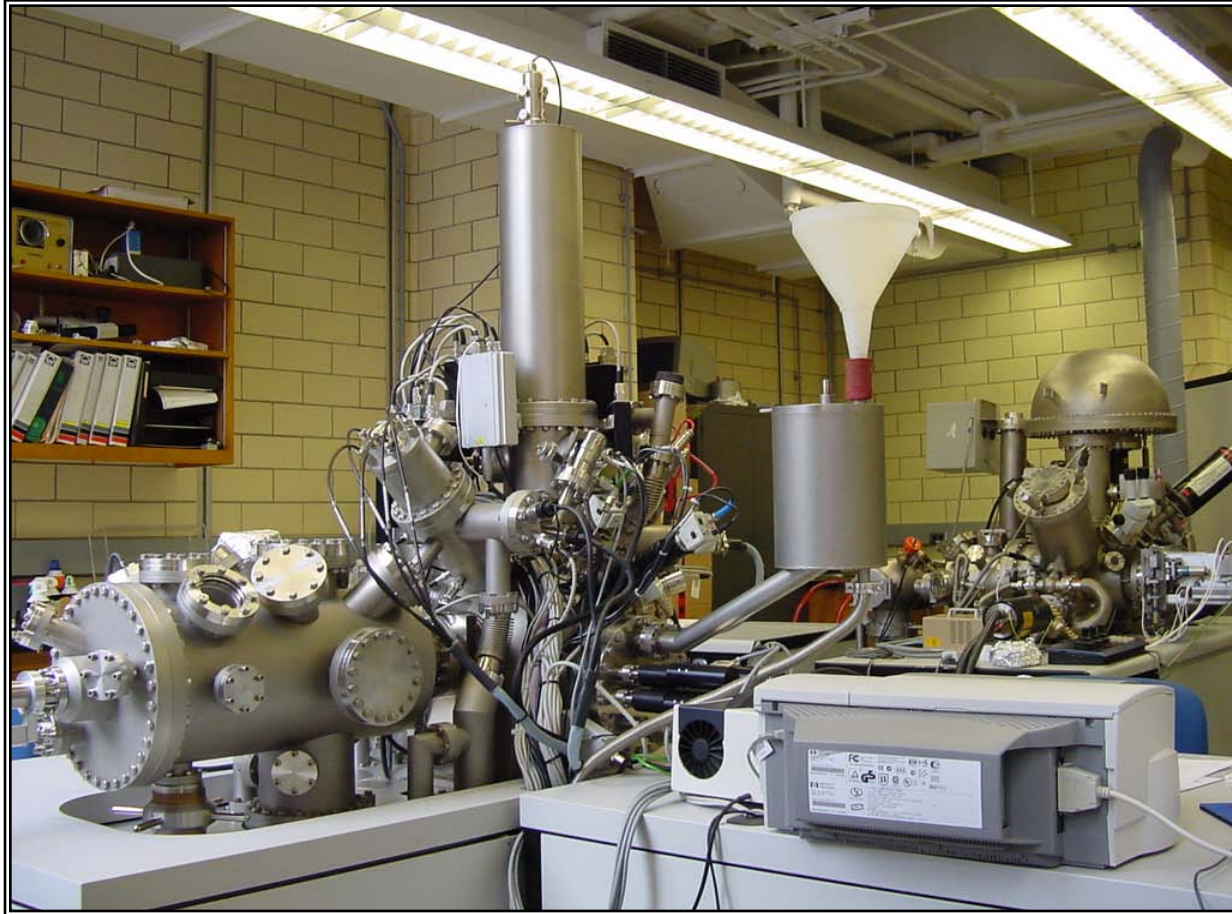


Secondary Ion Mass Spectrometry (SIMS)

A Conventional SIMS System

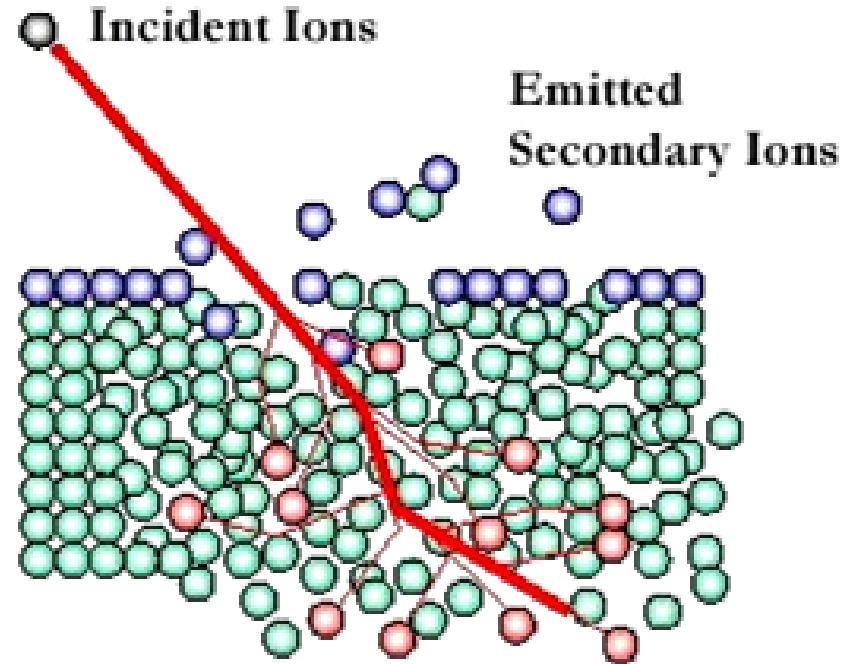


The MiniSIMS Instrument



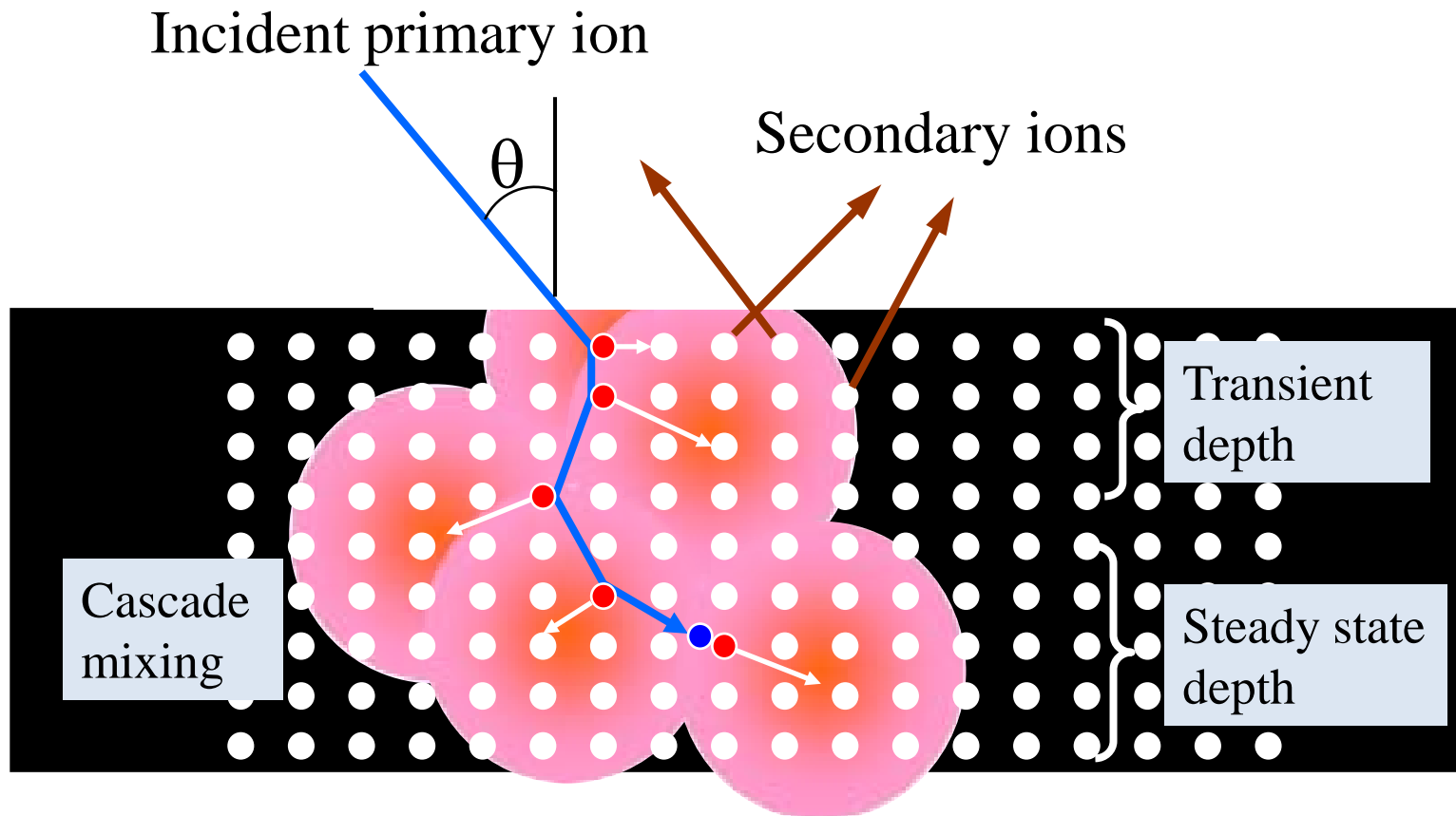
What is SIMS?

- SIMS is a surface analysis technique used to characterize the surface and sub-surface region of materials.
- It effectively employs the *mass spectrometry* of ionised particles which are emitted when a solid surface is bombarded by energetic primary particles (1-25 keV).
- The primary particles may be electrons, ions, neutrals or photons.

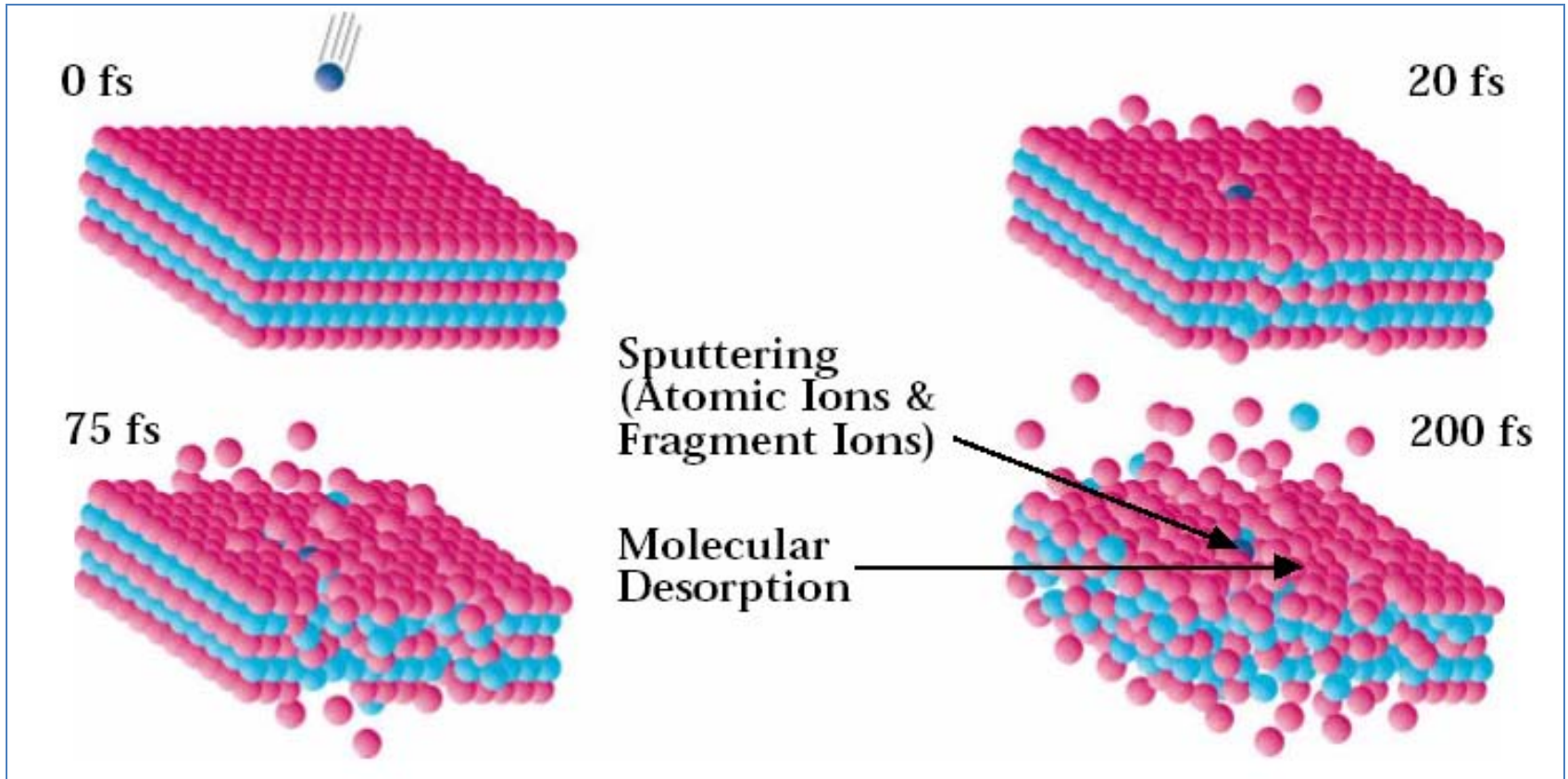


Ion – Solid Interactions

- ✓ The primary ions deposit energy into the surface layers. Around the impact site and to the depth of ~3 nm, many bonds are broken and there is much random displacement and movement of atoms. This region is called *the collision cascade*.



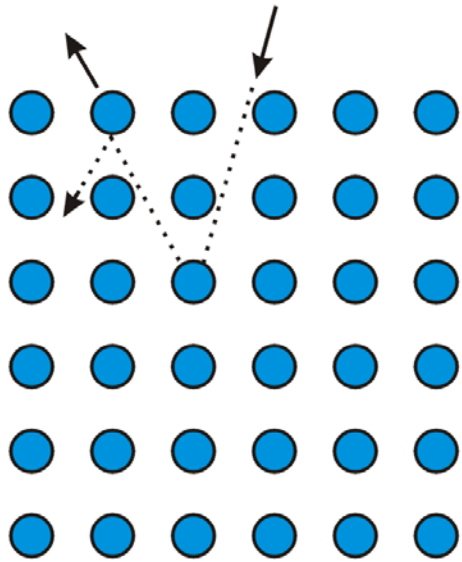
Collisions which result in translational energy being directed back to the surface layer lead to ejection of material. This process is termed *sputtering* of the surface.



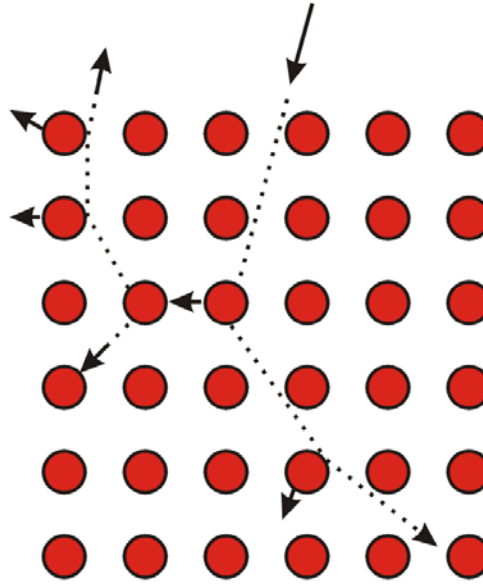
The Sputtering Process

- The process of sputtering can be described by the principles of classical mechanics through *binary collisions of primary ions with single target atoms*.
- Depending on the energy range of the primary particle, elastic and inelastic collisions take place. Dominating interactions in the **keV** range are **elastic** collisions.
- The number of inelastic collisions increases with rising energy. **Inelastic** collisions dominate in the **MeV** energy range.

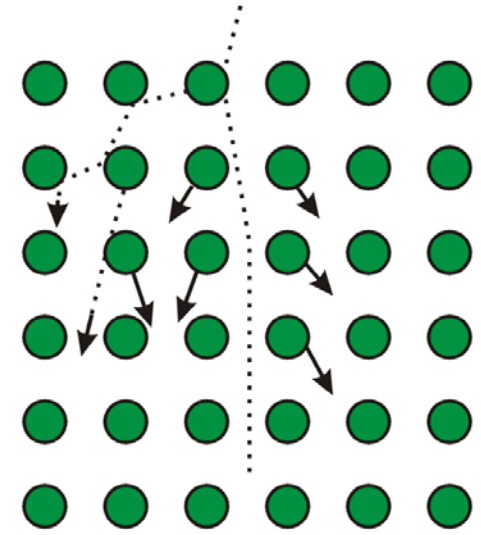
Sputtering by Elastic / Inelastic Collisions



Single knock-on
< 1keV
All secondary ions
virtually originate from
the uppermost atomic
layers



Linear cascade
1 keV – 1 MeV
sputtering yield
proportional
to beam energy



Spike > 1 MeV
High density of
recoil atoms

Ion Beam Sputtering

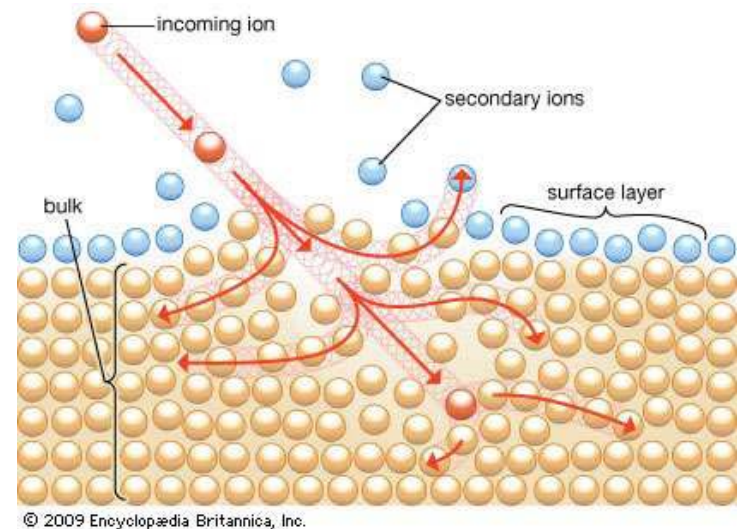
- The bombarding primary ion beam produces monatomic and polyatomic particles of sample material and resputtered primary ions, along with electrons and photons. The secondary particles carry negative, positive, and neutral charges and they have kinetic energies that range from zero to several hundred eV.

- Primary beam species useful in SIMS include Cs^+ , O^{2+} , O , Ar^+ , and Ga^+ at energies between 1 and 30 keV. Primary ions are implanted and mix with sample atoms to depths of 1 to 10 nm.

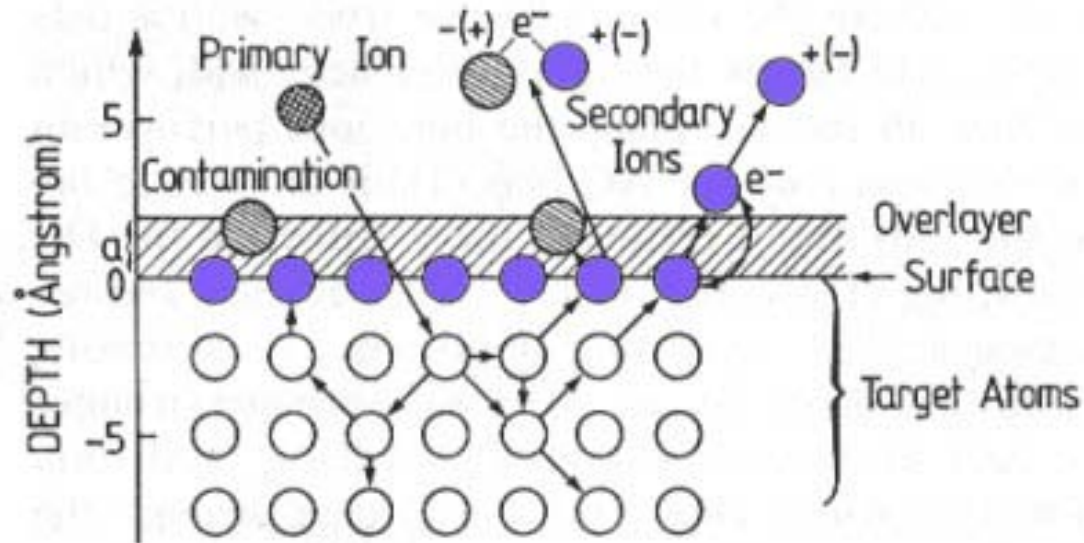
* A primary ion or particle causes a collision cascade amongst surface atoms and between .1 and 10 atoms are usually ejected. This process is termed sputtering. The sputter yield depends on the nature of the analyte.

- Sputter rates depend on primary beam intensity, sample material, and crystal orientation.

- The sputter yield is the ratio of the number of atoms sputtered to the number of impinging primary ions. Typical SIMS sputter yields fall in a range from 5 and 15.

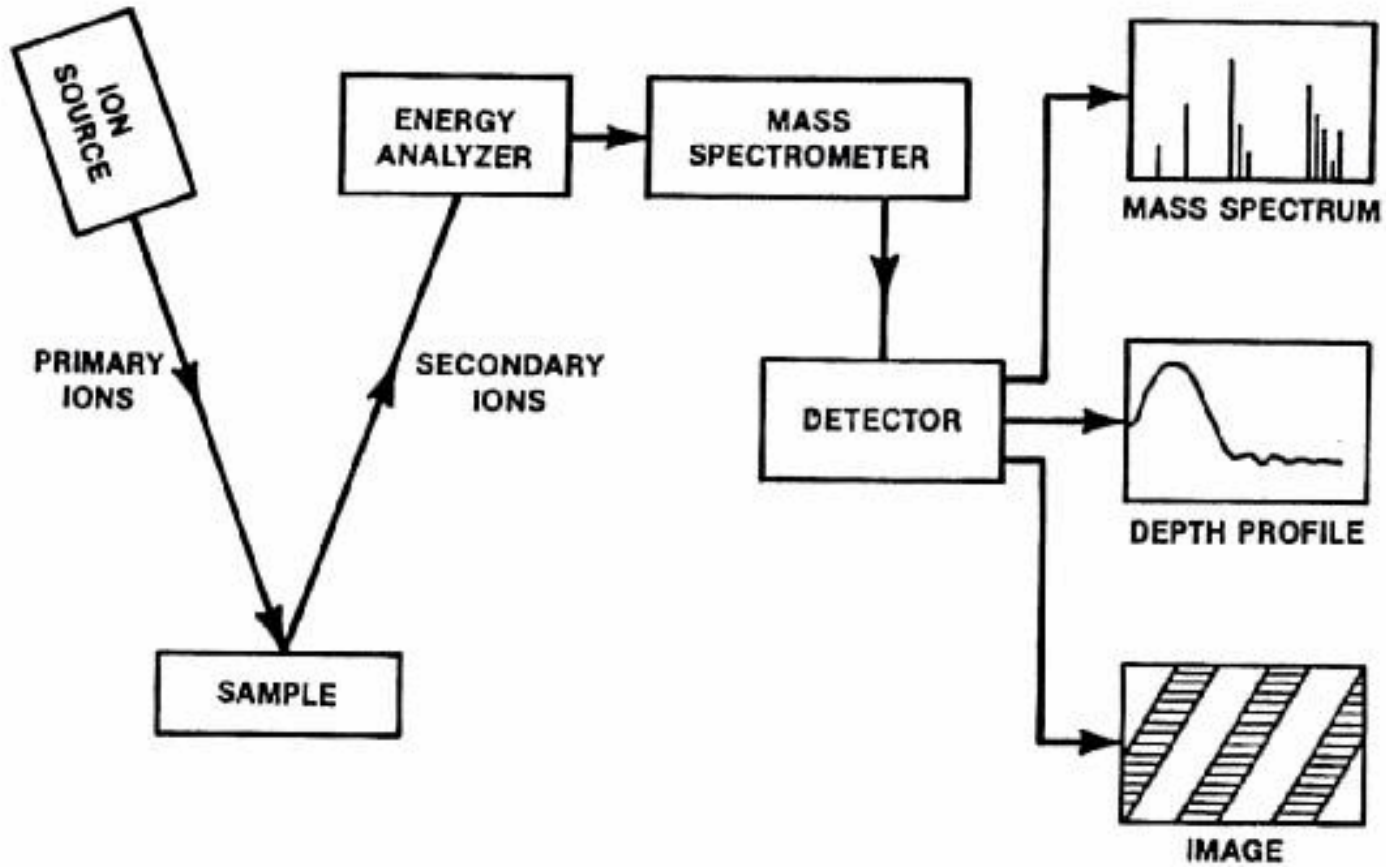


Collision Cascade



- Of these ejected atoms some are ionized (usually less than 10%), these are the secondary ions. The matrix of a sample must be known to accurately determine elemental concentrations, as ionization yields can vary as much as three orders of magnitude between nearly identical atomic sputtering yields.
- Secondary ions can then be analyzed using mass spectroscopy.

Basic Overview



Instrumentation

Ion Gun Sources

- Ion sources with electron impact ionization - Duoplasmatron: Ar^+ , O_2^+ , O^-
- Ion sources with surface ionization - Cs^+ ion sources
- Ion sources with field emission - Ga^+ liquid metal ion sources

Mass Analyzers

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

Ion Detectors

- Faraday cup
- Dynode electron multiplier

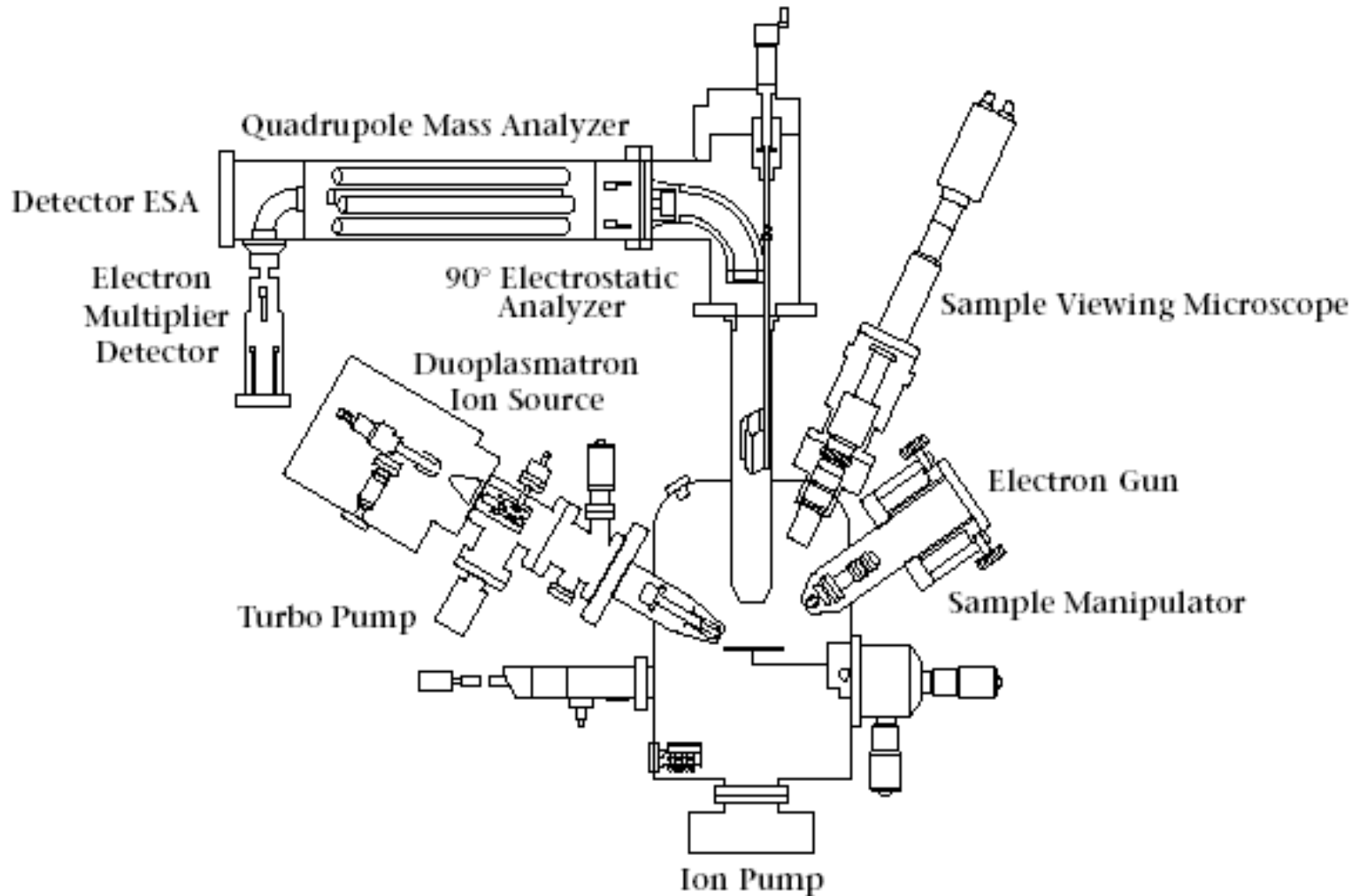
Mass Analysers

- Quadrupole
- Magnetic sector
- Time-of-Flight

Table 5.3. Comparison of mass analysers for SIMS

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

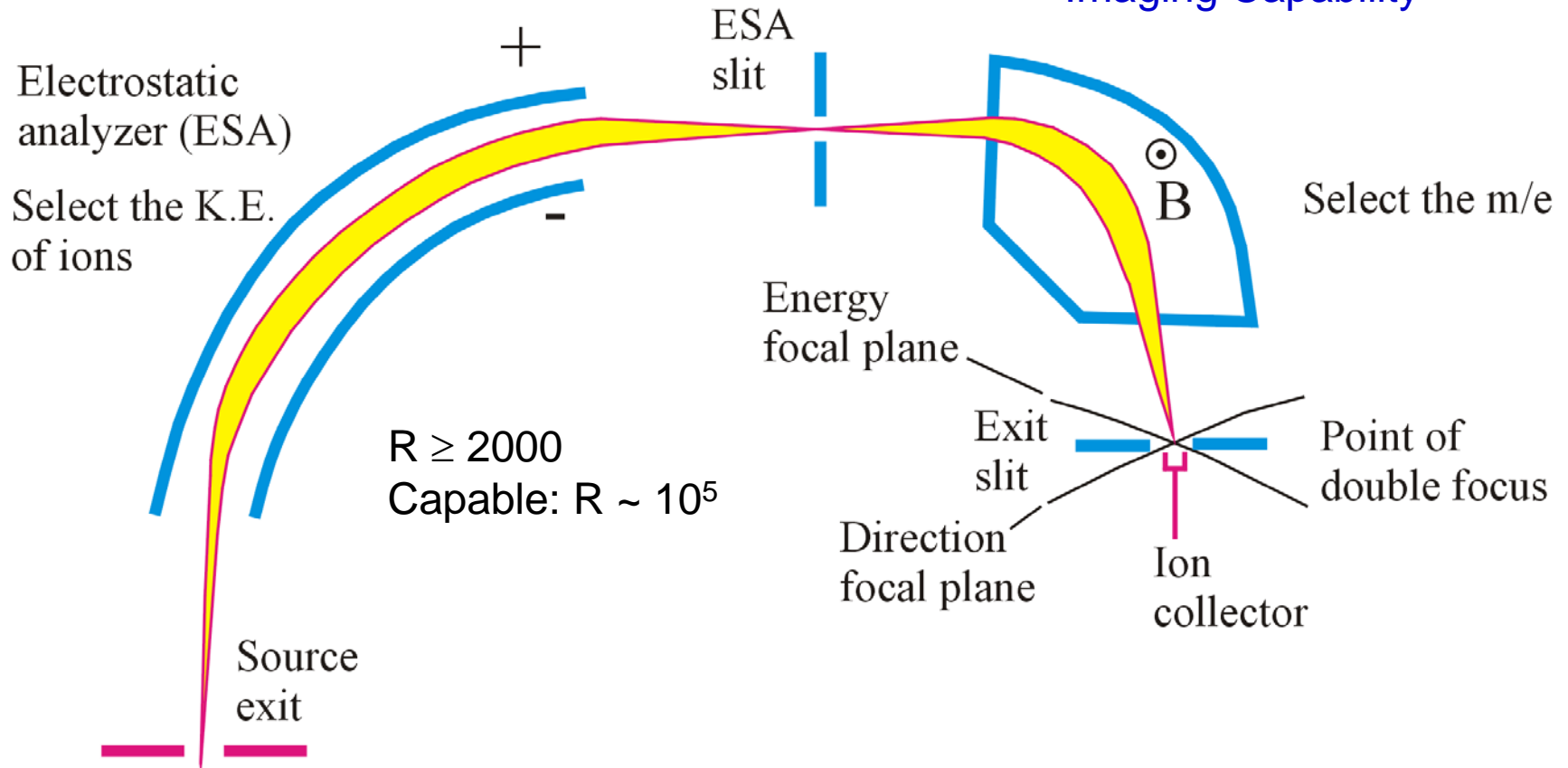
Quadrupole SIMS



Quadrupole - makes use of a combination of a DC and RF electric field applied to four parallel rods in order to separate ions according to their m/z ratio

Magnetic Sector Analyzer

High transmission efficiency
High mass resolution
Imaging Capability



- Radius of curvature R for an ion of m/z ratio travelling through a perpendicular magnetic field B after being accelerated by potential V is given by:

$$R = \frac{1}{B} \left(\frac{2mV}{z} \right)^{\frac{1}{2}}$$

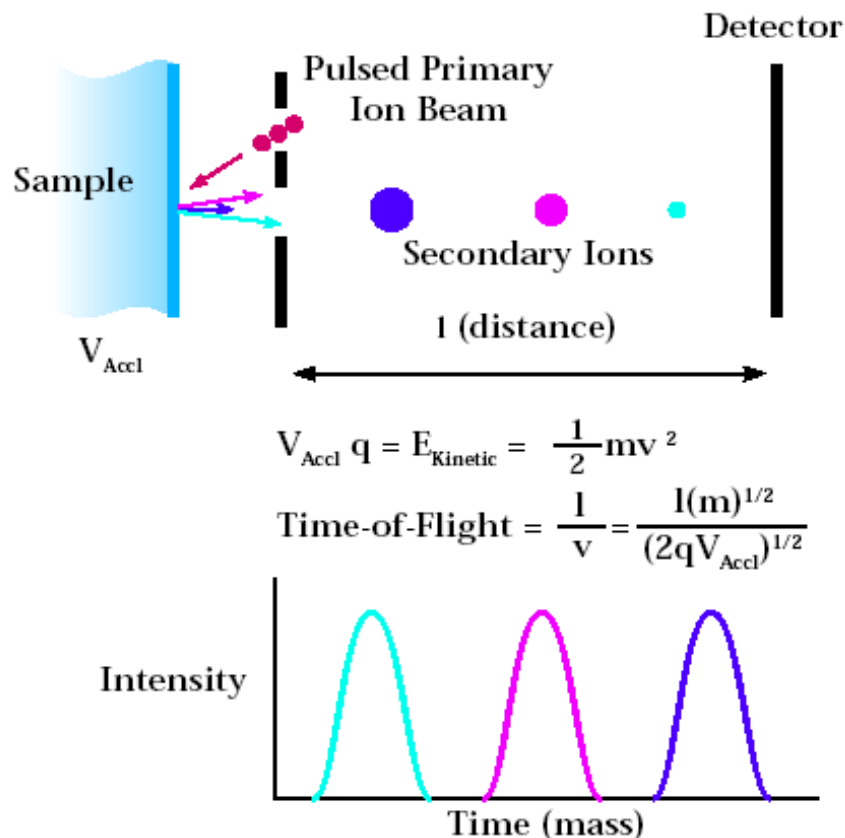
Time-of-Flight Mass Spectrometer (TOF-MS)

-pulses of secondary ions are accelerated to a given potential (3-8 keV) such that all ions possess the same K.E.; they are then allowed to drift through a field-free space before reaching the detector

- time-of-flight, t down a flight path length L is given by

$$t = L \left(\frac{m}{2zV} \right)^{\frac{1}{2}}$$

•Major advantages of this approach over quadrupole and magnetic sector type analysers are the extremely high transmission, the parallel detection of all masses and the unlimited mass range.

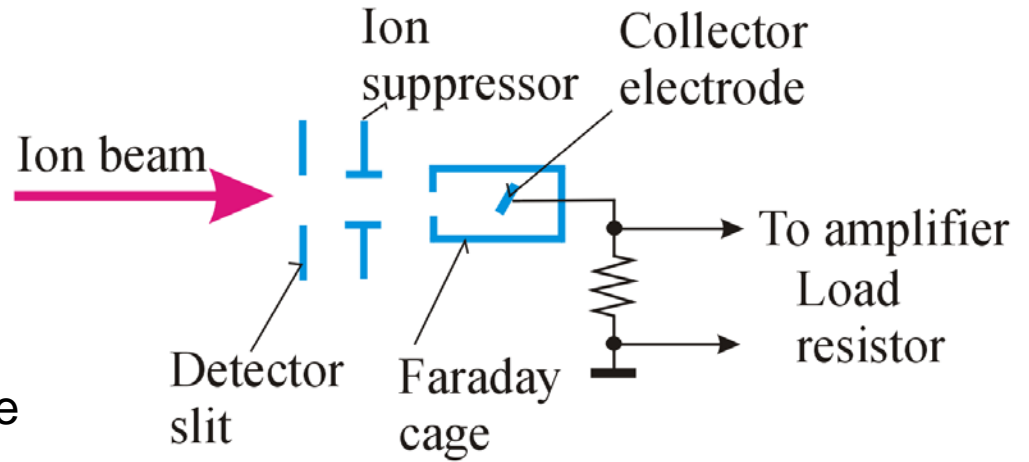


Complicating Issue

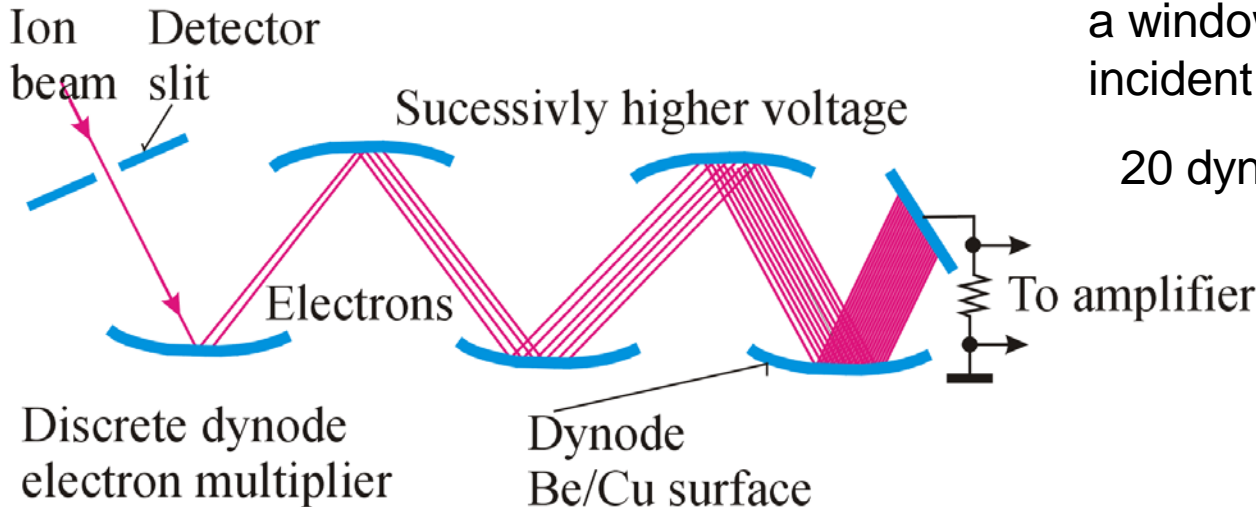
- Ions can be generated with non-zero initial kinetic energy
- Thus $E + D E = \frac{1}{2} m (v + Dv)^2$ causes broadening of peak at each mass (m)

Ion Detectors

Faraday Cup: A **Faraday cup** is a metal (conductive) cup designed to catch charged particles in vacuum. The resulting current can be measured and used to determine the number of ions or electrons hitting the cup.^[1] The Faraday cup is named after Michael Faraday who first theorized ions around 1830.



Secondary electron Multiplier:



An electron multiplier is a vacuum-tube structure with a window that multiplies incident charges

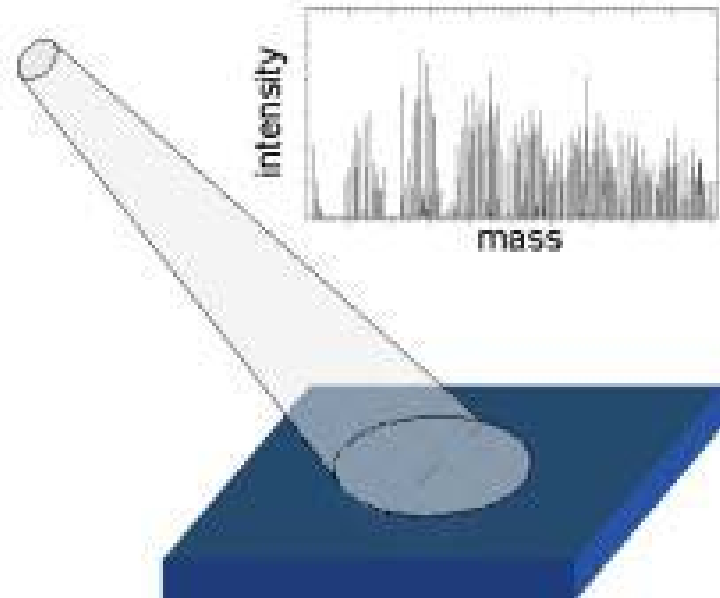
20 dynodes; Current gain 10^7

The 3 SIMS Analysis Modes

- **Static SIMS** are used to determine surface concentrations of elements and molecules without significantly altering the analyte.
- **Imaging SIMS** like static SIMS does not alter the analyte appreciably. This mode is used to generate images or maps of analytes based upon concentrations of one secondary ion representing either an element or molecule.
- **Dynamic SIMS** involves the use of a much higher energy primary beam (larger amp beam current). It is used to generate sample depth profiles.

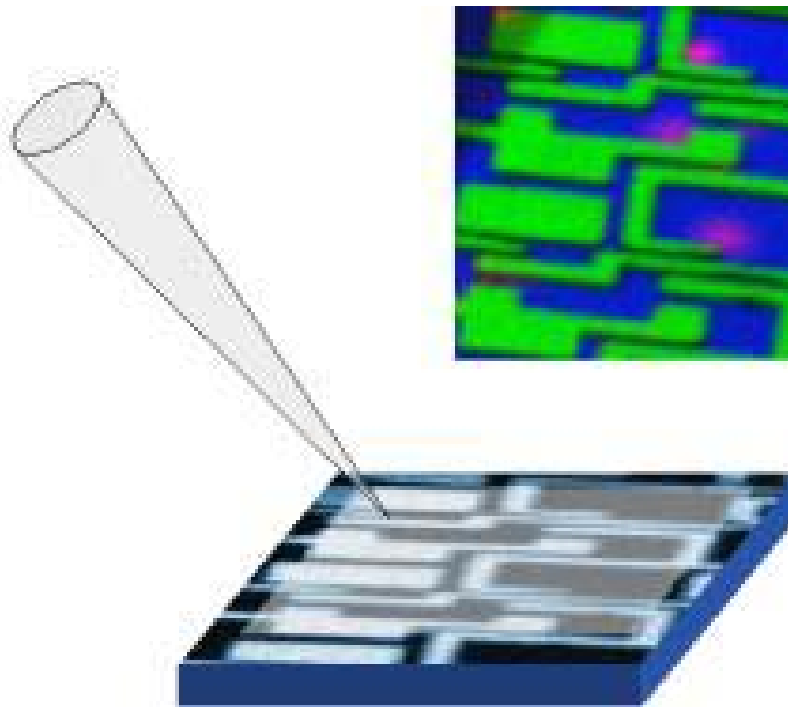
Static SIMS - Surface Spectroscopy

- The aim of a static SIMS investigation is the analysis of the original, non-modified surface composition.
- As SIMS in principle is a non-destructive technique this means that the contribution of those secondary ions to the spectrum originating from already bombarded surface areas must be negligible.
- This quasi non-destructive surface analysis can be achieved by the application of very low primary ion dose densities



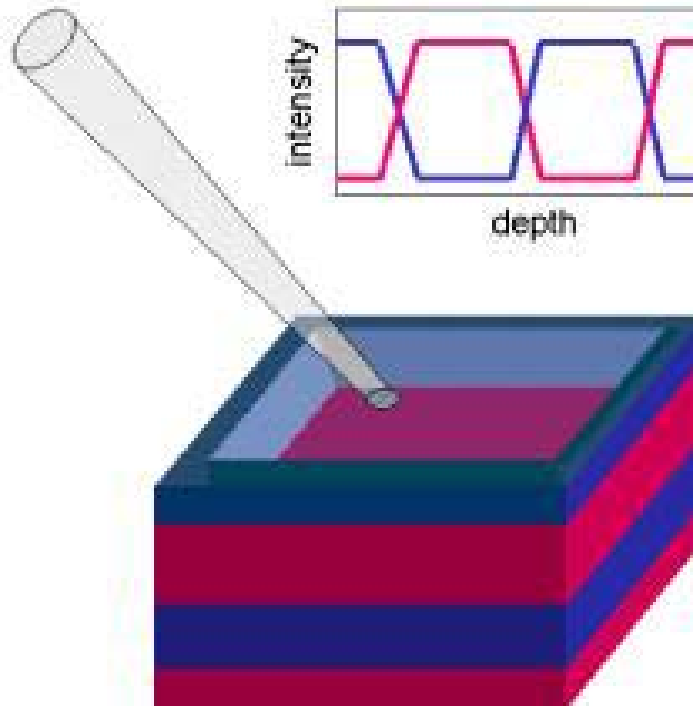
Imaging SIMS - Surface Imaging

- By rastering a finely focussed ion beam over the surface, like an electron beam in an electron microprobe, mass resolved secondary ion images (chemical maps) can be obtained simultaneously.

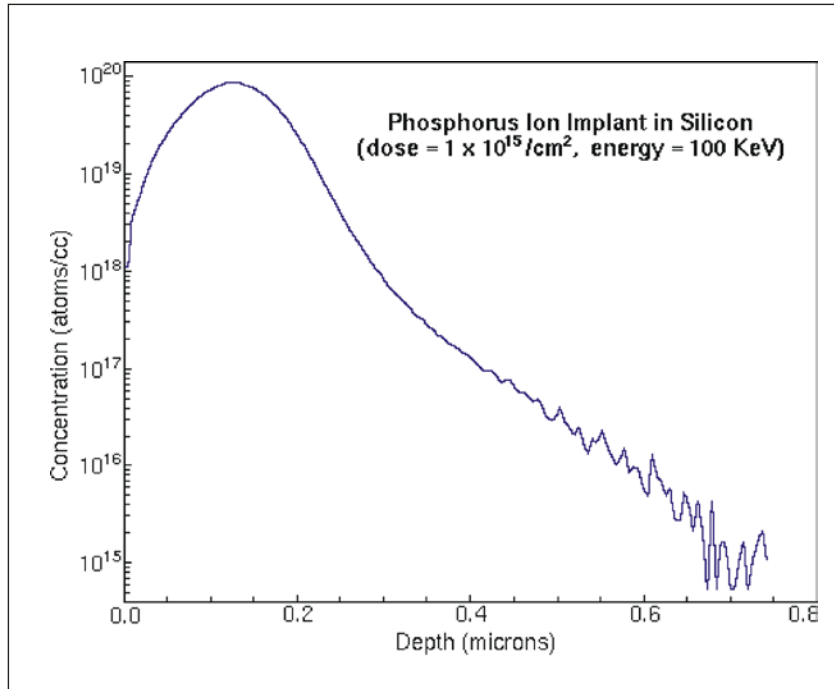


Dynamic SIMS - Depth Profiling

- In contrast to a static SIMS experiment, high primary ion dose densities are applied giving a successive removal (sputtering) of the respective top surface layers. By acquiring spectra during the sputtering the in-depth distribution of elements and small clusters (e.g. oxides) can be monitored.



Depth Profiling



- Monitoring the secondary ion count rate of selected elements as a function of time leads to depth profiles.
- The sample was prepared by ion implantation of phosphorous into a silicon wafer. The analysis uses Cs⁺ primary ions and negative secondary ions.

The following figure shows the raw data for a measurement of phosphorous in a silicon matrix.

Main Features

In the context of surface analysis, SIMS is complementary to

- * Ion Scattering Spectroscopy (ISS),
- * X-ray Photoelectron Spectroscopy (XPS or ESCA),
- * Scanning Electron Microscopy (SEM) and
- * Auger Electron Spectroscopy (AES).

- the main features of SIMS can be summarized as follows:
- Surface specificity is very high greater than for XPS, AES and XRF.
- Elemental sensitivity is also greater and can be of the order of ppm of a monolayer, whereas XPS, AES and XRF have sensitivities ~ 0.2 atomic percent.
- XPS and AES do not detect hydrogen, and XRF has zero or poor sensitivity to Lithium, Beryllium and Boron, whereas SIMS can detect all the light elements.
- SIMS also has the advantage of isotope specificity.
- The pattern of SIMS cluster ions contains a great deal of molecular/ structural information for both organic and inorganic surfaces.
- Total secondary ion images contain topographic contrast and provide surface visualization, as in SEM but with lower spatial resolution.

- Mass resolved images give chemical contrast and allow element mapping, as in XPS, AES or EDX, but the high sensitivity of SIMS means imaging is faster.
- Shallow depth profiling is straightforward because the same ion gun is used for both erosion and analysis.
- The main drawback to SIMS is that quantification is difficult except for the specific case of trace concentrations with calibration standards.

Figures of Merit

- At low frequency ion bombardment the outer most 5 nm of a sample can be characterized.
- Secondary ion images have resolution on the order of .5 to 5 μm .
- Detection limits for trace elements range between 10^{12} to 10^{16} atoms/cc.
- Detection limits are affected by stray ions and electrons in the vacuum instrument system and by cosmic rays. Their presence can create currents called **dark currents**, which can drown out a weak secondary ion signal.
- Spatial resolution is determined by primary ion beam widths, which can be as small as 100 nm.

Uses

- NASA first developed SIMS in the 1960s to investigate the composition of Moon rocks. The method proved so successful, that the apparatus was commercially produced.
- SIMS can be used to determine the composition of organic and inorganic solids at the outer 5 nm of a sample.
- To determine the composition of the sample at varying spatial and depth resolutions depending on the method used. This can generate spatial or depth profiles of elemental or molecular concentrations.
- These profiles can be used to generate element specific images of the sample that display the varying concentrations over the area of the sample.
- To detect impurities or trace elements, especially in semi-conductors and thin filaments.

- Today, SIMS is widely used for analysis of trace elements in solid materials, especially semiconductors and thin films.
- The SIMS ion source is one of only a few to produce ions from solid samples without prior vaporization.
- The SIMS primary ion beam can be focused to less than 1 μm in diameter.
- Controlling where the primary ion beam strikes the sample surface provides for microanalysis, the measurement of the lateral distribution of elements on a microscopic scale.
- .

- During SIMS analysis, the sample surface is slowly sputtered away.
- Continuous analysis while sputtering produces information as a function of depth, called a depth profile.
- When the sputtering rate is extremely slow, the entire analysis can be performed while consuming less than a tenth of an atomic monolayer.
- This slow sputtering mode is called static SIMS in contrast to dynamic SIMS used for depth profiles.
- Shallow sputtering minimizes the damage done to organic substances present on the sample surface.
- The resulting ion fragmentation patterns contain information useful for identifying molecular species. Only dynamic SIMS will be treated in this surface analysis computer aided instruction package because only dynamic SIMS yields quantitative information

Laser Microprobe Mass Spectrometry

* LMMS employs pulses from a UV laser focused to 1–5 microns, to evaporate and ionize a microvolume at the surface of a solid sample.

* The ions are subsequently separated according to their mass/charge (m/z) ratio.

* Depending on the power density during irradiation, ions containing the intact organic or inorganic molecules are formed in combination with specific fragments .

•The elemental composition of each ion can be derived from the m/z value.

• Knowledge of the ionization and fragmentation processes enables one to deduce the structural composition of the analyte.

• The main specimen requirement is stability in vacuum.