NACK NETWORK

Building College-University
Partnerships for Nanotechnology
Workforce Development

Secondary Ion Mass Spectrometry (SIMS)

Outline

- Secondary Ion Mass Spectrometry
  - Overview – History
  - Principles of Operation
  - SIMS Issues

Secondary Ion Mass Spectrometry (SIMS)

- SIMS is the most sensitive technique available for determining material composition. It can potentially detect down to one part per billion
- The measurement can be done at the surface of a sample, or utilizing simultaneous ion milling, composition as a function of depth can be determined.
- The measurement tells what atoms are present, but it does not give information on chemical bonding
- SIMS is destructive characterization method for determining the chemical composition of a material

Secondary Ion Mass Spectrometry (SIMS)

- The inspiration for this device started in 1910 when J.J. Thomson first observed the release of secondary ions from a surface by primary ion bombardment
- Successful work was done in the late 1940s by Herzog and Viehböck, at the University of Vienna, Austria
- SIMS provides elemental, chemical state, and molecular information from solid materials.
- Spatial resolution of less than 0.1 µm possible
- SIMS is a surface analysis technique with a typical analysis depth of less than 2 nm

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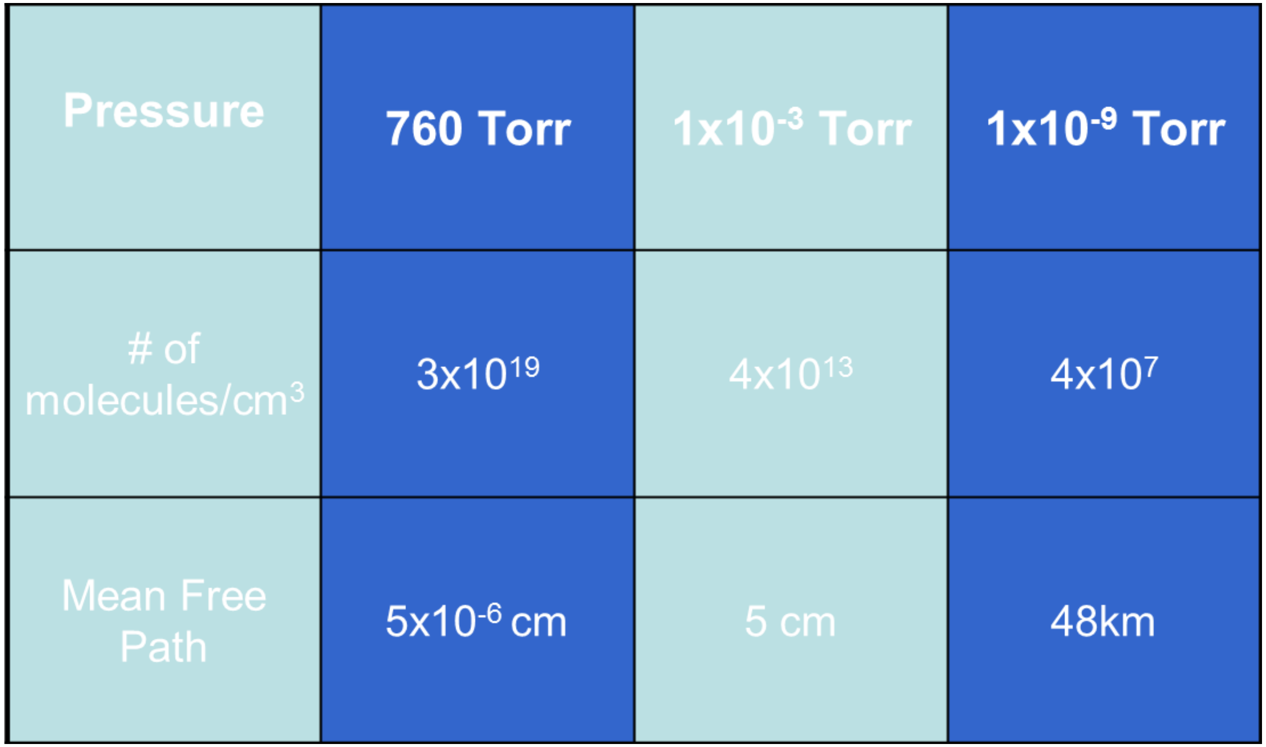
Principles of Operation

- Ions are accelerated into sample.
- A vacuum level of 10^{-6} Torr is needed to ensure that secondary ions do not collide with background gases on their way to the detector. Potential resolution of parts per billion.



Pressure	760 Torr	$1x10^{-3}$ Torr	$1x10^{-9}$ Torr
# of molecules/cm^3	$3x10^{19}$	$4x10^{13}$	$4x10^{7}$
Mean Free Path	$5x10^{-6}$ cm	5 cm	48km

Principles of Operation

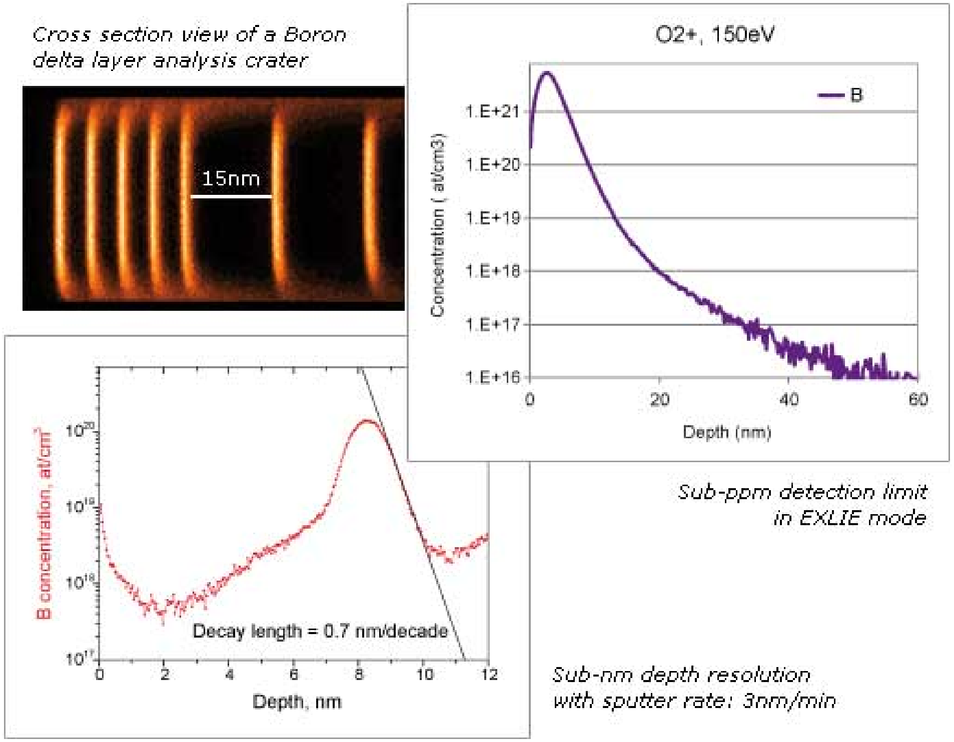
- When the primary ions strike the sample, secondary ions are emitted from the sample
- The scattered ions are accelerated and positioned by a series of magnetic fields.
- The ions then go through a mass analyzer to separate ions for analysis
- For Time of Flight (TOF) SIMS, the ion beam is pulsed, and secondary ions exhibit unique velocities influenced by a known electric field – hence time of the ion flight is indicative of mass

Principles of Operation

- Static SIMS is the process involved in surface atomic monolayer analysis, or surface molecular analysis, usually with a pulsed ion beam and a time of flight mass spectrometer. Uses low beam current and an low sputtering rate of about 0.1 nm per hour.
- Dynamic SIMS is the process involved in bulk analysis, closely related to the sputtering process, using a DC primary ion beam and a magnetic sector or quadrupole mass spectrometer. Uses high beam current and an high sputtering rate of about 10um per hour. This leads to a depth profile.

Principles of Operation

- A typical commercially available static/dynamic SIMS system is the Cameca SC Ultra. It is made by Cameca in France.
- The instrument capable of sputtering samples with a large range of impact energies: from high energy (keV range) for thick structures to Ultra-Low Energy (≤ 150eV) for ultra-thin structures.



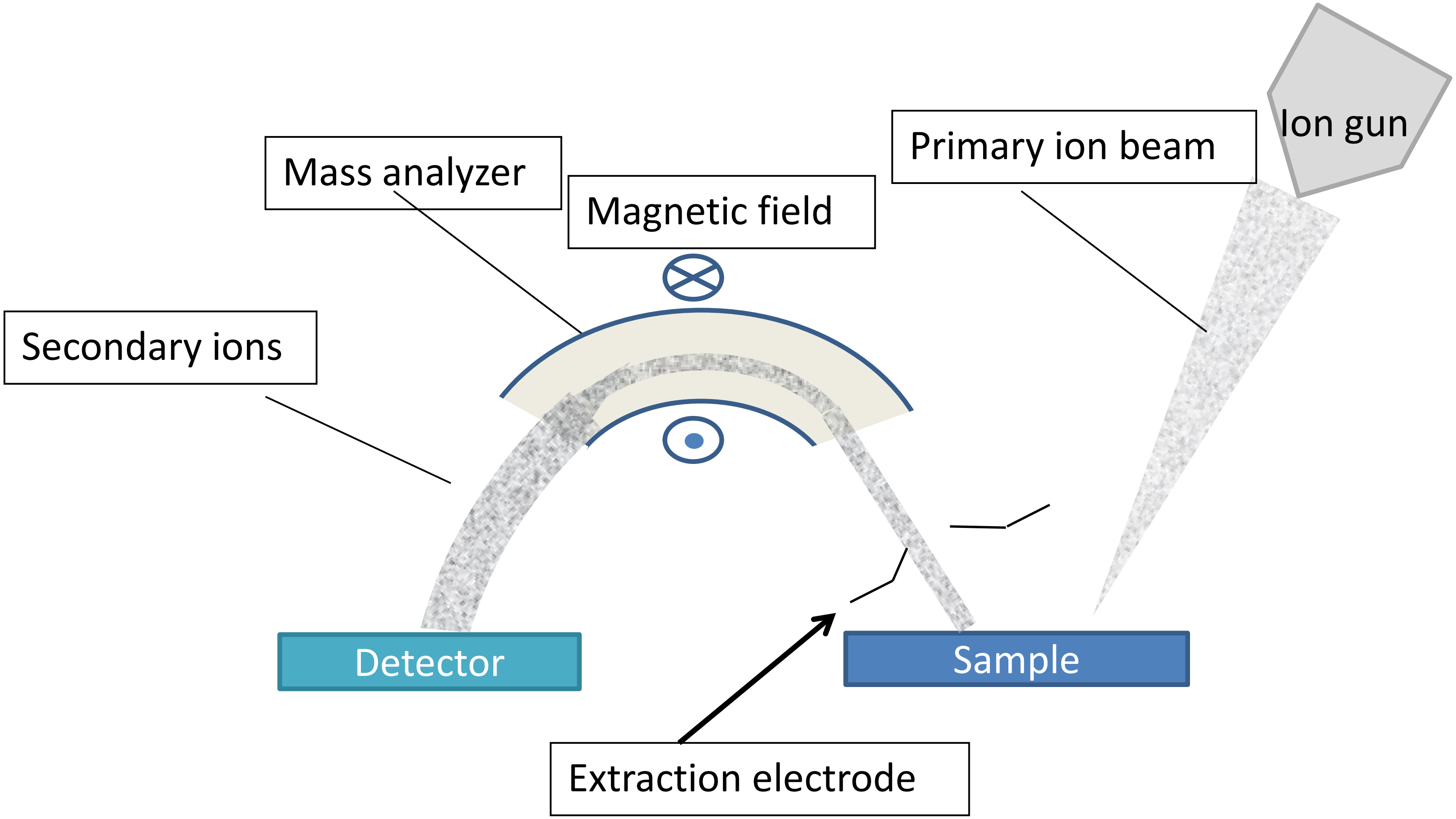
Cross section view of a Boron delta layer analysis crater

Sub-ppm detection limit in EXLIE mode

Sub-nm depth resolution with sputter rate: 3nm/min

www.Cameca.com

Simple SIMS Block Diagram



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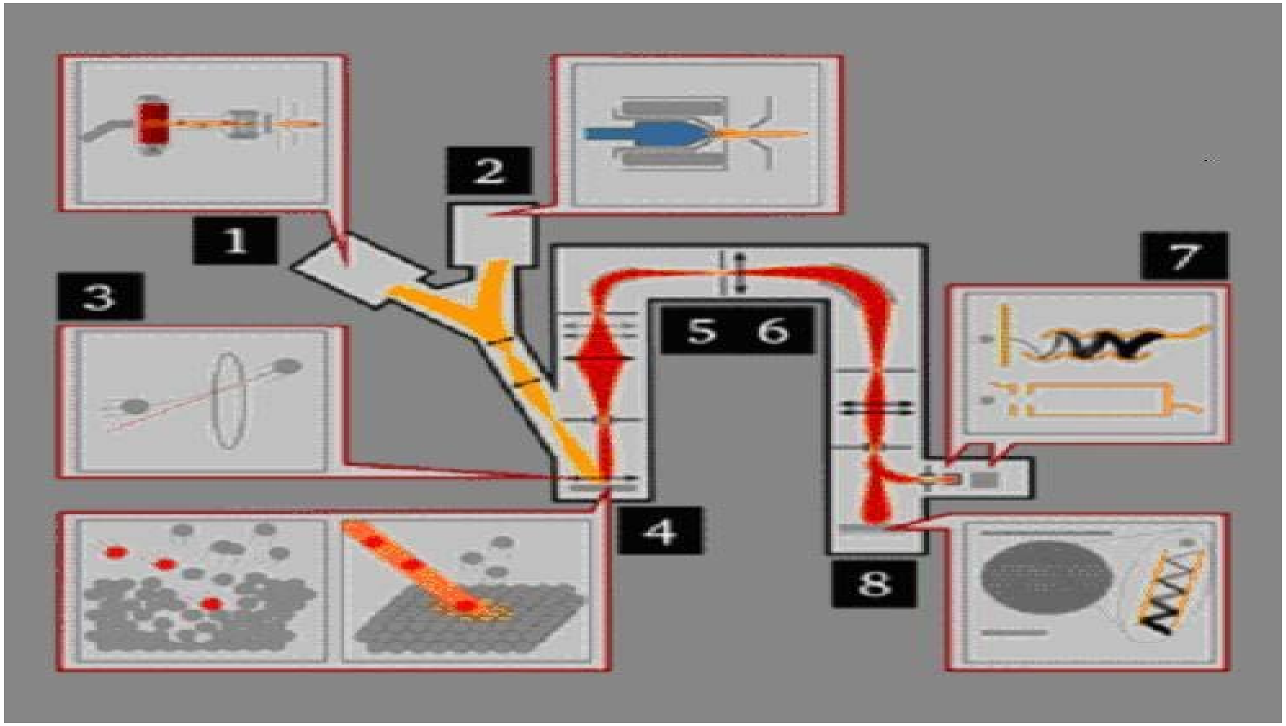
Principles of Operation

- Typical forward geometry SIMS/ion microprobe configuration (Cameca IM 6f) showing: 1) negative primary beam source, 2) positive primary beam source, 3) electrostatic lens for primary beam, 4) sample stage and sputtering, 5) electrostatic sector, 6) magnetic sector, 7) collectors, and 8) ion imaging detector.



www.Cameca.com

Principles of Operation

- The selected ion beam impinges on the sample, and atoms from the sample are “sputtered” from the sample.
- Incident beam atoms are also reflected and potentially implanted in the sample
- Most of the ejected atoms are neutral and cannot be detected by conventional SIMS
- About 1% of the atoms are charged and used for analysis
- The mass/charge ratio of the ions is analyzed and used to create a spectrum
- High vacuum minimizes contamination.

Principles of Operation

- The ion beam can be moved quickly across the surface for near surface chemical analysis, or the beam can be focused in one area to “dig” a profile into the sample.
- Typically the beam spot is approximately one half to one micron in diameter. Of course this varies by tool.
- The ion source is typically Cs+, O_2+, O , Ar+, and Ga+ at energies between 1 and 30 keV.
- The ion species will contaminate and interact with the surface depth of approximately 1 – 10 nm.

Ion Emission

- Three types of ion emitters
  - Gaseous ionization by electron ionization
  - Surface ionization of Cs ions
  - Liquid metal ionization

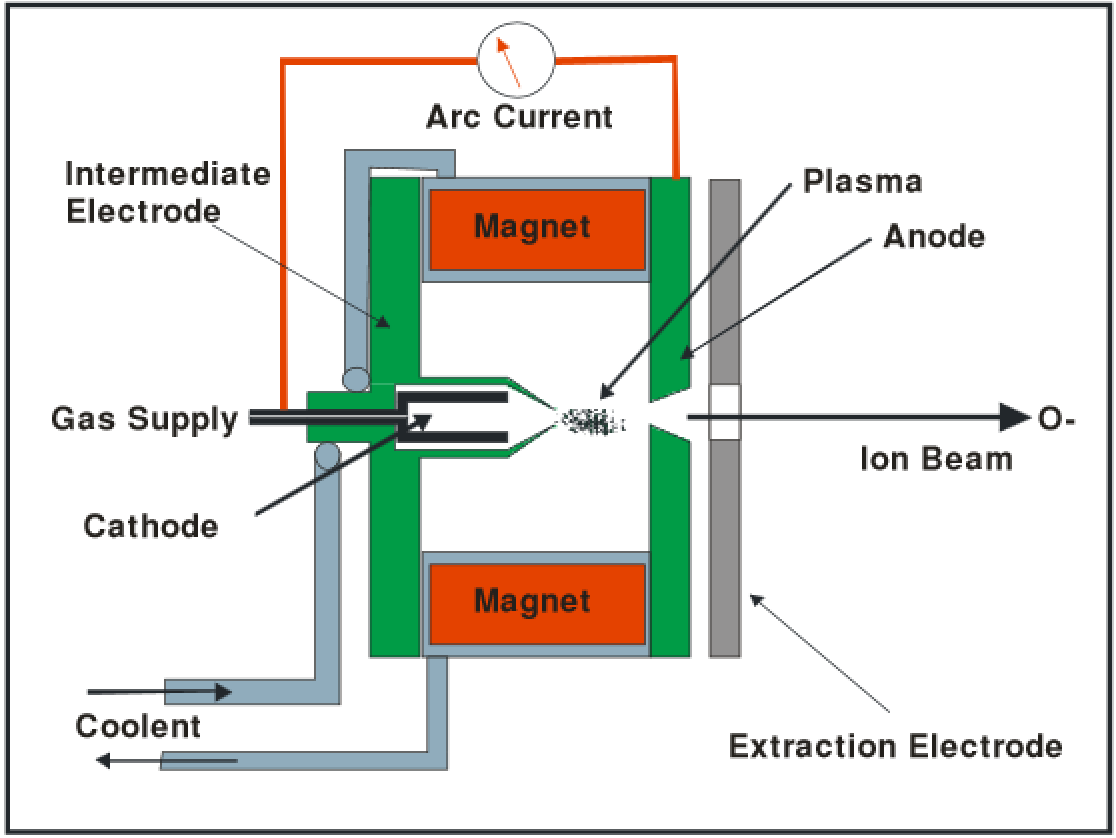
Ion Source	Beam Current	Beam Focus
Gaseous Ionization	High	Rough
Surface Ionization	Small-High	Fine-Rough
Liquid Metal Ionization	Moderate	Very Fine

Gaseous Ionization

- Gaseous ionization uses an electron gun to ionize a gaseous source of elements or molecules. The ion beam created by this technique has a high current but is roughly focused.
- The duoplasmatron can operate with almost any gas
- Oxygen primary ions are often used to investigate electropositive elements due to an increase of the generation probability of positive secondary ions
- The duoplasmatron may be used to extract either O- O2-, or O2+ depending upon the electrical polarity selected

Gaseous Ionization

THE DUOPLASMATRON

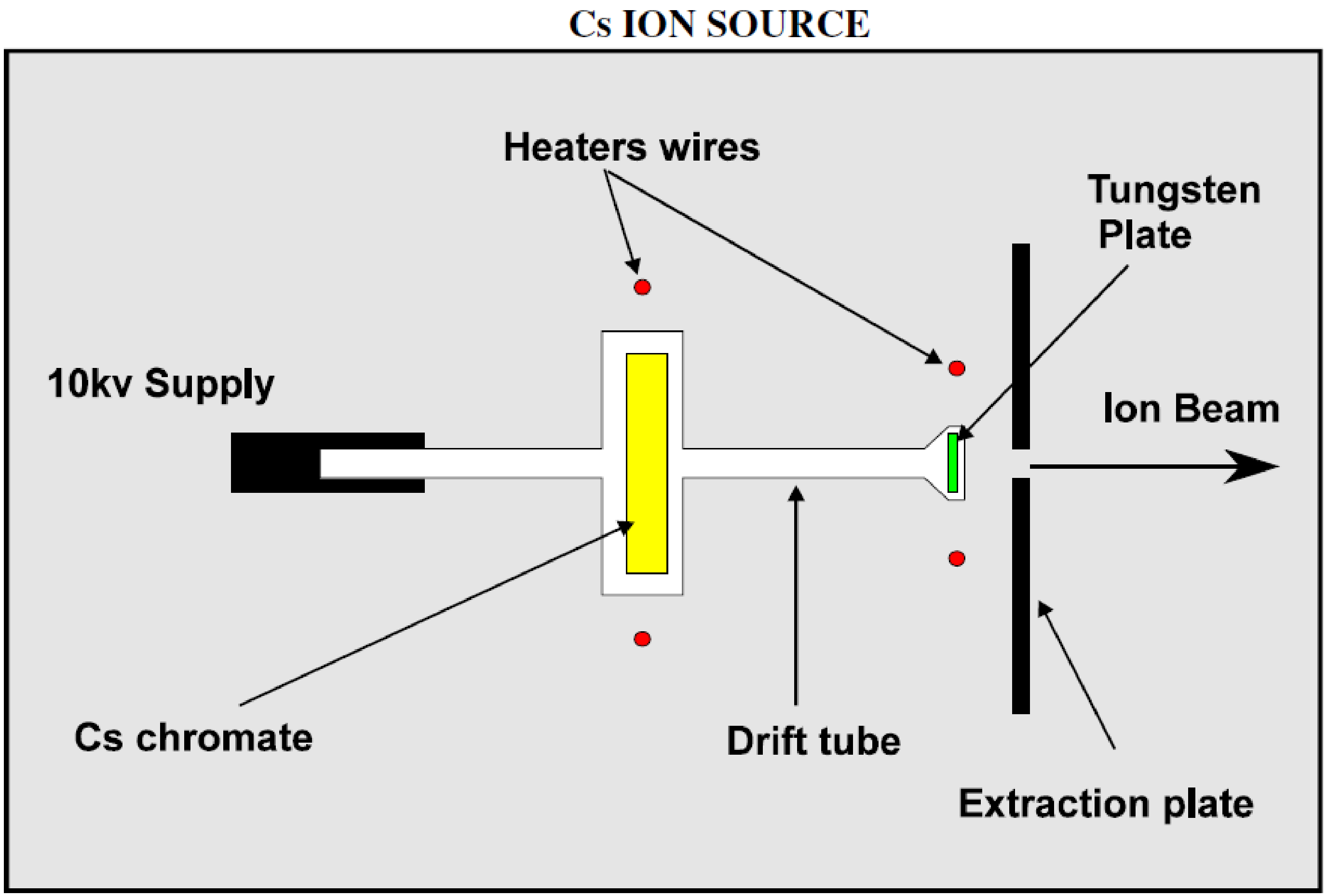


http://www.geos.ed.ac.uk/facilities/ionprobe/SIMS4.pdf

Surface Ionization

- In surface ionization, cesium is evaporated through a tungsten plug. This creates cesium ions. This technique creates either a tightly focused ion beam or a high current beam.
- Cesium primary ions often are used when electronegative elements are being investigated

Gaseous Ionization

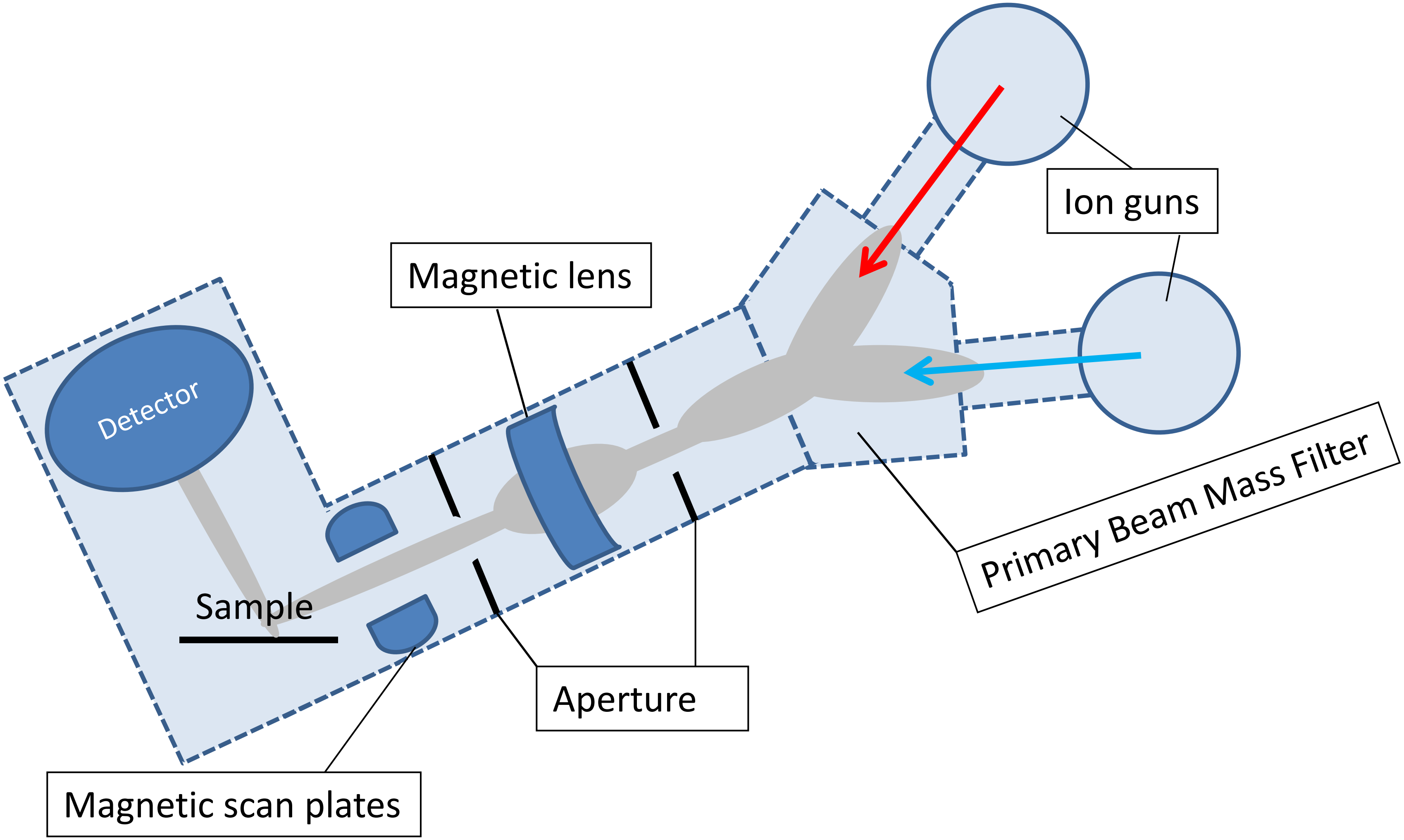


http://www.geos.ed.ac.uk/facilities/ionprobe/SIMS4.pdf

Liquid Metal Ionization

- For liquid metal ionization, a tungsten tip is covered in a metal or metal alloy that is typically liquid at or near room temperature.
- When the tip is subjected to a high electric field the tip will emit ions from the covering metal. This process is capable of producing very tightly focused ion beams of less than 50 nm.
- The electric field used to create the ions can be turned on and off in order to create pulsed ion beam.

Dual Ion Gun System



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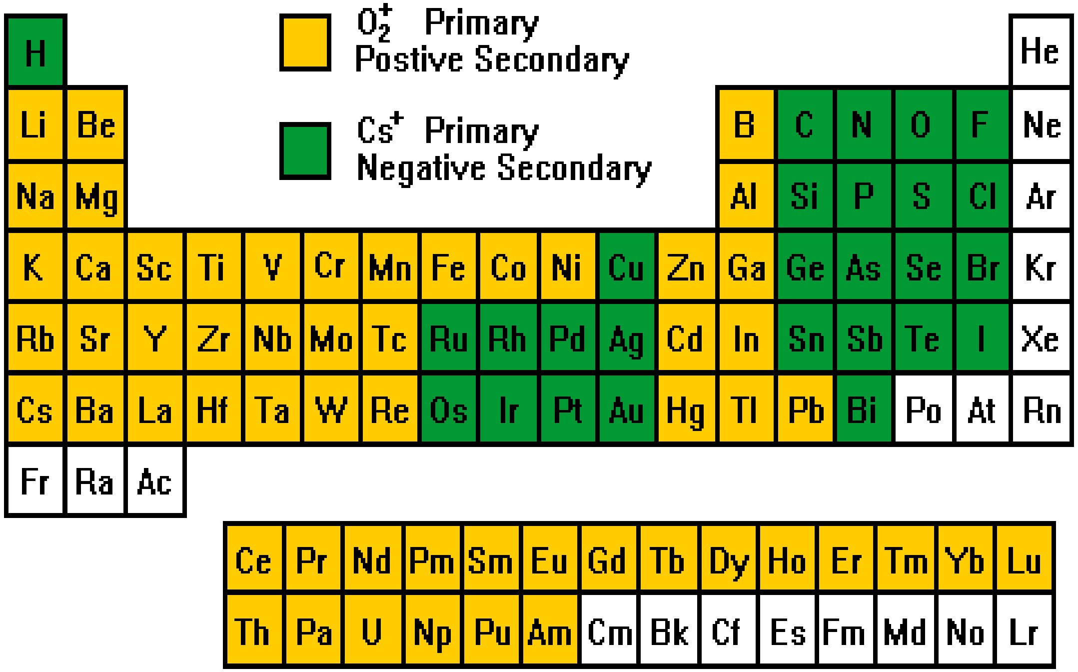
Some SIMS Issues

- Due to the large variation in ionization probabilities among different materials, SIMS is generally considered to be a qualitative technique, although quantitation is possible with the use of standards
- The ion source is typically Cs+, O_2+, O , Ar+, and Ga+ at energies between 1 and 30 keV
- These ions can chemically interact with the substrate
- Beam chemistry is selected to minimize this reaction.
- Beam chemistry and energy selection are part of the art of this procedure.

Cs and O_2 Ion Selection



🟨 O_2^+ Primary Postive Secondary

🟩 Cs^+ Primary Negative Secondary

🟩 H																	He
🟨 Li	🟨 Be											🟨 B	🟩 C	🟩 N	🟩 O	🟩 F	Ne
🟨 Na	🟨 Mg											🟨 Al	🟩 Si	🟩 P	🟩 S	🟩 Cl	Ar
🟨 K	🟨 Ca	🟨 Sc	🟨 Ti	🟨 V	🟨 Cr	🟨 Mn	🟨 Fe	🟨 Co	🟨 Ni	🟩 Cu	🟨 Zn	🟨 Ga	🟩 Ge	🟩 As	🟩 Se	🟩 Br	Kr
🟨 Rb	🟨 Sr	🟨 Y	🟨 Zr	🟨 Nb	🟨 Mo	🟨 Tc	🟩 Ru	🟩 Rh	🟩 Pd	🟩 Ag	🟨 Cd	🟨 In	🟩 Sn	🟩 Sb	🟩 Te	🟩 I	Xe
🟨 Cs	🟨 Ba	🟨 La	🟨 Hf	🟨 Ta	🟨 W	🟨 Re	🟩 Os	🟩 Ir	🟩 Pt	🟩 Au	🟨 Hg	🟨 Tl	🟨 Pb	🟩 Bi	Po	At	Rn
Fr	Ra	Ac															

🟨 Ce	🟨 Pr	🟨 Nd	🟨 Pm	🟨 Sm	🟨 Eu	🟨 Gd	🟨 Tb	🟨 Dy	🟨 Ho	🟨 Er	🟨 Tm	🟨 Yb	🟨 Lu
🟨 Th	🟨 Pa	🟨 U	🟨 Np	🟨 Pu	🟨 Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Detection Limits in SiO_2

O_2^+ Primary Ion Beam Positive Ions		Cs^+ Primary Ion Beam Negative Ions	
Element	DL (atoms/cm³)	Element	DL (atoms/cm³)
Li	1E+13	H	1E+18
B	5E+13	C	2E+17
N	2E+17	N	3E+16 – 2E+17[1]
Na	2E+13	P	1E+15
Mg	2E+13	S	1E+16
Al	1E+14	Cl	1E+16
K	1E+13	Cr	2E+16
Ca	5E+13	Fe	3E+16
Ti	5E+13	Ni	3E+15
Cr	2E+13	Cu	2E+15
Mn	1E+14	As	2E+15
Co	2E+14	Ge	2E+15
Fe	2E+14 – 5E+14	Au	1E+15
Ni	1E+15	-	-
Cu	5E+14	-	-
Zn	3E+15	-	-
As	2E+16	-	-
Mo	5E+14	-	-
In	2E+14	-	-
Ta	5E+15	-	-
W	5E+15	-	-

Note: For dynamic sector O_2^+ Primary Ion Beam sputtering, the maximum oxide layer thickness should be less than 1.5µm for proper charging compensation

[1] Higher detection limit for BPSG

Evans Analytical Group 2007

SIMS

- The ion beam will sputter at a approximate rate of 0.5 to 5 nm/s. Naturally, sputter rates are a function of primary beam intensity, sample material, and crystal orientation.
- Sputtered substrate ions will be approximately 1% of the incident ion stream.

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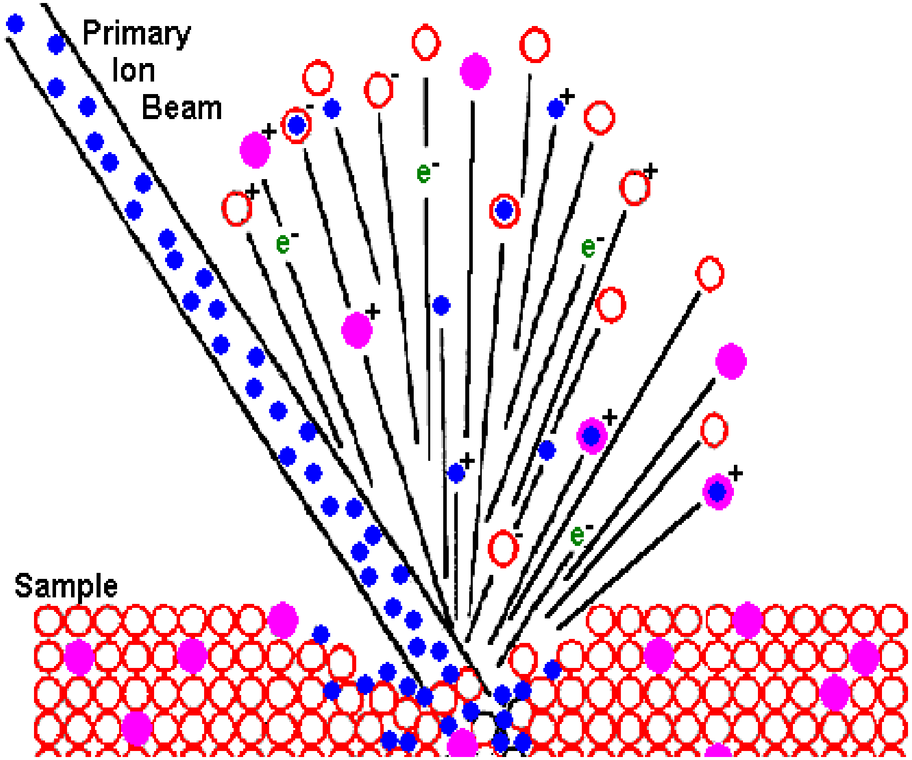
SIMS Issues

- Note the primary ion beam can contaminate the surface.
- The ejected species contain the incident ions, sample material, electrons, and photons.
- Yield is highly dependent on different elements, and matrix.
- The secondary particles carry negative, positive, and neutral charges and they have kinetic energies that range from zero to several hundred eV.



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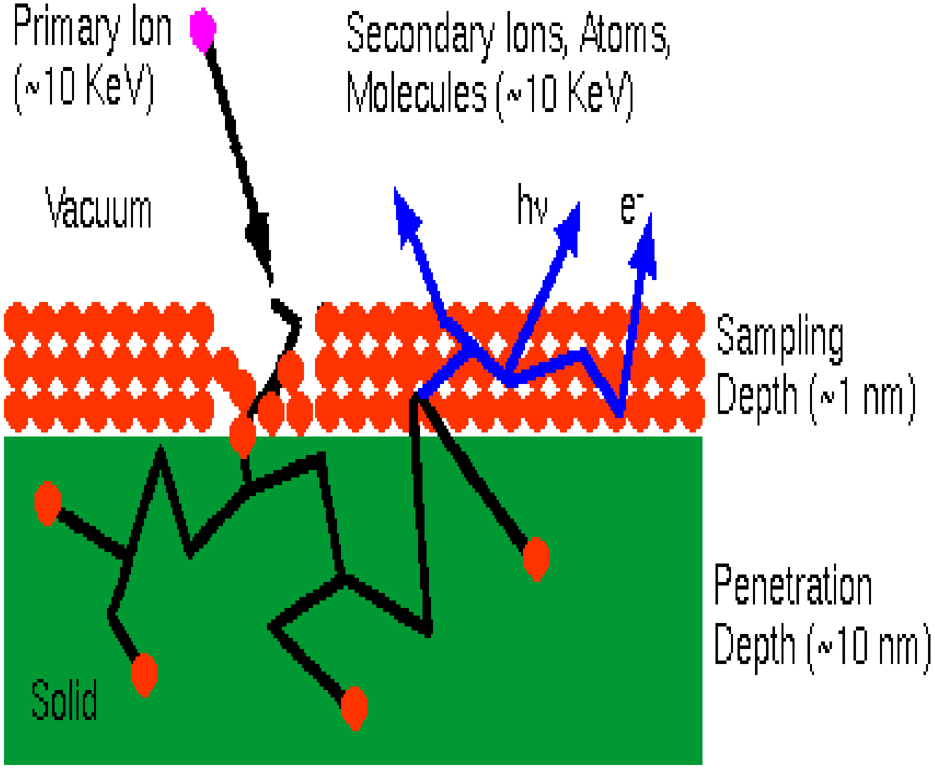
SIMS Issues

Atoms from the sample's outer monolayer can be driven in about 10 nm.

This type of damage is commonly called “surface mixing” or “knock on”.

Sputtering also creates surface roughness, lattice imperfections, roughness, etc.

It is a destructive test.



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Mass Analyzer Types

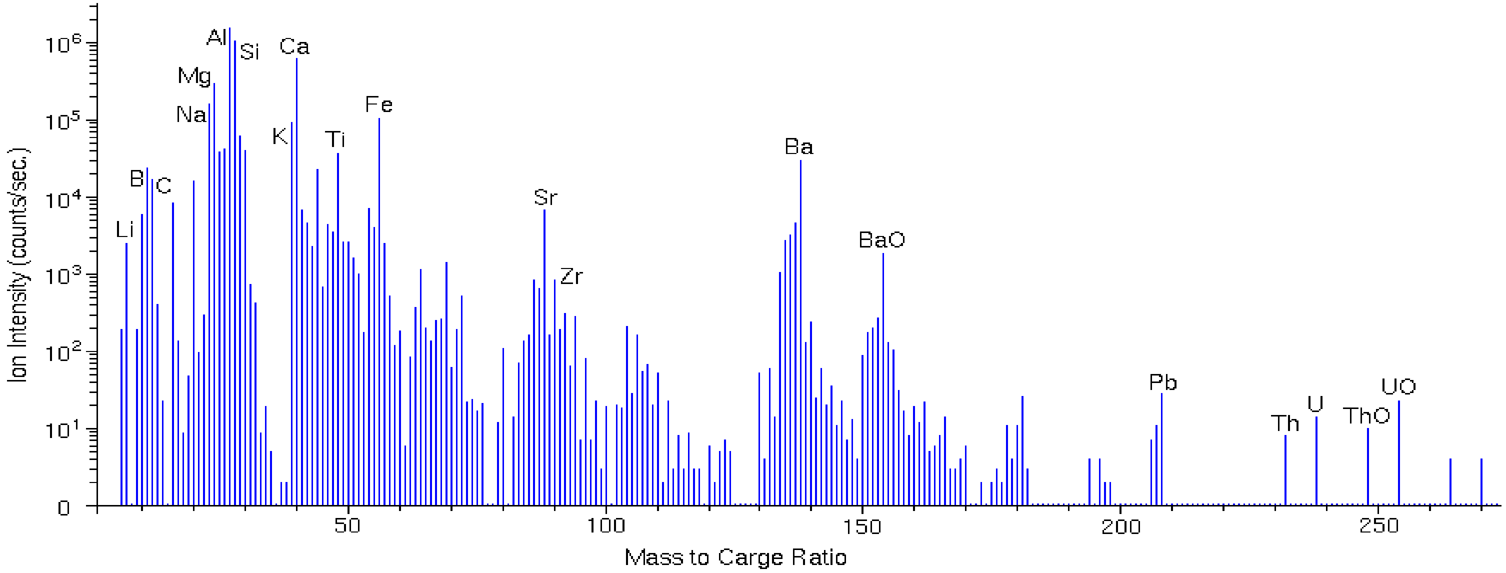
- A sector field mass spectrometer uses a combination of an electrostatic analyzer and a magnetic analyzer to separate the secondary ions by their mass to charge ratio
- A quadrupole mass analyzer separates the masses by resonant electric fields, which allow only the selected masses to pass through
- The time of flight mass analyzer separates the ions in a field-free drift path according to their velocity

SIMS Detection

The mass spectrum detects both atomic and molecular ions.

Mass to charge ratio can be misinterpreted.

Naturally the molecules can be dissociated into atomic fragments. This is especially true of organic media.



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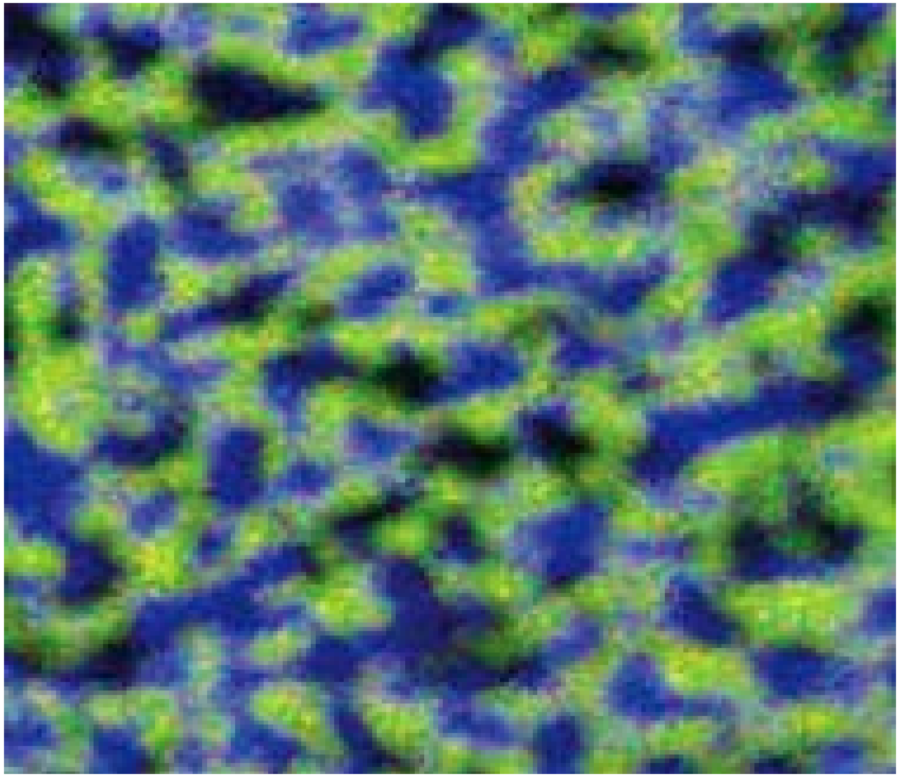
SIMS Detection



ToF-SIMS image of pharmaceutical ingredient distribution (Bentley).

SIMS Issues

- The secondary ion signal from the sample may be shielded from reaching the detector due to substrate charging.
- Dielectric samples may charge negatively and prevent positive ions from reaching the detector.
- In the case of a positive primary beam and negative secondary ions, the sample charges positively.
- Under these conditions the sample must be simultaneously bombarded with additional high- or low-energy electrons if charge build-up is to be reduced.

SIMS Issues

- There are a few ways of preventing this negative charge build up.
- High energy electron beams, are used to add negative charge to the sample. (This e-beam may interfere with the quadrupole detector).
- Dielectric samples can be coated with a conductive layer. Naturally, this layer will be included in the analysis.
- Software can add an offset voltage to compensate for the negative charging. Not a total solution, but more of an aid.

SIMS Summary

SIMS is considered one of the most sensitive surface analysis techniques, with elemental detection limits ranging from parts per million to parts per billion. Resolution is element specific, and SIMS is capable of detecting all elements as well as isotopes and molecular species

The measurement can be done at the surface of a sample, or utilizing simultaneous ion milling, composition as a function of depth can be determined.

Multiple ion sources are selected to give the best resolution

Unique methods to count the secondary ions can be used