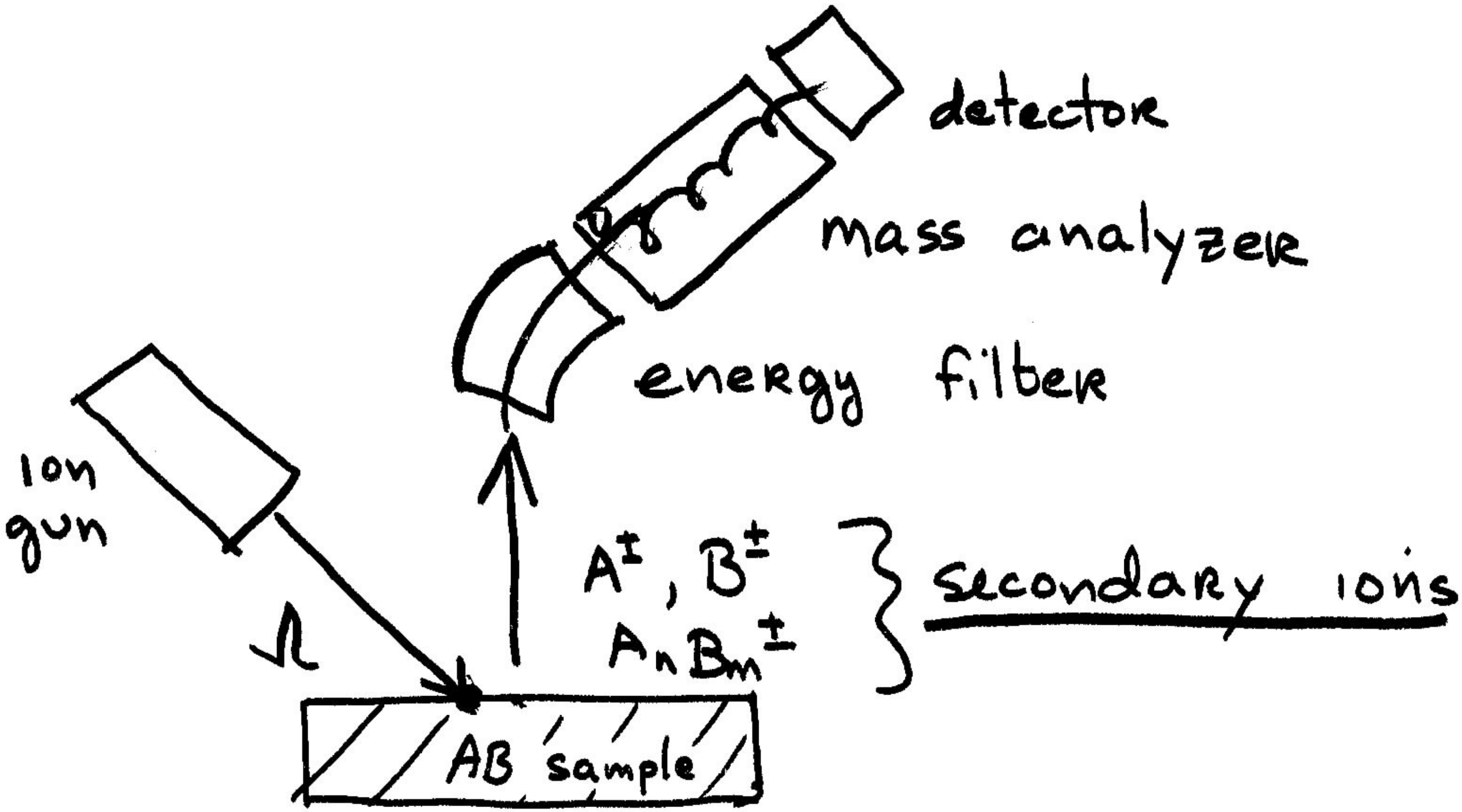
Secondary Ion Mass Spectroscopy (SIMS)

- SIMS is based on a beam of energetic primary ions sputtering away a solid surface, this produces sputtered particles (neutrals, +/- ions, clusters) which can be detected with a mass spectrometer.
  - A sputtered particle is a particle that was formerly a part of the solid surface that was removed due to ion bombardment.

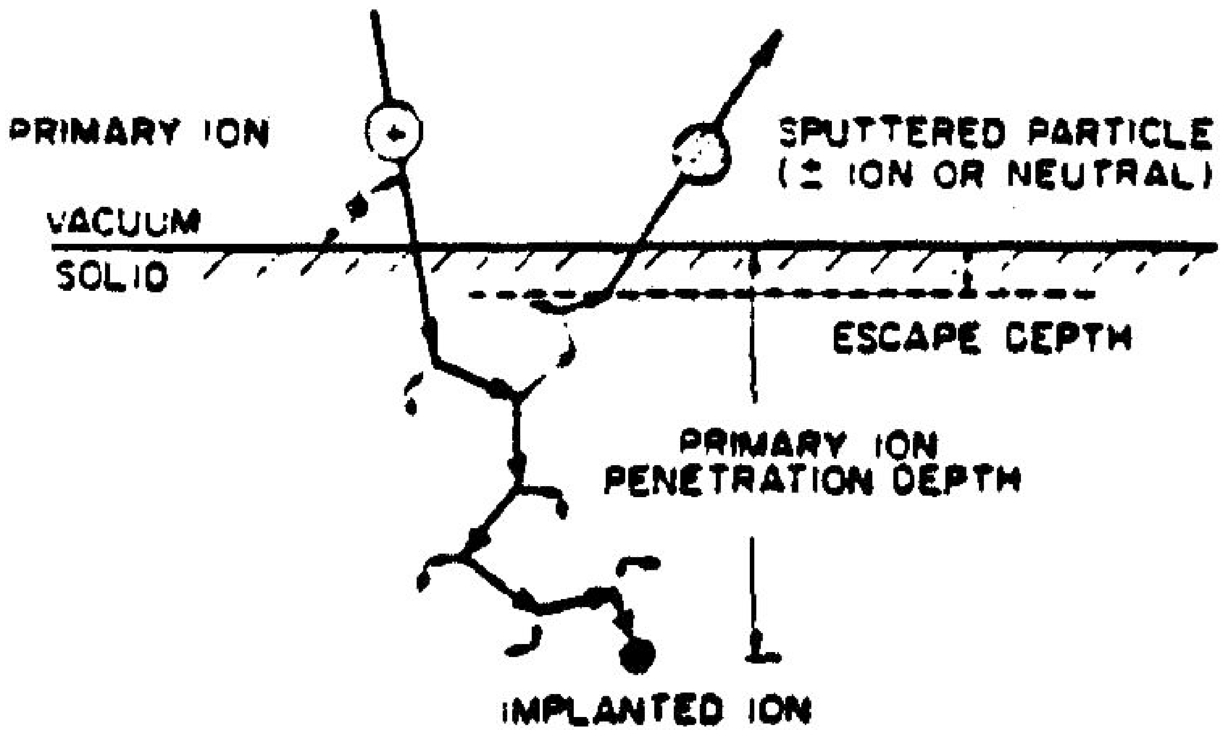
SIMS and Auger Profiling

- SIMS and Auger or XPS profiling are very similar. The main difference is that Auger (XPS) profiling probes the particles left behind on the surface while SIMS examines the particles that have been removed.

SIMS Schematic



SIMS Schematic



SIMS Schematic

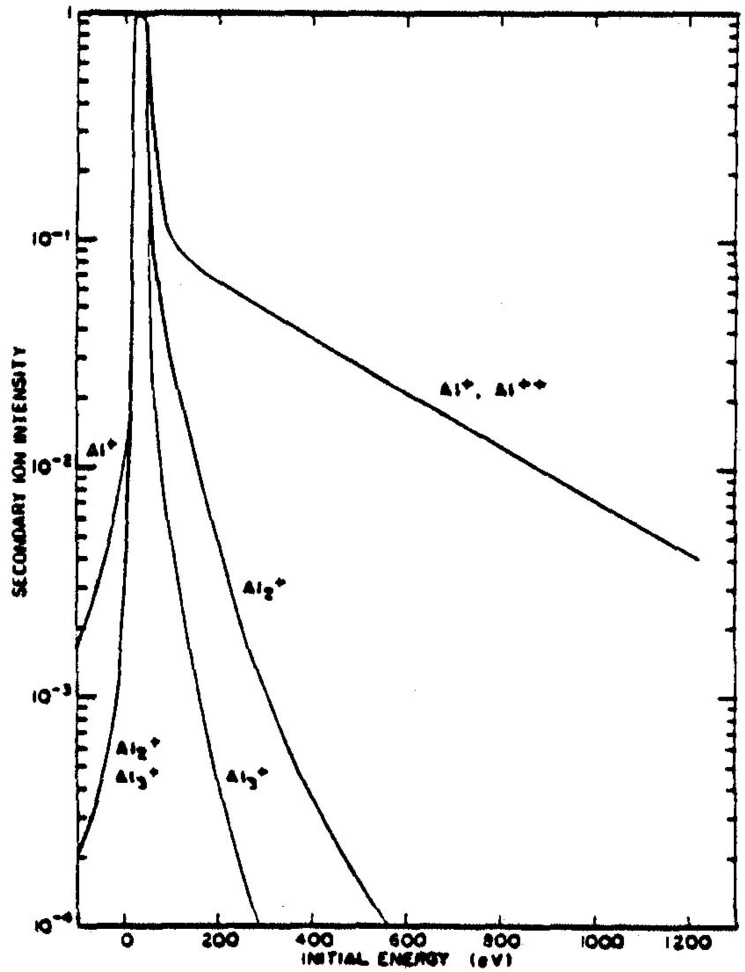


Fig. 5. Energy distributions for various Al secondary ion species sputtered from an Al—Mg alloy by 12 keV Ar^+. (From Herzog et al. [25].)

SIMS Advantages

- Depth profiling gives information on atomic composition as a funciton of depth
- High Detection Sensitivity for Most Elements
- Large Dynamic Range (Trace quantities are detectable)
- Can Detect Low-Z elements (H, Li, Be)
- Good Depth Resolution (~ 50 Å)

SIMS Pitfalls

- Complications arise because the most relevant experimental parameters are all coupled.
- Furthermore, they are poorly understood from a fundamental viewpoint.
  - Incident Ion Beam
    - Atom
    - Energy
  - Surface Removal Rate
  - Elemental Detection Sensitivity
  - Surface Conditions

SIMS Sensitivity versus Ion Beam Parameters

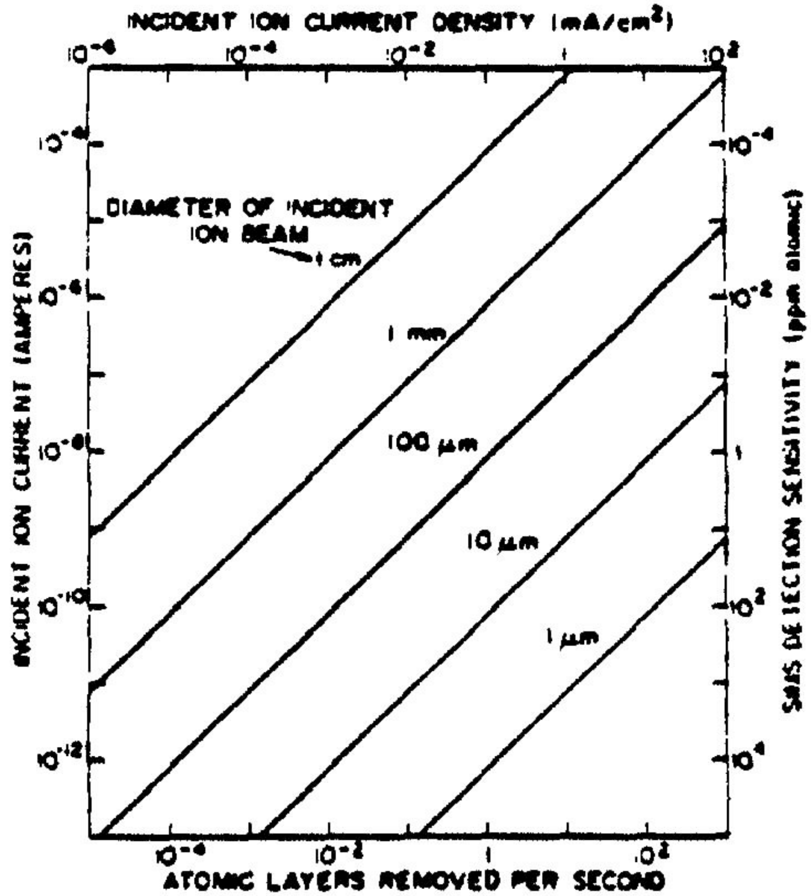


Fig. 1. Relationships between incident ion current, diameter and current density, atomic layer removal rate and SIMS detection sensitivity. The atomic layer removal rate is based on a typical matrix sputter atom yield and the SIMS detection sensitivity is based on experimentally derived sensitivities for a typical element—matrix situation.

SIMS Instrumentation

The principle behind SIMS is simple but the instrumentation is complex.

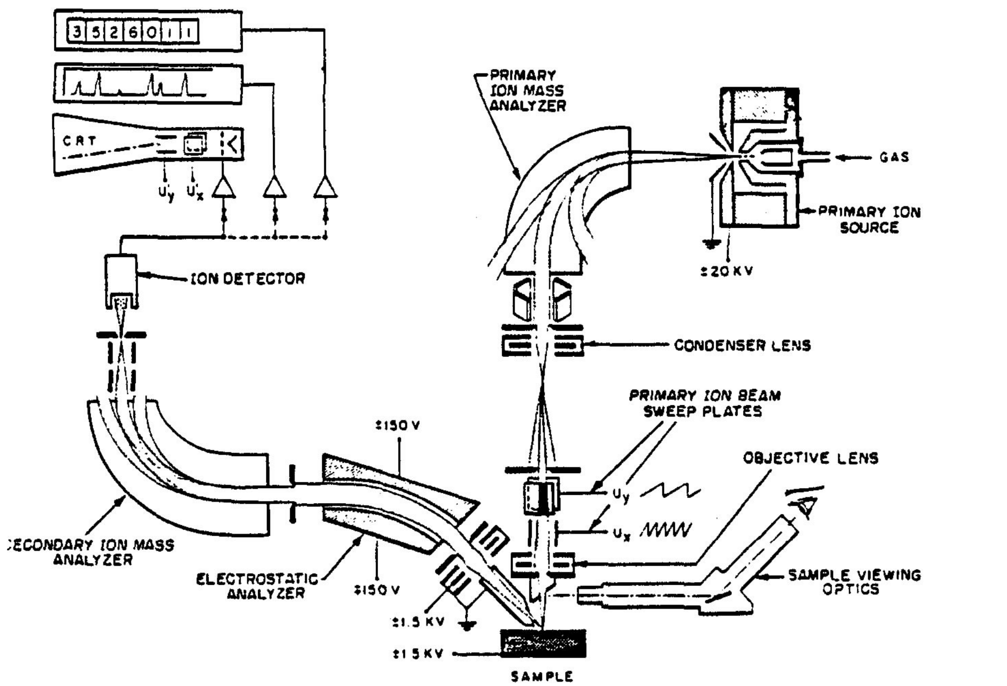


Fig. 10. Schematic drawing of the Applied Research Laboratories ion microprobe mass analyzer. (From McHugh and Stevens [134].)

Imaging SIMS (CAMECA)

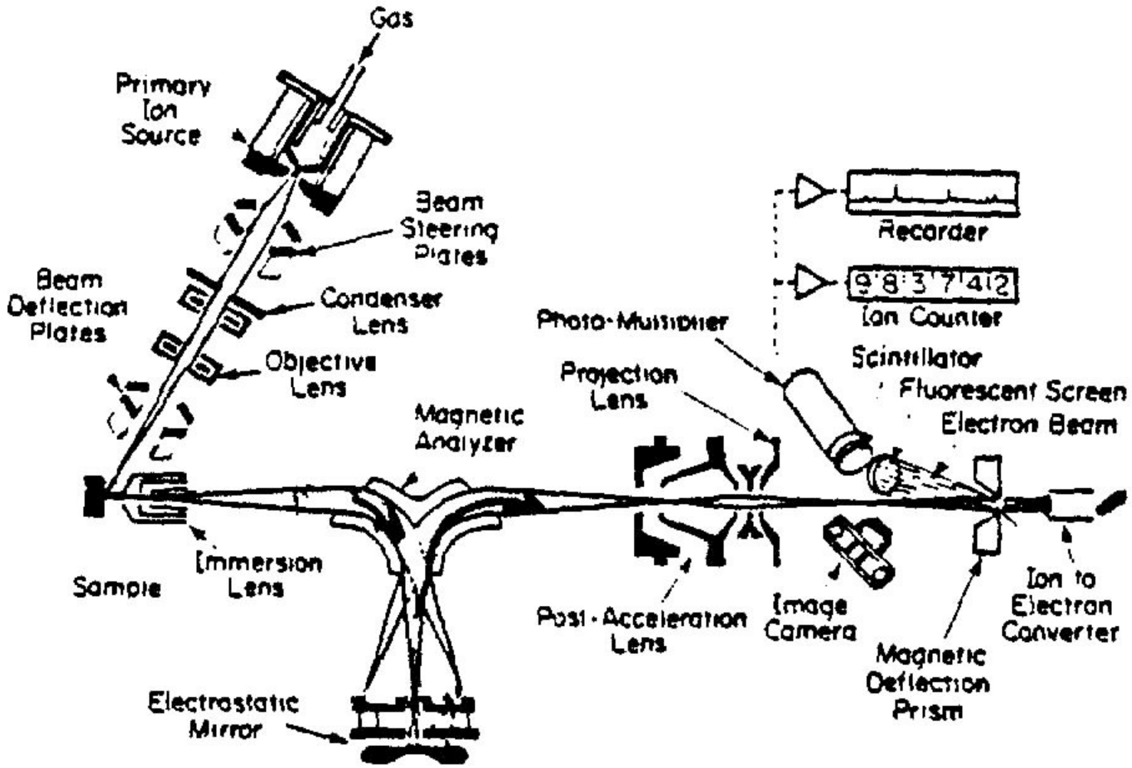


Fig. 11. Schematic drawing of the CAMECA Ion Microanalyzer. (From Evans [50].)

SIMS Particles

- The particles sputtered away from the surface can be either positive or negative or neutrals. In SIMS one refers to positive and negative ion spectra.
- Neutrals are the most abundant but must be ionized by some means (UV laser) before they can be detected.

Negative Ions

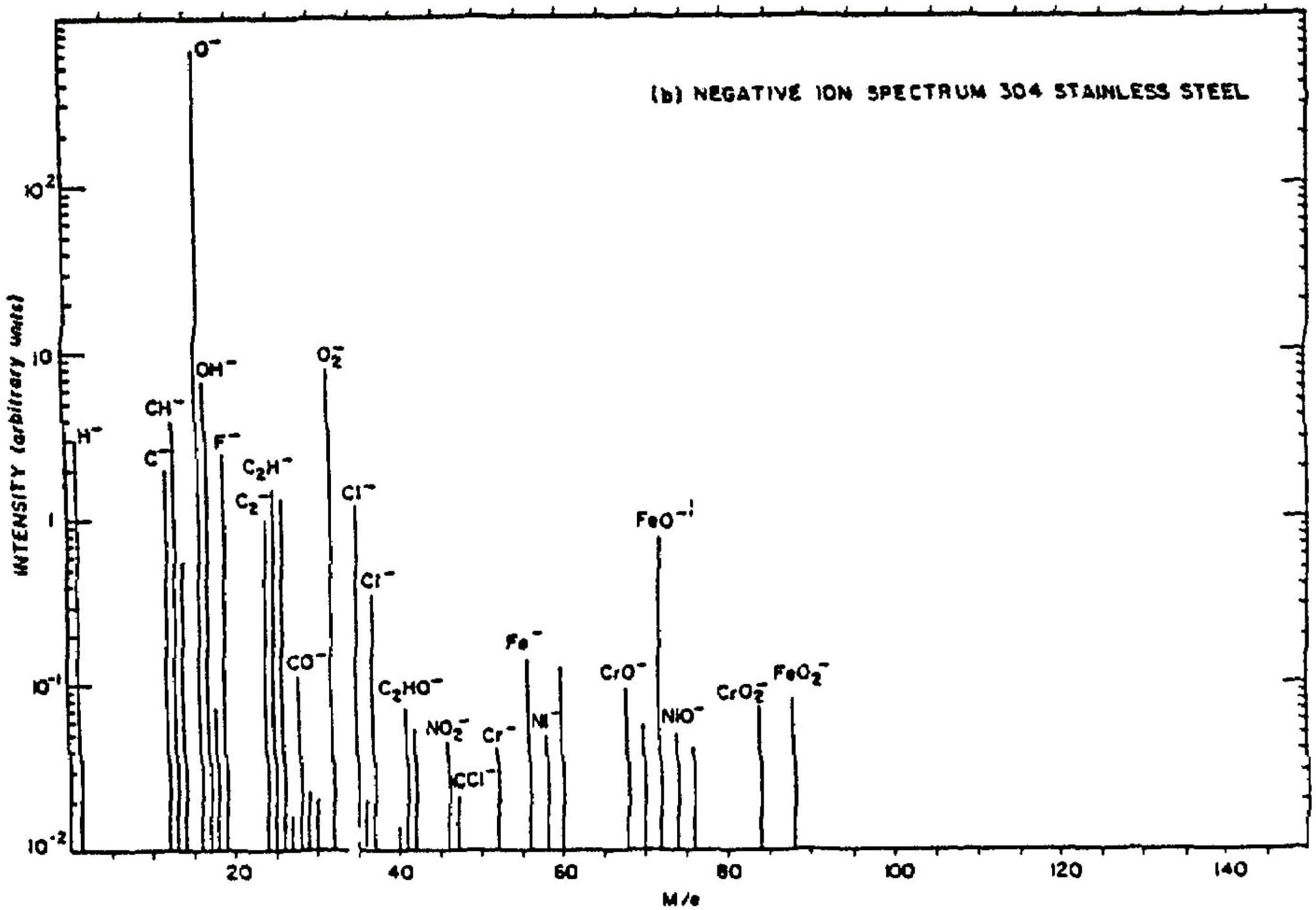
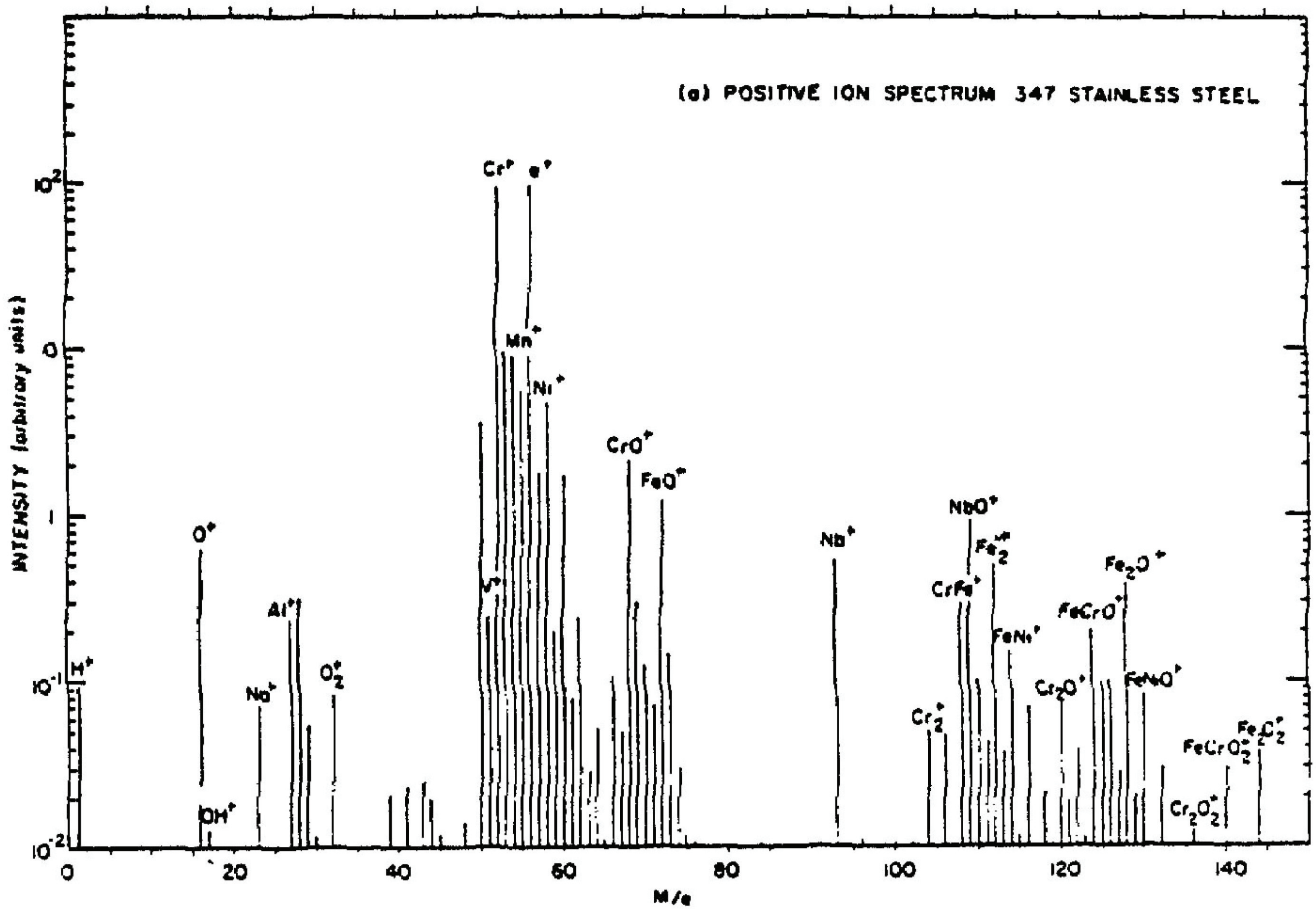


Fig. 6. Mass spectra for (a) positive secondary ions from a 347 stainless steel sample and (b) negative secondary ions from a 304 stainless steel sample. The incident $^{16}O^-$ beam energy and current were 15 keV and $\sim 10^{-9}$ A respectively. (From McHugh [54].)

Positive Ions



Secondary Ion Yield

$$S^{\pm} = \gamma^{\pm} C\, S$$

- C is concentration
- S is the total sputter atom yield (atoms per incident ion)
  - Determined by elemental binding energies or heat of atomization
- γ is the ratio of +/- secondary ions to to the total yield of ions
  - Sensitive to Electronic Structure of the material

Positive Ions

- Results through ionization of the excited atoms.
  - Excited atom travels through the surface
    - Velocity
    - Mean lifetime -- Influenced by electronic structure of matrix
      - Metals - fast de-excitation
        - low yield
      - Insulators - slow de-excitation
        - high yield

Negative Ions

- Less Clear Why Negative Ions Form
  - Gain electron in going through the surface
    - Must be influenced by electron affinity

Ion Yields in SIMS

- The secondary ion fraction of the sputtered atoms is small, typically 10^{-3} - 10^{-1}. Atomic ions are dominant for light elements, Z < 40, but ionized clusters and molecules are also present.
- The secondary ion yield changes rapidly with atomic number: For O^- primary ions, it changes about 4 orders of magnitude, roughly related to the reactivity of O with different elements; for Cs^+, a similar variation is observed depending upon electron affinity.

Ion Yields versus Atomic Number

Positive Ions

O^- bombardment

Negative Ions

Cs^+ bombardment

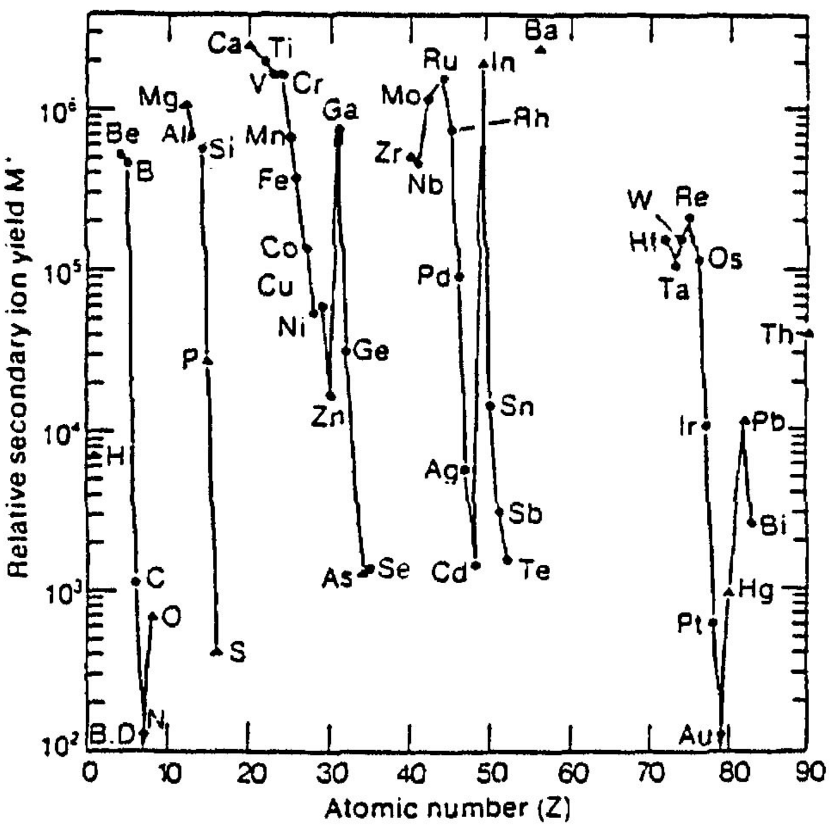


Fig. 4a Normalized positive secondary ion yields under O^- bombardment (*Storms* et al. 1977)

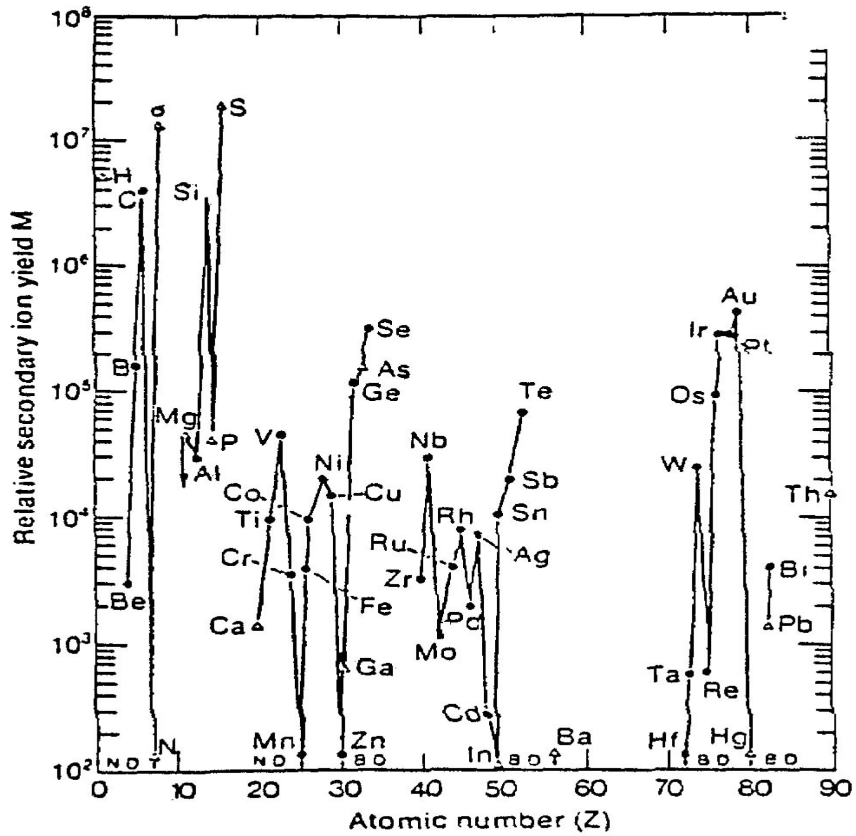
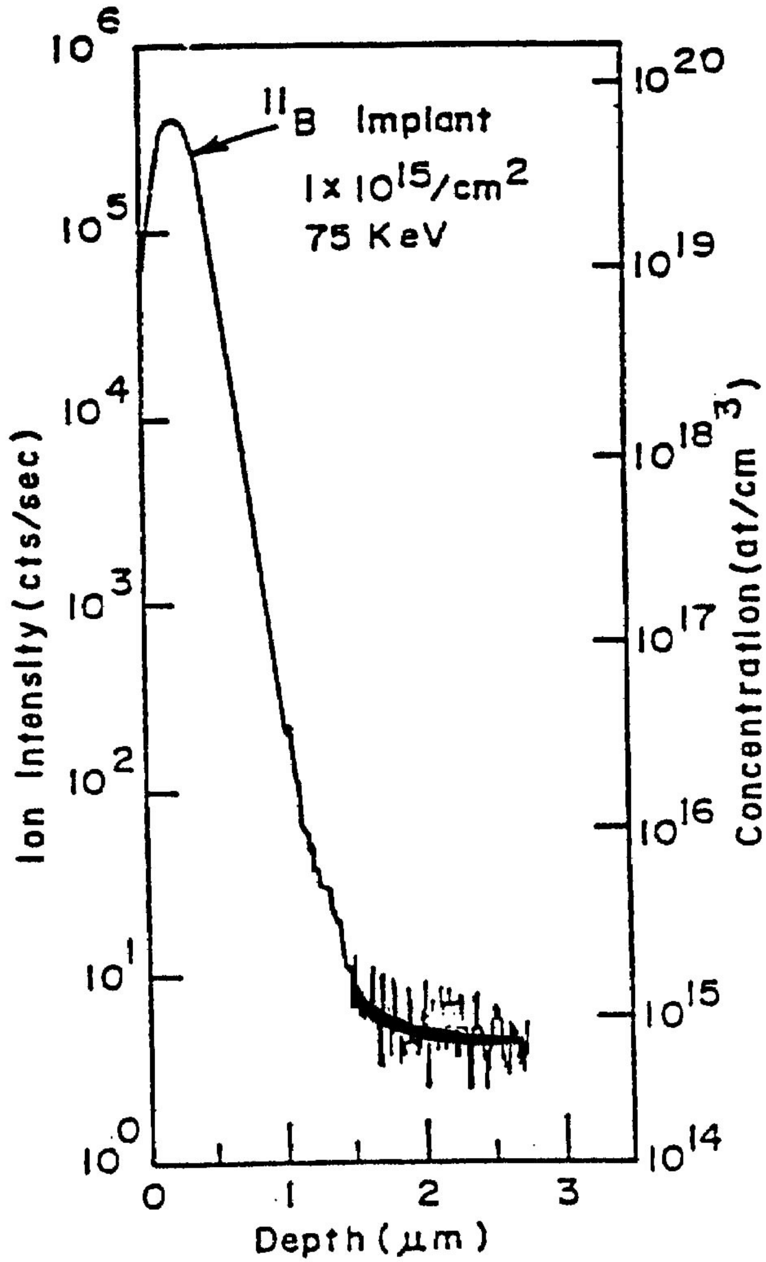


Fig. 4b Normalized negative secondary ion yields under Cs^+ bombardment (*Storms* et al. 1977)



Sensitivity

- Some important aspects of SIMS for surface analysis are shown below for a depth profile of boron in silicon
  - The dynamic range of detectability is about 5 orders of magnitude
  - The detection limit is ~ 5 ppb
  - With precautions, the ion intensity can be made proportional to the concentration over the whole dynamic range.

Profiling

- It is not possible to extract meaningful depth profiling information unless the primary ion intensity is constant and uniform over the detection area

Profiling

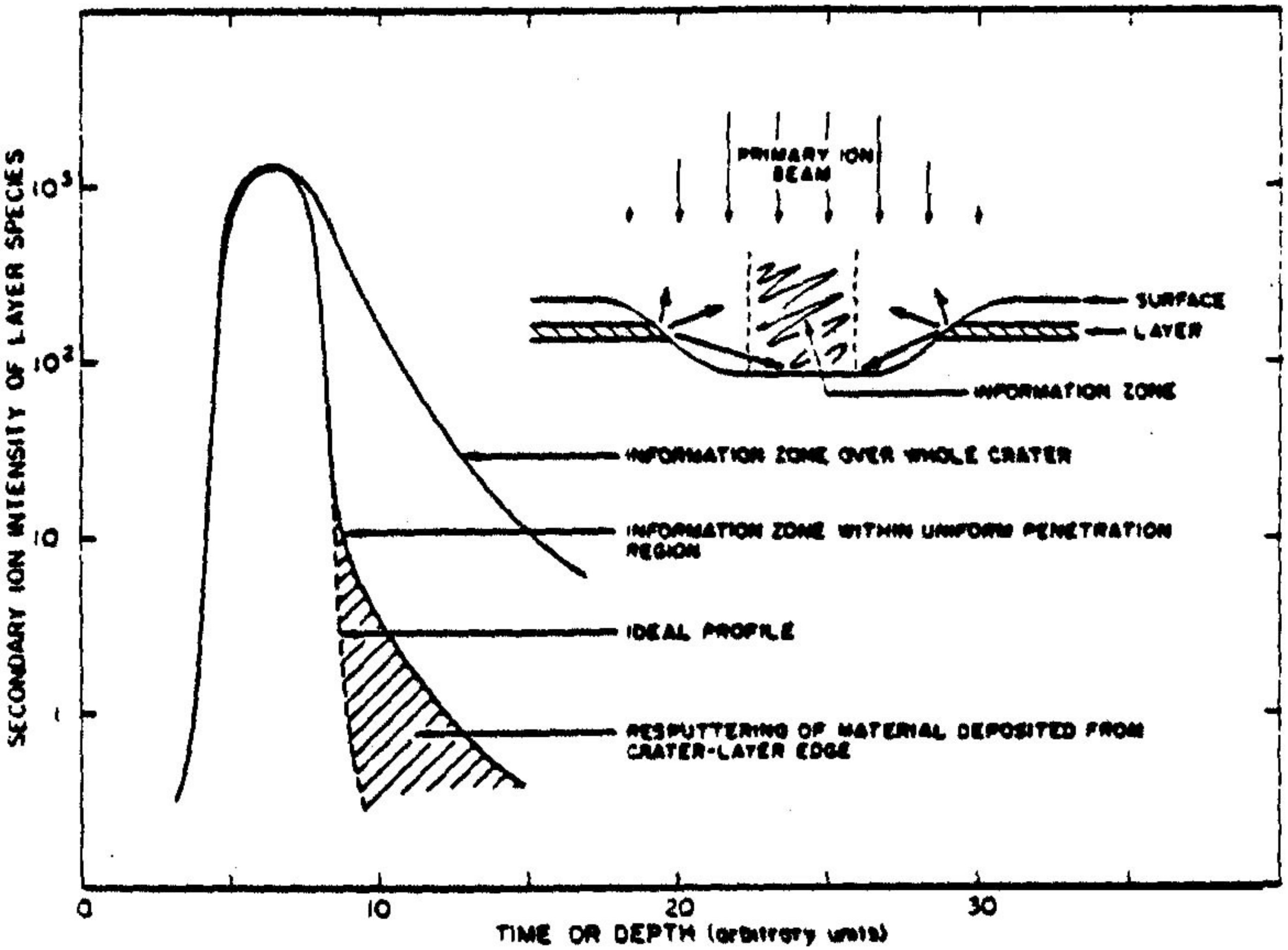


Fig. 20. Illustration of a concentration profile of a subsurface layer and various instrumental factors that produce a distorted profile of the true distribution.

Improving Depth Resolution

- Extreme measures must be taken if the optimal depth resolution is to be achieved
  - Rasterring a finely focussed primary ion beam over the sample surface and gating the secondary ion detector so that ions are only detected when the primary beam is over the selected central area can improve depth resolution

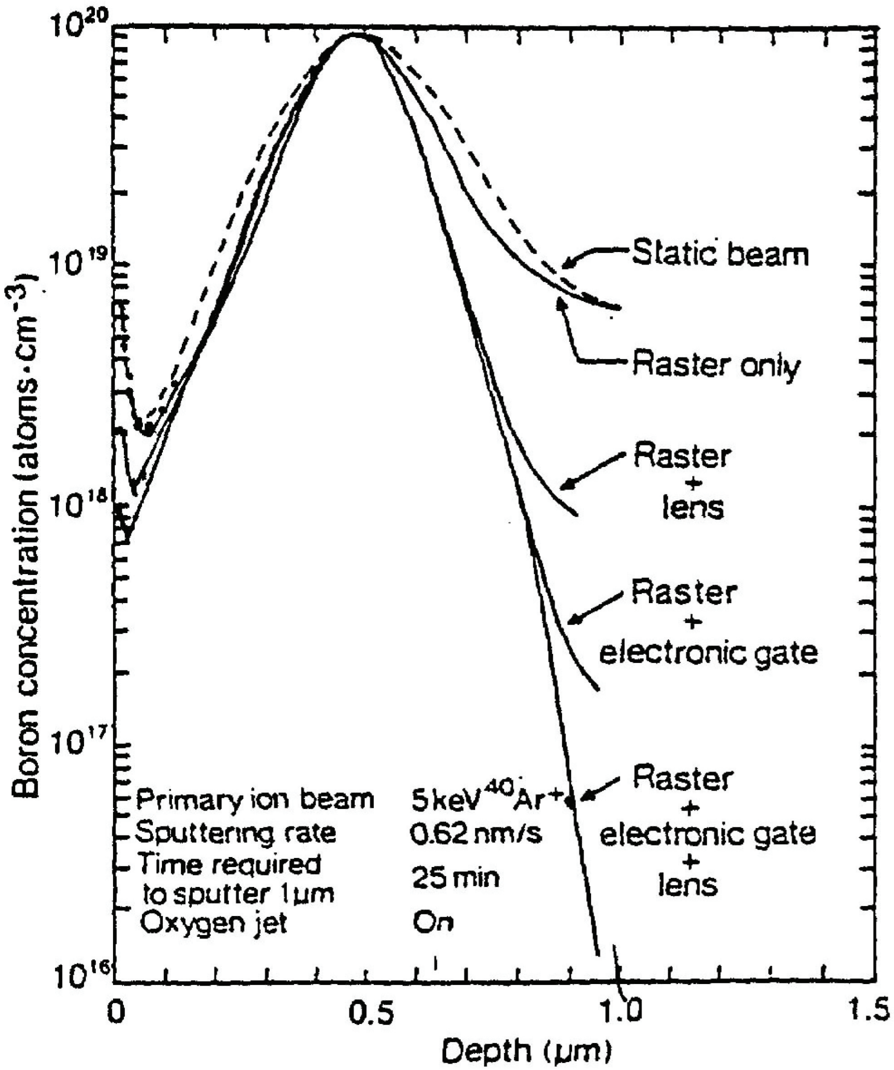


Fig. 2 Depth profiles of 150 keV boron implanted into silicon showing the improvements of depth resolution and background suppression by the use of increasingly sophisticated primary beam techniques and secondary ion optics. (From *Magee* et al. 1978).

Improving Depth Resolution

ISOTOPES

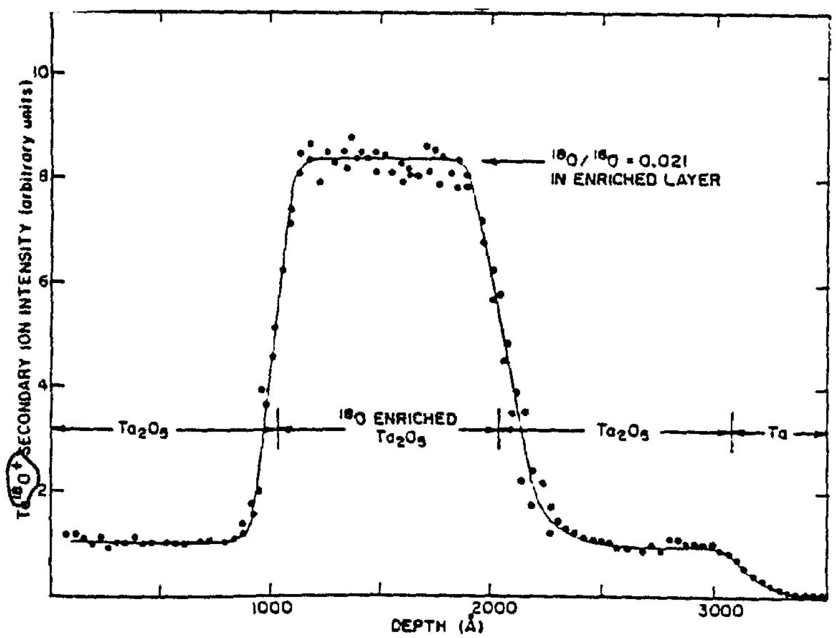
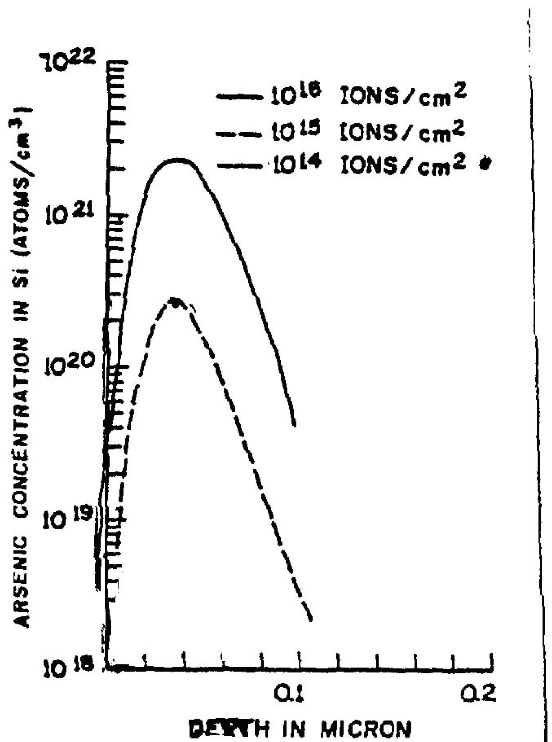


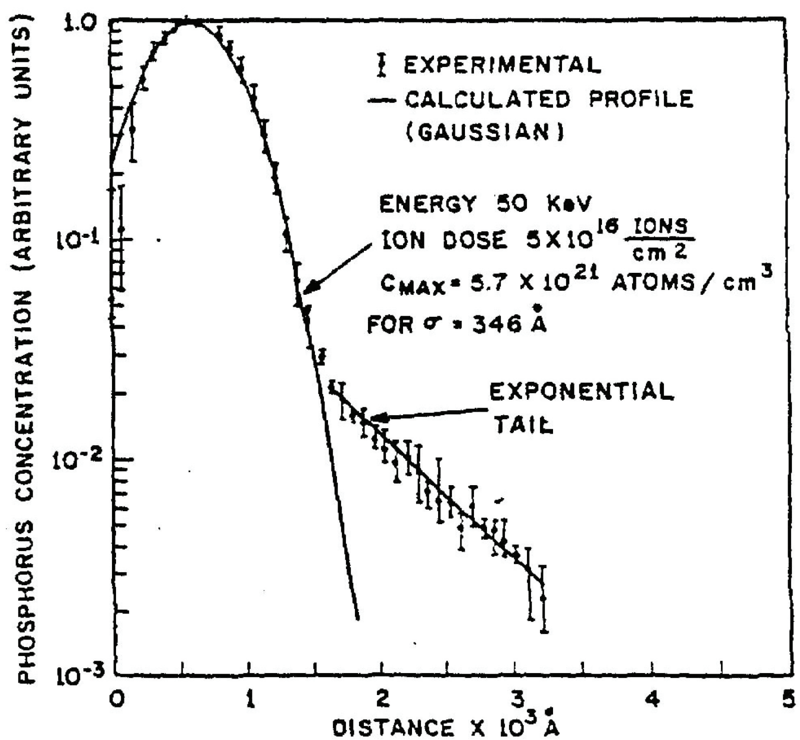
Fig. 25. The depth concentration profile of ^{18}O in a Ta_2O_5 sample containing a layer enriched in ^{18}O. The profile was performed with an ARL ion microprobe using 8.5 keV N_2^+ and the monitor of the ^{18}O concentration was Ta $^{18}O^+$. The ^{18}O is ~2% of the oxygen in the enriched layer. The Ta $^{18}O^+$ signal preceding and following the enriched layer peak is due to the ^{18}O level in normal oxygen. (From McHugh [54].)

- SIMS is one of the few techniques that can detect Isotopes.
  - The figure shows a Ta surface depth profile by SIMS. The sample was anodized in 3 stages. Each contributing 1000 Å to the total oxide thickness. The middle layer used an electrolyte enriched in O18. Clearly, a difference was observed in O18 concentration in the middle layer.

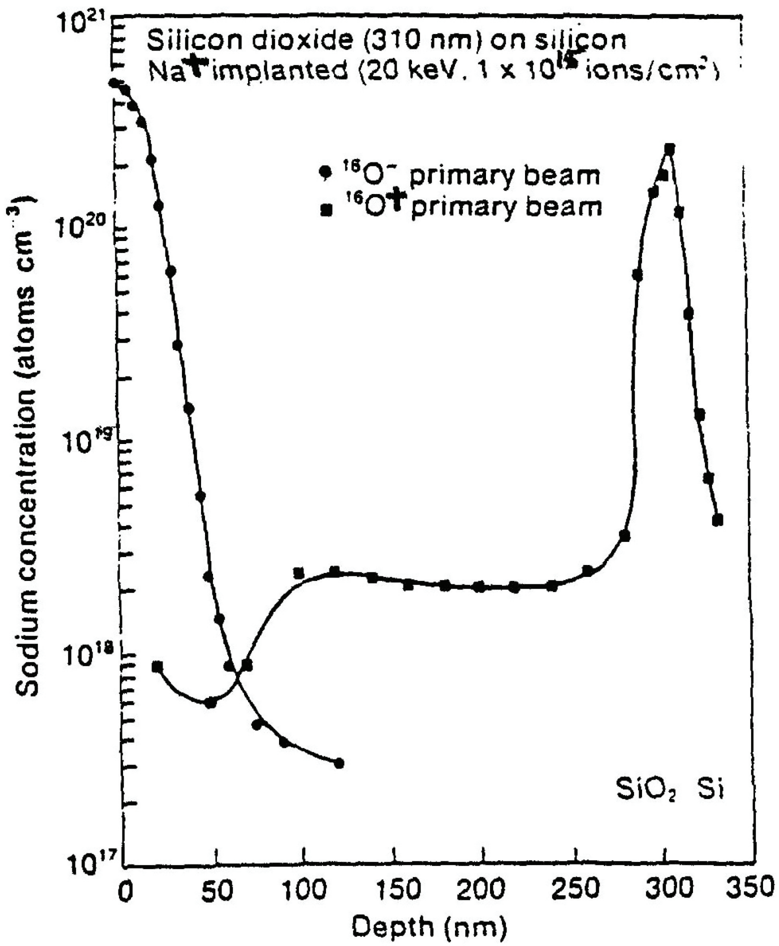
Typical SIMS Profiles

- Ion intensity is proportional to the doping concentration
- Left Right
- As implanted into Si P ion implanted in Si





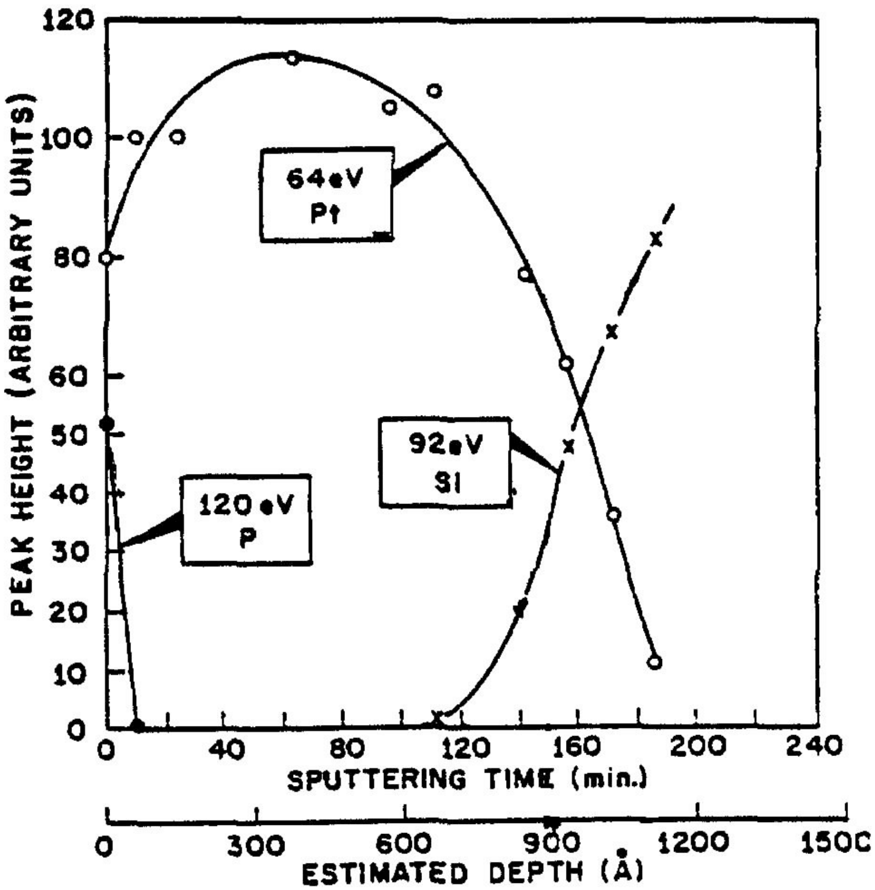
Artifacts



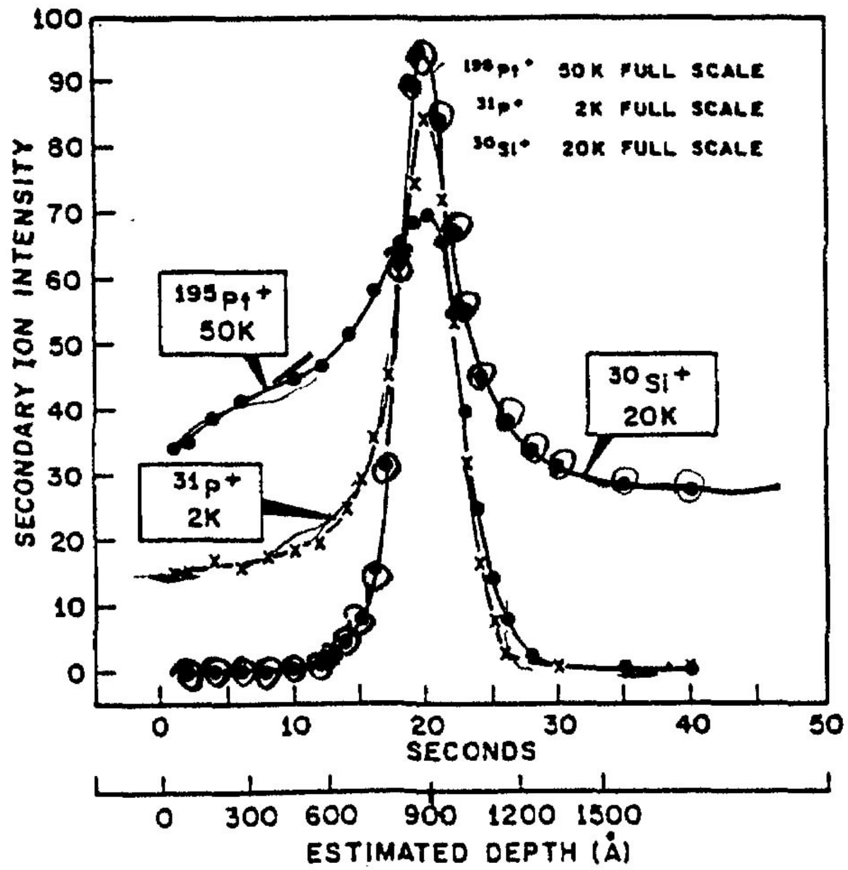
- An example of a large experimental artifact in SIMS depth profiling
  - Charged primary beam causes surface charging in insulators.
  - Na migration due to ion beam charging is shown here for an SiO_2 surface.
  - When O^+ is used as a primary ion beam, the Na will migrate away from the surface to the SiO_2-Si interface. The opposite occurs, (Na segregates to the surface) when O^- is used as the primary ion beam.

Auger versus SIMS Depth Profiles

Auger Profile



SIMS Profile



Auger and SIMS profiles of CVD Pt on Si as deposited at 225C.
SIMS profile taken with oxygen primary ions at 4.5 keV.

SIMS Depth Profiling Summary

- Depth Resolution: given by atomic mixing range and flatness of crater within the acceptance area of the detection system
- Dynamic Range: mainly given by the flatness of the sputtered area, neutral beam effects (neutrals in primary beam), contamination effects, redeposition of sputtered materials
- Sensitivity: mainly given by ion yield of the examined elements and the sputtered area

SNMS and TOF SIMS
Experimental Apparatus

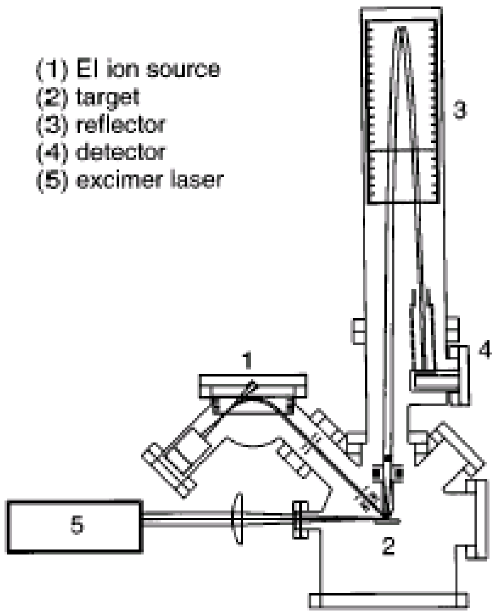


FIG. 1. Scheme of the time-of-flight mass spectrometer.

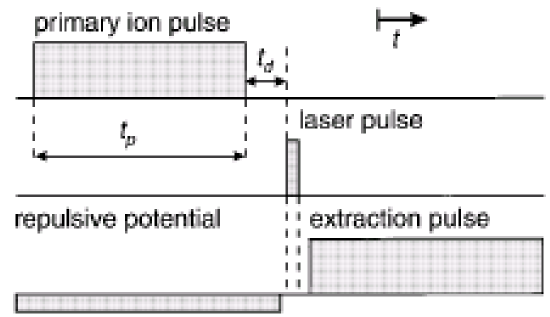


FIG. 2. Timing diagram of one acquisition cycle in Laser-SNMS.

Pulsed ion beam used to generate signal
Static ion beam can be used for sputtering
Timing critical for mass resolution
SNMS uses laser to ionize neutrals
Pulsed voltages remove ions in SNMS

Improving Matrix Effects in SIMS

Oxygen dosing improves yield and reduces surface matrix effect

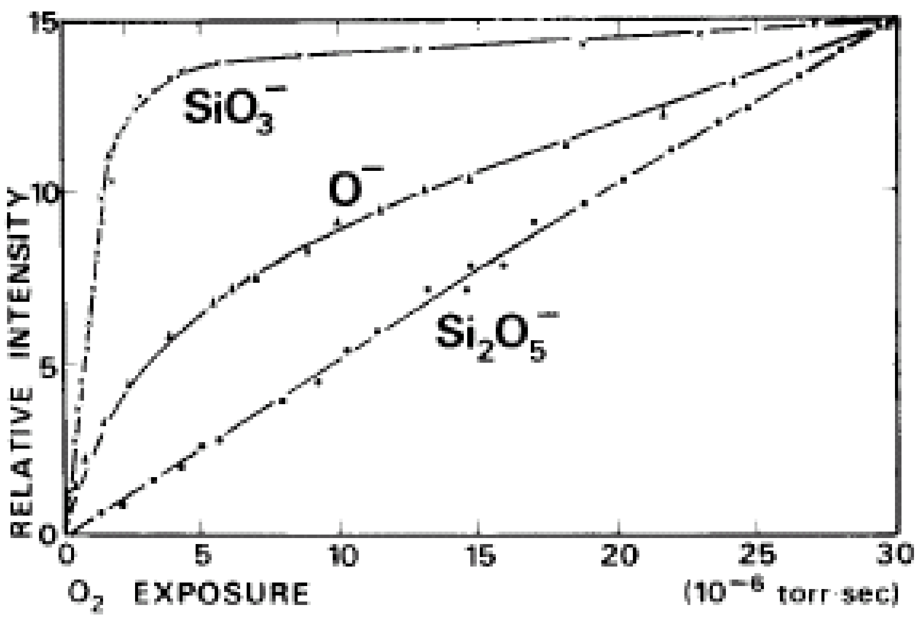


FIG. 3. Increase of secondary ion intensities during oxygen exposure of a Si (111) surface. Total primary ion flux during the complete measurement: 10^{-6} A · s · cm^{-2} (Ref. 8).

Detection Limits for Laser SNMS

TABLE II. Laser-SNMS: Relative sensitivity factors and detection limits for metals on Si wafer surfaces. Detection limits may originate from different factors (see Sec. V B 1).

	Relative sensitivity factor $S(\mathrm{Me}, \Sigma \mathrm{Si})$		Detection limits in cm^{-2}		
Element	193 nm	248 nm	193 nm	248 nm	limited by
Al	0.9	0.9	8×10^{9}	3×10^{10}	useful yield
Ti	1.9	9	5×10^{9}	5×10^{9}	mass interference
V	2.1	42	3×10^{8}	3×10^{8}	data rates
Cr	2.9	28	3×10^{9}	3×10^{9}	mass interference
Fe	1.6	31	5×10^{9}	5×10^{9}	mass interference
Co	1.1	6.9	5×10^{8}	5×10^{8}	data rates
Ni	0.9	14	1×10^{9}	1×10^{9}	isotopy, data rates
Cu	1.2	24	5×10^{9}	5×10^{9}	mass interference
Ga	4.4	0.4	5×10^{8}	8×10^{9}	isotopy, data rates
As	1.9	10	3×10^{8}	3×10^{8}	data rates
Mo	1.8	32	3×10^{8}	3×10^{8}	isotopy, data rates
W	5.1	39	5×10^{8}	5×10^{8}	isotopy, data rates

Detection Limits for TOF SIMS

TABLE III. TOF-SIMS: Relative sensitivity factors and detection limits for metals on Si wafer surfaces (30 min UV/ozone treated). Detection limits may originate from different factors (see Sec. V B 1).

Element	Relative sensitivity factor $S(\mathrm{Me},\Sigma\mathrm{Si})$	Detection limits in cm^{-2}	Limited by
Al	1.6	5×10^{8}	background
Ti	0.9	3×10^{9}	background
V	1.1	2×10^{9}	useful yield
Cr	1.5	1×10^{9}	useful yield
Fe	1	3×10^{9}	useful yield
Co	0.5	2×10^{9}	useful yield
Ni	0.4	4×10^{9}	useful yield, isotopy
Cu	0.5	5×10^{9}	useful yield, isotopy
Ga	1.8	2×10^{9}	useful yield, isotopy
As	0.1	2×10^{10}	useful yield
Mo	0.2	3×10^{10}	useful yield, isotopy
W	···	$>1\times10^{12}$	useful yield, isotopy

Note use of UV/ozone treatment prior to measurement