF-SIMS depth profile of a 100 Angstrom ONO gate oxide structure.
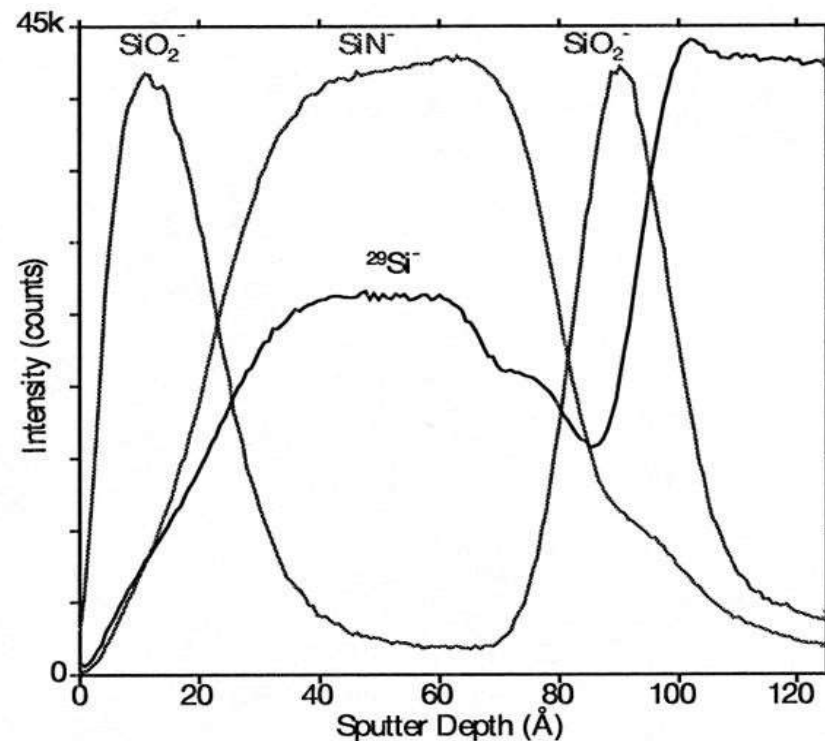
Secondary Electron & Secondary Ion Images

- Combined secondary electron (SE) and secondary ion images of a metal surface indicating localized areas rich in magnesium (Mg+). The topography of the surface is clearly shown in the secondary electron image.

TOF SIMS Secondary Electron image

Mg+

Al+

255

0

Colour Index

100 x 100 um²

20 µm
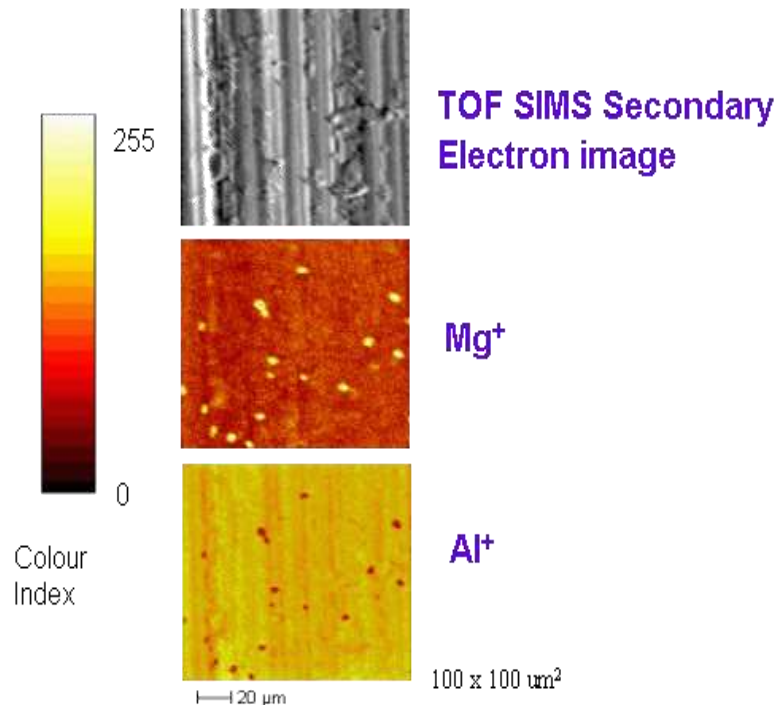
# Organic Contamination on Surfaces

TOF-SIMS images showing, from left to right, the total ion image, the distribution of fluorolubricant, and a series of organic peaks in the range of 320-500 daltons. The mass spectrum from the droplets is shown above.

The TOF-SIMS spectrum of the droplets showing peaks in the mass range from 320-500 daltons is shown in the top figure, while the bottom figure is from a control region on the surface. The droplets were determined to be pentaerithrytol tetraoctanoate.

Imaging of Long-Chain Organic Molecules

- Crystals of stearic acid are revealed by secondary ion imaging of molecular ions using ToF-SIMS.

Stearic acid on aluminum surfaces

50 µm

Mg+   Al+   Mg stearate

(Stearic acid-OH)+   (Stearic acid +H)+   Dimer
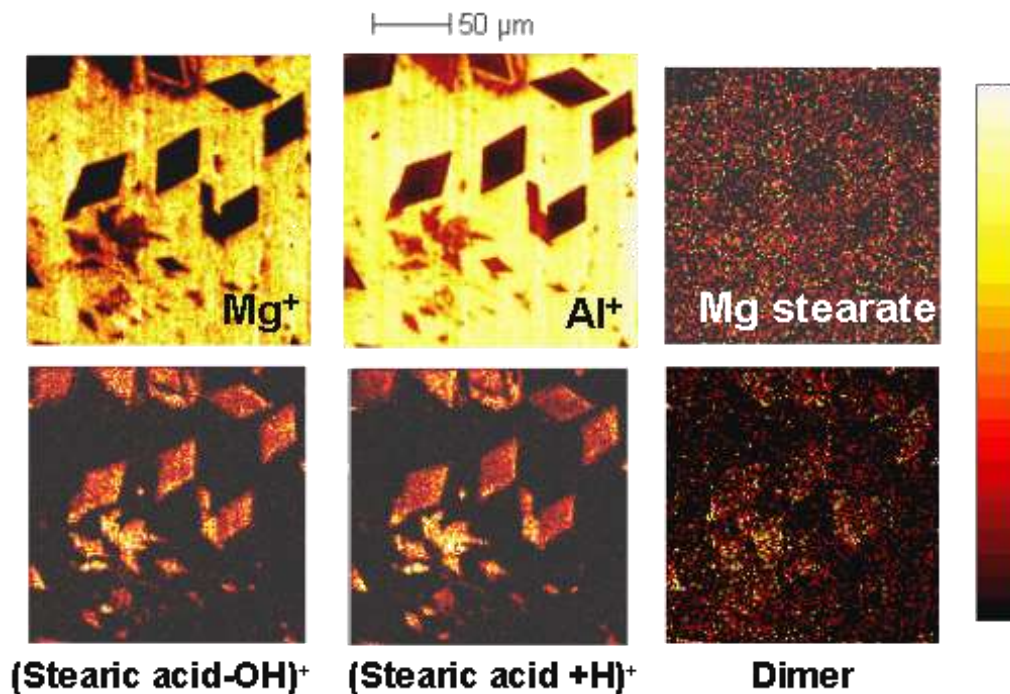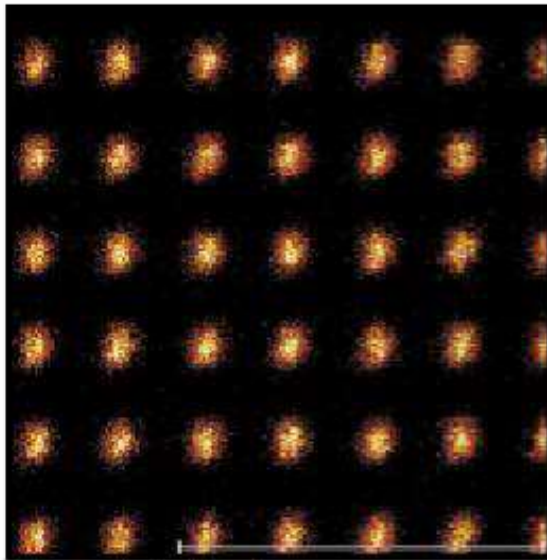
TOF-SIMS Analysis of Device Vias
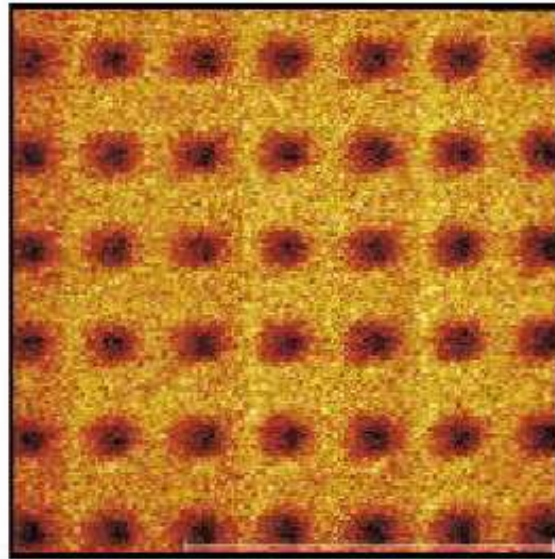

Figure 1. Ti ion image.
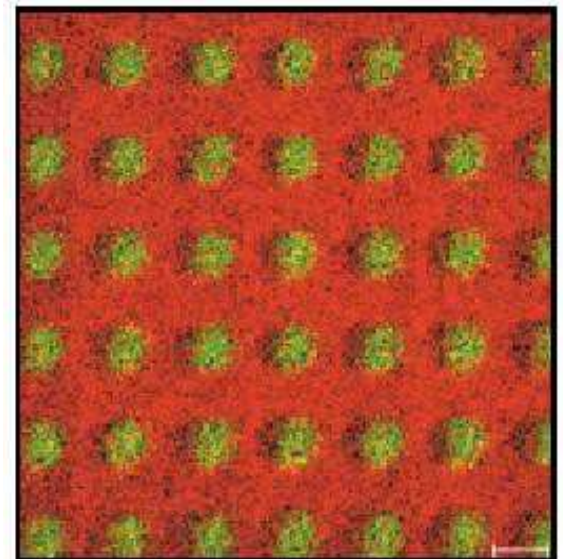
Figure 2. Si ion image.

Figure 3. Overlay of Si/Ti.

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