

Secondary Ion Mass Spectroscopy

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General Uses

- Surface compositional analysis with approximately 5- to 10-nm depth resolution
- In-depth concentration profiling
- Trace element analysis at the parts per million to parts per trillion range
- Isotope abundances
- Hydrogen concentration analysis
- Spatial distribution of elemental species by ion imaging

Examples of Applications

- Identification of inorganic or organic surface layers on metals, glasses, ceramics, thin films, or powders
- In-depth composition profiles of oxide surface layers, corrosion films, leached layers, and diffusion profiles
- In-depth concentration profiles of low-level dopants diffused or ion implanted in semiconductor materials
- Hydrogen concentration and in-depth profiles in embrittled metal alloys, vapor-deposited thin films, hydrated glasses, and minerals
- Quantitative analysis of trace elements in solids
- Isotopic abundances in geological, lunar and extra-terrestrial samples
- Tracer studies (for example, diffusion and oxidation) using isotope-enriched source materials
- Phase distribution in geologic minerals, multiphase ceramics, and metals
- Second-phase distribution due to grain-boundary segregation, internal oxidation, or precipitation

Samples

- *Form:* Crystalline or non-crystalline solids, solids with modified surfaces, or substrates with deposited thin films or coatings; flat, smooth surfaces are desired; powders must be pressed into a soft metal foil, such as indium or compacted into a pellet
- *Size:* Variable and depends on the machine, but typically about a cm cube.
- *Preparation:* None for surface or in-depth analysis; polishing as needed for microstructural or trace element analysis

Limitations

- Analysis is destructive
- Qualitative and quantitative analyses are complicated by wide variation in detection sensitivity from element to element and from sample matrix to sample matrix
- The quality of the analysis {precision, accuracy, sensitivity, and so on} is a strong function of the instrument design and the operating parameters for each analysis

Estimated Analysis Time

One to a few hours per sample depending on sample and the analysis needed

Capabilities of Related Techniques

- *XPS and Auger electron spectroscopy:* Qualitative and quantitative elemental surface as well as in-depth analysis is straightforward, but the detection sensitivity is limited to > 1 000 ppm; microchemical analysis with spatial resolution to <100 nm
- *Rutherford backscattering spectroscopy:* Nondestructive elemental analysis; quantitative determination of film thickness and stoichiometry
- *Electron microprobe analysis:* Quantitative elemental analysis and imaging only with depth resolution of that of an electron probe.

Introduction:

Secondary Ion mass Spectroscopy (SIMS), as the name suggests, involves characterizing metallic and other materials through the spectroscopic analysis of secondary ions emanating from the surface of the material to be characterized by the impact of the high energy primary ions. The primary ion source including the choice of its gun, voltage and current can be selected and used depending on the purpose of the analysis. In most instruments more than one primary ion gun is lined up to the sample stage and can be activated with selected accelerating parameters (voltage and beam intensity). The impingement of primary ions on to the sample surface generates positive, negative or neutral ions, electrons, atoms and atomic clusters. Majority of these sample fragments being neutral, could not be utilized as such fragments cannot be manipulated through the use of electromagnetic or electrostatic lenses. Secondary ions that are positively or negatively charged possess large variation in velocity, charge, and mass. These ionic fragments eventually travel through a system of several lenses in very high vacuum to reach detector/counter. Relative amounts of alloying elements or impurities in an alloy can be calculated from the counts of related ions accumulated in the detector/counter.

Sir J.J. Thompson, well known physicist and Nobel laureate, first observed the release of positive ions and neutral atoms from a surface bombarded by charged ions (Ref.1, page 5). While this happened in 1910, during 1936 – 1937 time frame, F. L. Arnot and J. C. Milligan investigated the secondary ion yield and energy distribution of negative ions by positive ions with the help of a magnetic field and may be credited as the forerunners (Ref. 1, page 5) of the SIMS instrument. In 1949 Richard F. Herzog and F. Viehboeck develop the instrument that generated an ion source from electron impact. Some ten years later, a complete SIMS was constructed by R. E. Honig, R. C. Bradley, H. E. Beske, and H. W. Warner (Ref. 1 page 5). With the development of effective vacuum systems, rapid developments took place in instrument developments and SIMS applications. First commercial SIMS was built by Herzog, Liebl and co-workers at GCA Corporation of Bedford, Massachusetts. Beske and Warner have shown its application in semiconductor technology which is the most important analytical field for various types of SIMS instruments (Ref. 1, page 5).

SIMS technique has developed exponentially in recent years which is largely due to the advent of semiconductor technology. As the electronic devices get smaller and smaller, chemical analysis in micro scale has become increasingly important and SIMS plays a huge role in this development. Microchips are made from single crystals of silicon, GaAs, InP or from several other base materials made by Czochralski or Bridgeman methods. Various insulators and conductors are then deposited on to these crystals. The deposition can be made by ion implantation or by diffusional processes. Areas are masked where depositions are not needed. Dopants are also added to the required levels by these processes. SIMS is extensively used to characterize these materials for impurity as well as dopant level analysis. Depth profiling employed when various deposited layers need to be characterized for depth, composition and dopant levels.

There are two types of SIMS depending on the type of instruments and their analysis rate: Static and Dynamic. A static SIMS erodes only the surface at a rate that removes material only less than 1.0% of the surface. It also shows higher mass molecular species in the spectrum. On the other hand, a dynamic SIMS erodes more material from the surface as well as from inside of the specimen producing large volumes of secondary ions. This helps perform bulk analysis of the material and covers ion intensities in a broad range covering seven orders of magnitude. This is a tremendous advantage compared to other analytical techniques such as Energy Dispersive X-ray (EDS), Auger and x-ray photo-electron analysis (XPS) which normally show limits of about 0.1%. A common data obtained from a SIMS instrument is mass spectra

which displays intensity in seven orders for various masses. Impurities at levels of ppb can be measured by a dynamic SIMS.

The simplistic method described above can not only be used for elemental characterization of bulk alloys but also can be used to acquire a variety of information of the surface as well as near surface of an analytical sample depending on the analytical requirement and the instrument used. SIMS is considered as a destructive method as the primary impinging ions leave a crater behind on the sample surface by removing the material for analysis, part of the material removed end up at the detector giving needed information. There are three types of SIMS each designed to provide specific analytical information on materials to be analyzed. The three types are: (a) Quadruple Mass Spectrometer, (b) Magnetic Sector machines, and (c) Time-of-flight (TOF) spectrometers. Quadruple spectrometers are simplest and are extensively used in Residual Gas Analyzers (RGA). When employed in analyzing solids, they generally provide information of the surface of about 5 nm deep. They come under static SIMS due to their low erosion rates. Magnetic Sector SIMS are more sophisticated and are designed to erode more materials from the sample and are designed to perform depth profiles in electronic components. They come under dynamic SIMS. They are highly sensitive, designed to measure levels of dopants and contaminants at levels of ppm, even ppb for some elements. They have high mass resolutions to resolve interferences in a SIMS spectrum. TOF SIMS are still in the process of development with as good a resolution as the magnetic sector SIMS and with many advantages but are considered as static SIMS due to their low erosion rates. They are extensively used to characterize polymeric materials.

SIMS instrument provides a spectrum of a large number of peaks even from a piece of pure metal. This is because the primary beam reacts with the metal to generate complex ionic species. For example, a piece of Al will show ions of Al^+ , Al^{2+} , AlO^+ , Al_2O^+ etc. when an oxygen primary beam is used. Therefore, interference is an inherent part of SIMS analysis and high-resolution instruments are required for the separation of the interfering species to isolate the peaks of interest. Multiple peaks generated from the fragmentation of a matrix can be used in identifying a compound or a polymer wherein the spectrum reflects how the matrix is broken by the impinging primary ion. TOF SIMS is extensively used in characterizing polymers who otherwise would simply indicate the presence of carbon and oxygen when used by conventional microanalytical techniques such as the Energy Dispersive X-ray analysis (EDS) using an electron microscope. Other unique utilization of SIMS analysis is the quantitative and localized measurement of light elements such as H, Li and Be in small amounts that are otherwise not possible in conventional techniques. Isotopic ratios of elements are yet another application of the SIMS instruments as an accurate estimation of such ratios can be related to the origin (terrestrial or otherwise) of these elements.

The modern SIMS is intricate and the analysis of the spectrum is difficult but its capability is so unique that its benefits outweighs the difficulties associated with these interpretations and expensive operations of these sophisticated machines. Instrumental sophistications are needed to counteract the inherent limitations such as the mass and ionic interferences, large variations in secondary ion yield for different elements and matrices, flat surfaces are needed for analysis. The following are the unique capabilities of the SIMS instruments.

- All elements are detectable and the quantities can be measured with the use of standards and Relative Sensitive Factors (RSFs)
- Detection limits are in the order of parts per million (ppm) and for some elements parts per billion (ppb), very useful for impurity and dopant analysis
- Relative isotopic analysis can be made
- Polymers can be analyzed using relative molecular ion abundances

- Spatial resolutions are high, suitable for microelectronics characterization

General Principles

Fig. 1 (Ref.2) is a schematic illustration if the SIMS process. It consists of two steps: (a)incidence of the primary beam and (b) collection and processing of the species generated by the impact of the primary beam. As mentioned earlier, the bombardment of a solid surface with a flux of energetic particles in the primary beam can cause the ejection of electrons, monoatomic species, and clusters. The species thus generated may have one or more electronic charge or neutral. This process is termed as sputtering (Ref. 3), and in a more macroscopic sense, it causes erosion or etching of the solid often creating a crater on the impinging solid surface with a geometry consistent with the scanning pattern of the primary beam. The incident projectiles are often charged ions, as they facilitate production of an intense flux of focused energetic particles into a directed primary beam. How ever, in principle, sputtering (and secondary ion emission) will also occur under both charged or neutral beam bombardment. Secondary ion mass spectroscopy is typically based on ion beam sputtering of the sample surface, although new approaches to SIMS based on Fast Ion Bombardment (FIB) are constantly being developed.

The interaction between the energetic primary ions and the solid surface is complex. At incident ion energies from 1 to 20 keV, the most important interaction is momentum transfer from the incident ion to the target atoms. This occurs because the primary ion penetrates the solid surface, travels some distance (termed as the mean free path), then collides with a target atom. Figure 1 shows schematically that this collision displaces the target atom from its lattice site, where it collides with a neighboring atom that in tum collides with its neighbor. This succession of binary collisions, termed a collision cascade, continues until the energy transfer is insufficient to displace electrons or the target atoms from their lattice positions.

The ejection of target atoms and atomic clusters occurs because much of the momentum transfer is redirected toward the surface by the recoil of the target atoms within the collision cascade. Because the lifetime of the collision cascade produced by a single primary ion is much smaller than the frequency of primary ion impingements (even at the highest primary ion beam cur rent densities), this process can be viewed as an isolated, albeit dynamic, event. The ejection of target species due to a single binary collision between the primary ion and a surface atom occurs infrequently.

The primary ion undergoes a continuous energy loss due to momentum transfer, and to the electronic excitation of target atoms. Thus, the primary ion is eventually implanted tens to hundreds of angstroms below the surface. In general, then, the ion bombardment of a solid surface leads not only to sputtering, but also to electronic excitation, ion implantation, and lattice damage. The effects of ion implantation and electronic excitation on the charge of the sputtered species are discussed in the section "Secondary Ion Emission" in this article.

The sputtering yield, S , is the average number of species sputtered per incident primary ion. This number depends on the target material and on the nature, energy, and angle of incidence of the primary ion beam. The sputtering yield is directly proportional to the stopping power of the target (because this determines the extent of momentum transfer near the surface), and it is inversely proportional to the binding energy of the surface atoms. Therefore, the sputtering yield also exhibits a dependence upon the crystallographic orientation of the material being sputtered. In most SIMS instruments, Cs^+ , O_2^+ , O^- , Ga^+ and Ar^+ primary ions are used in the energy range

from 2 to 20 keV at angles of incidence between 45° and 90°. Under these conditions, the sputtering yields for most materials range from 1 to 20. Information on the effects of the primary ion beam and the target material on sputtering yields is provided in Ref 4 (Sec. 1.2).

Selective sputtering, or preferential sputtering can occur in multi-component, multi-phase, or polycrystalline materials. Thus, it is possible for the alloy surface to get modified during sputtering, where, the species with the lowest sputtering yield become enriched in the outer most monolayer, while the species with the highest yield are depleted. In the case of multiphase materials, those phases with the higher yield will be preferentially etched. This alters the phase composition at the surface, and introduces microtopography as well as roughness. For polycrystalline materials, the variation in sputter yield with crystallographic orientation can also lead to the generation of surface roughness during sputtering. All of these effects can influence the quality and interpretation of a SIMS analysis.

Secondary Ions and Species (Ref.3):

The species ejected from a sample surface due to the primary ion impact could be monoatomic, polyatomic, multi-component atomic clusters, or even electrons. The ions could be singly charged or multiply charged with either positive or negative charges or could simply be neutrals. There may be one or few are of interest in an analysis. Electrons emitted are gathered for creating a secondary electron images of the scanned primary ion areas. Whether it is one or multiple ions are of interest, the secondary ion yield is an important parameter because it determines the relative intensities of the various SIMS signals. The secondary ion yield depends on the same factors as the sputter yield, but it also depends on the ionization probability. Although a complete and unbiased theory of secondary ion emission, particularly the ionization probability, has not yet been reported, most models emphasize the importance of chemical and electronic effects. Accordingly, the presence of reactive species at the surface is believed to modify the work function, the electronic structure, and the chemical bonding, and all of these can influence the probability that a sputtered species will be ejected in a neutral or charged state. The secondary ion yield, which determines the measured SIMS signal, is a very sensitive function of the chemical and electronic properties of the surface under bombardment. Thus, it exhibits a dependence upon the element, its matrix, and the bombarding species being implanted in the surface during the analysis; moreover, it is influenced by residual gas pressure and composition during the analysis because adsorbates can modify the chemical and electronic state of the surface monolayer.

The matrix dependence of the secondary ion yield is the characteristic of secondary ion emission that has received perhaps the most attention. In the case of inert primary beam bombardment, for example, Ar+ on aluminum versus aluminum oxide, the positive metal ion yield is recognized to be three to four orders of magnitude higher in metal oxides than in their pure metal counterparts. This ion yield dependence is due to the ionization probability, which is approximately 100 times greater for Al₂O₃ than for aluminum metal, not to the sputtering yield, which is approximately two times greater for the metal than for the metal oxide.

Similarly, Ar+ bombardment of a pure aluminum metal sample is known to produce a larger Al+ signal in a dirty vacuum or in the presence of an intentional oxygen leak (capability available in some machines) than in a nonreactive UHV environment. Therefore, most modern approaches to SIMS analysis, at least when quantitative elemental analysis is of interest, use reactive primary ion beams rather than inert ion beams; an oxygen beam (O₂⁺ or O⁻) or a cesium (Cs+) beam is typically used. Thus, the surface is always saturated with a reactive species (due to the primary ion implantation) that enhances the ion yield and makes the elemental analysis less sensitive to matrix effects and/or to the residual vacuum environment during analysis.

Crystallographic orientation further compounds the matrix dependence of the secondary ion

yield. This is due primarily to the difference in electronic properties (for example, work function or band structure) from one crystal face to another and to the difference in adsorptivity or implantation range from one face to another (and much less so due to variation in sputtering yield). In the case of polycrystalline and/or multiphase materials, the emission intensity can vary considerably from one grain to another. This can be an important source of contrast in secondary ion emission imaging of polycrystalline materials.

Regarding the energy and angular distribution of the ejected species, the secondary ions are ejected with a wide distribution of energies. The distribution is usually peaked in the range from 1 to 10 eV in energy, but depending on the identity, mass, and charge of the particular secondary ion, the form of the distribution will vary. In general, the monatomic species (for example, B⁺ or Si⁺) have the widest distribution, often extending to 300 eV under typical conditions; the molecular species (such as O₂⁻ or Al₂O⁺) cut off at lower energies. The energy distribution of the ejected secondary ions is relevant to the design of the SIMS instrument (because it must be energy filtered before mass analysis) and to the mode of operation because ions can often be resolved on the basis of energy.

Systems and Equipment:

There are three types of SIMS instruments prevail today. They are: (a) Quadruple SIMS, (b) magnetic Sector SIMS and the (c) Time-of-flight (TOF) SIMS. While the instrument could be very sophisticated, it could be presented in a simple form in block diagram as shown in Fig.2 (Ref.4 page 1-8). As Fig.2 indicates, the instrument needs to have a primary ion source; the ejected secondary ions pass through an energy analyzer and mass spectrometer. The charged ions of interest, after their separation from the other ions by virtue of their mass and velocity, enter into a detector or counter where they are used for displaying either a mass spectrum, a depth profile of the sample, or a spatial image of the location of the different ions on the sample surface. High vacuum levels, of the order of 1.0 e⁻⁹ torr or better is maintained throughout the path of the ions. This is accomplished by using turbo, ion, or cryogenic vacuum pumps all being backed by one or more rotary mechanical pumps. An electron gun or charge neutralizer is also an essential part of the SIMS instrumentation since the location being analyzed ejects a number of charged ions leading to localized charging. Unless the charge is neutralized for insulating samples, secondary ion energies will be affected.

Quadruple SIMS:

A quadruple SIMS is rather a relatively simple instrument. The instrument consists of one or more primary ion source and an electron gun for charge neutralization. See Fig.3 (Ref.5). The ejected secondary ions travel along the length of strategically placed four rods and are detected at the other end of the rods. The rods are charged with alternating charges and the charged ions reached the detectors at the end of the rods based on their masses. The quadruple SIMS are relatively inexpensive and are used mostly to identify materials and alloys with light elements. They have wide acceptance angles and can rapidly sweep through masses. Their disadvantages include low mass resolution of the order of 300 m/Δm, where m is the atomic mass, and low ion transmission, less than 0.1%, through the rods. Low resolution does not allow accurate count of the intensity of the mass of interest, the counts being higher than the actual being inflated by the interfering mass species. Low secondary ion transmission warrants higher levels of solutes or alloying elements in an alloy to be detected by the instrument, raising its detection limit. Quadruple SIMS generally have either an argon or a cesium primary ion gun or both.

Magnetic Sector SIMS:

The magnetic sector instruments are complex, expensive and are most useful of all SIMS instruments. Magnetic sector SIMS will be discussed in greater details in this chapter. As the name suggests, the secondary ions are separated by an electro-magnet and the whole spectrum of secondary ions could be focused on to the detector by varying the magnetic field strength. Fig.4 (Ref. Cameca website) illustrates a schematic layout of a magnetic sector SIMS. This represents schematic for a IMS-1270 machine designed by Cameca Instruments (now a part of AMETEK Materials Analysis Division). The instrument comes with an oxygen primary source, an additional Cs source can also be added to enhance secondary ion yield. The oxygen primary source is known as the Duoplasmatron that can generate O_2^+ and O^- ions. The source can also use Ar gas to generate Ar^+ ions. A schematic of Duoplasmatron is shown in Fig. 5 (Ref. 6) where a plasma is created between the anode and the cathode through the aid of the coil. A very small amount of oxygen or argon can be introduced to create this plasma. O_2^+ ions are present at the center of the plasma whereas O^- ions are present at the periphery. The Z electrode is utilized to move the location of the plasma to make this selection. The entry gas pressure, positions of electrodes and the voltages need to be adjusted for a stable plasma and a constant beam current.

The design of the Cs source is completely different. Fig. 6 (Ref.5, page 107) shows a schematic of a microbeam Cs source. In this source Cs vapors come from a Cs chromate pellet when the pallet is heated by the reservoir filament and the Cs gas atoms are ionized at the other end of the tube by an ionizer, a tungsten plate heated to 1100° C. The charged Cs^+ ions are then extracted by an electrostatically charged plate and then focused on to a Primary Beam Mass Filter (PBMF). Both the oxygen and the cesium primary ions are filtered by the PBMF by simply deflecting away the unwanted species coming out along with the ions of interest. The unwanted species would be the impurities and the ions of isotopes with different masses. The PBMF is simply a magnet, the strength of which could be adjusted by the magnetizing current to deflect unwanted ionic species.

The mass-filtered primary ion beam now enters a set of lenses to focus the beam and to squeeze it to make it round and fine. In the IMS-6f machine, See Fig. 7 (Ref. 2) for a schematic, the beam is then scanned to obtain scanned ion images or large area analyses. It is important to point out that the ion beam is more difficult to focus than an electron beam due to its large mass and the range of ionic velocities. This makes the image resolution in SIMS inherently poorer than those obtained from an electron microscope. The scanning ion beam hits the sample surface and erodes the surface atoms and molecules for the generation of secondary ions and subsequent analyses. To obtain a fine and circular primary beam the primary column of IMS-6f machine in Fig. 7 has several stigmators, quad lenses as well as slits.

The depth of focus for ion beams is very small and requires flat samples. In case of IMS-6f the sample not only needs to be flat but also at a fixed distance from the scanning and emersion lenses at all locations. A precise and flat sample holder needs to be designed to maintain this equidistant locations for all samples. The sample is made to enter from the bottom of the sample holder with its flat end up and held with the aid of a spring from bottom. The sample holder is isolated from the ground and has a charge of several kilovolts to attract ions with higher velocities.

The ejected secondary ions not only come out at different angles to the sample normal, they also have different velocities. That means that Al^+ ions coming from a pure Al sample have a wide range of velocities. The IMS-6f machine attempts to collect ions with different velocities and integrate them on to the total count of a mass of 27 amu (atomic mass unit) for Al^+ ions. Fig.7 shows a detailed schematic view of the secondary section of the instrument in blue color. In the electrostatic sector of the machine (E.S.A. in Fig. 7), the various ions with different velocities are focused on to an image plane (energy slit) which can be opened or closed to allow only ions of smaller or larger range of energies to the magnetic section of the instrument. As the ions pass through the spectrometer, the magnet separates out ions of different masses and focusses them on to either an electron multiplier or to a channel plate serving as detectors. The primary beam could be used as a static beam or it could be scanned. With the static beam, the beam could widen to fall over a wide area and the secondary ions ejected form images of various species in the path of the beam, image intensity being proportional to their spatial

concentrations on the channel plate. This arrangement is called as the ion microscope. In the scanned mode, as the fine primary beam hits the sample surface at scanned locations, ions of various masses are counted by the electron multiplier point by point which eventually integrates an ionic image of the sample.

Time-of-Flight (TOF) SIMS:

TOF SIMS utilizes pulsed primary ion beam mostly Cs or Ga (other primary ion sources such as Bi, Ar, Xe, SF₅, C₆₀ are also available) to remove material only from the very surface to analyze the chemistry and characterize the surface contaminants. Species are removed from the atomic monolayer of the surface by a ‘soft’ primary ion bombardment and accelerate through a ‘flight tube’, and the masses of the species are determined by the time taken for them to reach the detector from the pulsing time from the time pulse is initiated. The heavier species take longer to reach the detector. Since longer the flight path longer is the detectable time difference between different masses (hence, better resolution), the instruments are designed either with a circular path (TRIFT by Physical Electronics) or a ‘reflectron’ design by Cameca IonTOF systems to increase the travel path. Schematics of these designs are shown in Fig.8.

TOF SIMS are also known as ‘static’ SIMS whereas the magnetic sector SIMS are known as ‘dynamic’ SIMS due to their low and high sputtering rates respectively. The high sputtering rate of dynamic SIMS breaks the bonds in polymeric materials and changes the structure underneath the sputtered layer. TOF SIMS has a softer impact and analyzes the broken species away from the primary ion impact site. The TOF SIMS has a mass range of 10,000 amu, much higher than other instrument types, which enables TOF SIMS to gather a very wide mass spectrum, and used effectively in characterizing polymeric materials and organic compounds. The merits and limitations of TOF SIMS are as follows:

Merits –

- Surveys of all masses on surfaces including atomic ions, large molecular fragments
- High mass resolution of the order of few thousandth of an amu
- High sensitivity for trace elements of the order of ppm, even of the order of ppb
- Surface analysis of metals as well as non-metals
- Considered as non-destructive when surface analysis is performed
- All species (elements) are analyzed at the same time unlike the magnetic sector SIMS where the magnetic strength is continuously varied to get a mass spectrum

Limitations –

- Large amount of data is generated, each sputtered point generates an entire mass spectrum and takes a significant time to review
- Slow for depth profiling
- Generally, does not produce quantitative data
- Requires a pulsed beam
- There is an image shift when gathering data changes from positive to negative ion data collection mode, exact location for analysis can not be reached in two modes.

Primary Ion Sources:

Ion guns are inherent to the SIMS instruments as they supply the primary ions for the sputtering process. Two types of ion sources, duoplasmatron for oxygen and argon ions and Cs ion sources have already been discussed earlier as they are the most common ion sources. Cluster ion sources have been developed in recent years. Cluster ion sources such as C₆₀ and SF₅ are the common ones. They have softer impact on samples compared to monoatomic ion sources, have. Fig.9 (Ref. 9)

shows a schematic for the cluster ion gun. Older focused ion beam instruments used a liquid-metal ion sources (LMIS) often with gallium. In a gallium LMIS, gallium metal is placed in contact with a tungsten needle and heated gallium wets the tungsten and flows to the tip of the needle where the opposing forces of surface tension and electric field produce the cusp shaped Taylor cone. The tip radius of this cone is ~2 nm. The electric field at this small tip is very high causing ionization and field emission of the gallium atoms. The ions are then accelerated to an energy of 1–50 keV and focused onto the sample with electrostatic lenses. LMIS produces a high current density ion beam with a small energy spread and can deliver a high current density with a fine spot size.

Vacuum Systems:

The capacities of the vacuum systems are such that the vacuum levels at the sample chamber and the secondary ion path is maintained very low to have a long mean free path for the ions generated. Vacuum levels of the order of 1.0×10^{-9} or 1.0×10^{-10} torr is obtained using ion, cryogenic or turbo pumps of adequate capacity attached to the various segments of the SIMS instrument. These pumps are most efficient at high vacuum level and therefore are backed by a conventional mechanical rotary or dry pump generating a vacuum level of around 1.0×10^{-3} millibar. In most instruments, there is also a sample preparation chamber prior to the analytical chamber to introduce the sample from air and to expel volatiles. The vacuum level in this chamber is maintained at a lower level (around 1.0×10^{-6} torr). Samples with holders are introduced to the analytical chamber after they spend enough time to remove most volatiles in this sample preparation chamber.

Charge neutralizers:

When secondary ions leave the surface of a sample, the surface is electrically charged either with a positive or a negative charge depending on the polarity of the secondary ion leaving the surface. In conductive samples this polarity is neutralized by electrons coming from ground (provided there is a good connection to ground). For non-conducting samples, and for sample holders that are charged to several kilovolts, the sample charging needs to be compensated external electron sources known as Charge Neutralizers. The electronic charge on the sample surface attracts the ejected ions reducing its kinetic energy. Erroneously, due to the reduction in kinetic energy, these ions appear to be coming from a different location and lead to a distorted energy distribution. A charge-neutralizer attempts to compensate this effect by simply spraying low energy electrons onto the sample surface. Thus, a charge neutralizer is nothing but an electron gun. It may appear simple, but the ion interaction spot has varying intensity needing more electron at the center of the spot for compensation which is not easily done. Modern SIMS machines have complex charge neutralizers to counteract this effect. Schematic of one such patented (by Physical Electronics) dual-beam charge neutralizer is shown in Fig 10 (Ref. 9).

Modes of Operations:

Magnetic sector SIMS have several modes of operation mainly to obtain desired results from the analysis. The primary beam in IMS-6f needs to be manipulated to generate a fine beam for possible better lateral resolution. This is accomplished by adjusting the four primary column lenses, for their size, astigmatism and focus. The image quality and mass resolution is further improved by adjusting energy, entrance, and exit slits along with the manipulation of contrast aperture and spectrometer and projector lenses.

The mode changes for the magnetic sector SIMS such as IMS-(3f, 4f, 6f and 7f) involves the selection of primary beam and the secondary beam polarity. This mode selection depends on the

species of interest that in turn, increases secondary ion yield for the species of interest. For example, if a secondary ion of interest has a higher ionization tendency such as Mg, Ca, Na, Pb, or in general a metal ion (may be present as an impurity), primary O₂⁺ and secondary positive ion extraction is selected. Similarly, if an element of higher negativity, or a non-metallic element (C, O, N, S) is of interest, Cs⁺ source and a secondary negative extraction is used.

Both magnetic sector and TOF SIMS could be operated by either one of the two imaging modes: ion microscope or ion microprobe. In case of the microprobe mode or the probe imaging mode, a fine and focused primary beam scans over the analysis area like a scanning electron microscope and creates an integrated image of various points with respect to a particular ion of interest. Most of our discussions in this chapter will encompass this mode of operation. The ion microscope mode or the direct imaging mode is analogous to the optical microscope where-in the primary ion beam is broadened and the ejected secondary are focused through stigmatic focusing mass analyzer and form a mass-filtered ion image at the detector. Spatial resolution for the ion probe is governed by the fineness and characteristics of the primary beam whereas for the ion microscopic mode the spatial resolution depends on the of aberrations in the secondary ion optics.

Tandem Mass Spectrometry: Tandem mass spectroscopy, though not common, is worth mentioning at this point. This type of spectrometry is gaining use for the analysis of biomolecules, peptides and proteins. In a Tandem Mass Spectrometer, the secondary ions (generally, high mass fragments) are further broken down (fragmentation) by one of several techniques, and the resultant fragments are detected by a second detector. An example of this type of spectrometer is the PHI nanoTOF II (Ref. 9) shown schematically in Fig. 11. In this design, a parallel imaging MS/MS machine, a precursor ion of choice (Precursor Selector in Fig. 11) is selected from the secondary ion stream and deflects to a high energy collision induced dissociation cell (CID) while the rest of the secondary ion beam is collected as usual in the first detector (MS1 detector). In the CID cell the precursor ions collide with argon gas causing fragmentation. These ions are then mass separated in a linear TOF and counted by a second detector. In this system additional information is obtained from the same analytical areas along with the spectrum from the normal TOF SIMS.

Specimen Preparation:

SIMS specimens need to be flat since the primary beam enters at an angle to the sample surface. A rough surface with peaks and valleys would cast shadows with reference to the primary ions and the shadow areas would not get analyzed. Also, the emersion lens generally located very close to the sample surface and perturbances on the sample surface can change electrostatic field around it. The sample surface could be polished for flatness and for metals and alloys grain boundaries and precipitates may be revealed if the analysis at such locations is of interest. Generally, optical magnification of sample features is very limited (about 500 times maximum) and therefore not all the microscopic features are visible. This is due to lack of close proximity of the objective lens of SIM's optical microscope to the sample surface (the other electrostatic lenses need to be closer to attract ions of interest).

The analytical chamber of the instrument is maintained at a very high level of vacuum, around 1.0 e -9 torr or better. Porous or mounted samples cannot be readily analyzed due to the effusion of trapped gases. For magnetic sector SIMS such as IMS-6f the sample is charged up to 5KV and is insulated. Fig.12 shows one of the sample holders for the machine. The holder is designed for analyzing microchips and are of correct size to be loaded from bottom of the holder and supported by a spring. For each specimens it is important that the openings on the holder are covered entirely by the specimen and the specimen makes good contact with the holder all around.

Even a well-polished and clean surface can adsorb gas molecules from the atmosphere or it can be contaminated. If the contamination is of interest, static SIMS (quadrupole or TOF SIMS) may be employed for surface analysis. If the needs are for the analysis of material underneath, the specimen can be analyzed in a dynamic SIMS (magnetic sector SIMS) where the sample can be cleaned by sputtering prior to analysis.

Calibration and Accuracy:

The data output from a SIMS instrument is mass-to-charge ratio (m/z) along the x-axis and intensity or counts (number of ions detected) along the y-axis. Fig.13 shows spectrum obtained from an Al sample under O_2^+ ion bombardment. It is seen from Fig.13 that the detection of Al^+ ion is at the saturation limit whereas there are also Al^{2+} and Al^{3+} ions with significant intensity. These are ions with two and three ionic charges, respectively. There are also Al ionic clusters such as Al_2^+ and Al_3^+ with O_2^+ from the primary beam. In addition, interactions with oxygen ions have generated ions such as AlO^+ , Al_2O^+ , AlO_2^+ , and $Al_2O_2^+$ etc. with in a mass range of 100 amu. There are also other peaks that are not identified in Fig.13. They could be impurities or the products of interaction of impurities with oxygen. They could also be the products of interaction among impurities themselves. Identification of the intensity lines or peaks depends on the position of the line on the m/z axis. Under high resolution conditions, the m/z axis must be calibrated to up to four or more places after the decimal point. For example, the mass for Al should be calibrated to 26.9815. If we consider the AlO^+ line, O having three isotopes and all three would produce three lines with Al (since Al has only one isotope). The most abundant O isotope (with mass 15.994915) would produce the most intense line. However, in machines such as IMS-6f, there is the PBMF (Primary Beam Mass Filter) that filters the primary beam and isotopes other than the most abundant have negligible intensity. Let us now consider the primary beam Cs^+ on an Al specimen. The spectrum is shown in Fig.14. The use of Cs source with negative secondary increases yield for species of O, C, N, F, Cl etc. and therefore, the dissolved elements show up, even AlO^- ion, on the spectrum. The Al peak is rather small compared to Fig.13, indicating lower yield for Al^- ions.

Calibration of the mass axis (x-axis) is accomplished by using known substances such as O, Al, Cu, Cs etc. for which the intensity lines are obvious. To calibrate higher masses, ions such as Cs_2 are used. In case of magnetic sector SIMS, the magnetizing current for the spectrometer magnet is precisely controlled to identify a particular ion. It is expected that the same amount of magnetizing current should be needed in repetitive experiments. Unfortunately, this current varies somewhat due to the residual magnetism and other factors. For depth profiling analysis in magnetic sector SIMS, where same elemental analysis is performed cyclically, the peak calibrations are made periodically as the sputtering and profile analysis progresses.

TOF SIMS have similar limitations except for the magnetizing current which effects the peak positions. In case of TOF SIMS, the pulse duration and the time measurement are critical to the accuracy of the measurement. Traditional TOF SIMS suffer from mass inaccuracy and mass resolution. Also, the spectrum display may miss the higher mass peaks. In any case, the mass calibration is performed in the same manner as the magnetic sector machines, with materials of known spectrum.

This far, we have discussed the line/peak positions along the m/z axis of the spectrum. The peak heights which is a measure of peak/ion intensity, represented in the y-axis, depends on many factors such as stability of the primary current, secondary lens adjustments, primary beam shape, size, and

energy. It also depends on the mass resolution since higher resolution allows only the secondary ions with close masses and kinetic energies. It is possible to generate reproducible results (mass spectrum) with stable primary sources and within the same grains and in very fine-grained structures (when the primary beam covers several grains). To address the calibration and accuracy in SIMS instruments, one must realize how the various SIMS instruments are used in industry. Modern SIMS are used to:(a) obtain a mass spectrum to learn about the general alloy chemistry or compare the mass spectrum for a material with known spectrum, (b) depth profile to determine various material layer thicknesses, (c) determine isotopic ratios, (d) quantitative analysis of light elements such as H and Li, and (e) to determine the doping or impurity contents in microchips (or trace element analysis). In the following paragraphs various applications and the associated accuracies are discussed.

(a)*Mass Spectrum*: All SIMS produce mass spectrum. As described above, they all are plots of m/z vs. intensity of each m/z. They are plotted to identify an unknown material or to verify the identity of a known one. Quadrupole and magnetic sector SIMS scan the secondary ions starting from 1.0 amu to any upper limit within the specification of the machine. Often there are several lines clustered together making the peak wider, and therefore, there are software which produce bar graphs where the clustered peaks are integrated to produce one fine line at each amu integrating intensities on both sides of the peaks between +/- 0.5 amu. Bar graphs are in a simple form to compare intensities or bar heights but completely ignore the interferences. Bar graphs have been discussed in the next section and are useful to get a qualitative assessment of elements present in a specimen (Fig. 17). The instrument is calibrated using materials with known chemistry prior to analysis.

(b)*Depth Profiling*: Depth profiles (DP) are needed to verify exact amount of deposition in a layered structure and is an important application for dynamic SIMS in micro-electronics. In a depth profiling process, constant monitoring of species take place as the sputtering continues. Often the doping profiles are also monitored as the depth of analysis progresses through various layers. It is therefore important that the primary current remains constant throughout the process. The depth of a crater formed during DP is a function of time and primary beam intensity and time.

Depth of a crater is measured by either by a profilometer or using a high-resolution electron microscope. Depth profiles can also be measured by sectioning, polishing the section and measuring by a high-resolution electron microscope. Calibration methods have been standardized by ISO/TR-15969. Also, there are several multi-layered reference materials developed by various National Institutes. Some of them are, Ni/Cr multilayer, AlAs/GaAs superlattices, Ta₂O₅/Ta multilayer, SiO₂/Si. These materials are manufactured with precise thickness by ion implantation or vapor deposition techniques. Chemical analysis of various species is performed with the help of a stable and scanning primary beam over the area of interest. This operation forms a crater and secondary ions only from the center of the crater are gathered for analysis to avoid erroneous effects from the edge of the crater. Fig. 14 and Fig.15 illustrate the DP analysis procedures. With proper standards, quantitative estimation in a DP analysis is better than +/- 10%.

(c)*Isotopic Ratios*: Determination of isotopic ratios or natural abundances are important to identify origin of material/specimen. It is believed, and perhaps rightly, that extraterrestrial materials such as the ones found in meteorites, moon rock, and star dust etc. have different isotopic ratios than what is known or found on earth. Historically, magnetic sector SIMS have been used to verify isotopic ratios of such materials. High resolution SIMS with multiple detector to record isotopic peak intensities simultaneously have been designed and used. Cameca Instruments has several models designed to establish natural abundances in geological samples where samples of different ores present in very fine scales. Reference for isotopic ratios is the well-established in physics databases

(Ref. CRC handbook) and their ratios need to be accurately determined by precise instruments.

Magnetic-sector SIMS and perhaps TOF SIMS and quadruple SIMS can provide isotopic information. However, the intensities of interfering species must be subtracted to obtain the correct isotopic ratios. The instrument must have a very high resolution and the secondary ion yields must be high. To counteract the effects of grain size, the specimen should be amorphous or have large grains.

(d) *Quantitative Assessment of Light Elements:* Light elements such as H, He, Li, and Be can be analyzed effectively using SIMS. There is very little or no interference at this low end of mass spectrum and therefore, high resolution instruments are not required. Concentration of hydrogen within grains, at grain boundaries and triple points can be successfully determined to investigate hydrogen embrittlement or stress corrosion cracking. Li concentrations at various locations in Li containing alloys such as the Al-Li alloy 2195 can be determined and imaged. Homogeneous alloys containing the element of interest can be used as the standard for this type of analysis. Unknown and alloys of known analysis can be analyzed side-by-side on the sample holder to improve accuracy. Commercially available standards are made from Si chips on to which other ions such as H are implanted. It is important to note that the secondary ion yield of a Si matrix can be significantly different from that of the alloy matrix being analyzed.

(e) *Trace-element Analysis:* Traces of a certain element, level of doping in semiconductor materials, impurity analysis can be performed by magnetic-sector SIMS as the secondary ion yield is high and the secondary ion intake is also high for these machines. However, the levels of dopants or trace elements must be above the detection limit of the species being detected for the same matrix. Detection limit (DL) depends on the matrix as well as the background spectrum intensity.

There are several considerations that the operator must consider for a good trace element analysis. They are:

- The count rate must be high enough otherwise low counts of the trace elements will not reach the detector,
- A contaminated instrument, contaminated from previous analyses can show trace elements (which are also the contaminations from the previous analyses) that may not be there in the sample being analyzed,
- Trace element being sought has the same mass as a interfering species,
- Poor vacuum can lead to gases such as H, C, O, N, and other species from vacuum system to appear in the spectrum,
- If the specimen being analyzed has an alloying element or impurity that can produce species for which DL is being sought.

To address accuracy of the SIMS analysis process in a magnetic sector SIMS (Cameca IMS-6f), a small experiment was carried out. A polished and lightly etched Niobium (Cb) sheet was used for this purpose. Partition of interstitial elements such as C, H and O was investigated at ten locations both inside the grains and at grain boundaries (G.B.). Table 1 shows the variation of counts for ^1H , ^{16}O , and ^{12}C with a constant intensity Cs^+ beam, continuous scanning, and negative secondary collection for a fixed time. It can be seen from table 1 that despite variations in counts, the average indicates there exists a segregation of all elements to the grain boundaries in this material.

Location	1	2	3	4	5	6	7	8	9	10	Average
$\text{H} \times 10^3*$	1.22	0.625	0.85	1.20	1.57	1.33	1.17	1.46	1.29	1.27	1.20

H x 10³	0.65	0.72	1.04	0.98	0.89	0.96	0.56	0.87	0.82	1.24	0.87
C x 10^{2*}	4.9	3.13	3.39	3.43	4.57	3.76	3.76	5.50	4.30	3.58	4.02
C x 10²	4.13	3.60	3.55	3.62	3.76	3.90	7.70	3.28	2.54	3.80	3.98
O x 10^{4*}	2.48	1.77	1.95	2.48	3.16	2.79	2.37	2.90	2.45	2.29	2.46
O x 10⁴	2.21	2.40	2.69	2.45	2.07	2.34	1.45	1.96	1.90	2.63	2.21

Table1 – Distribution of C, H, and O in term of counts between the matrix and the G.B. in a Niobium sheet. * means at G.B.

Data Analysis and Reliability:

Mass Spectrum and bar graph: Data gathered during the mass spectrum analysis is a continuous scan for the available masses in the ejected secondary ions. It is displayed as a graph of mass number or amu divided by the charge on the ionic species in the x-axis (m/z), and the intensity of each available of that species. The scan could be faster or slower based on the available sample material and the objective of the experiment. It could be displayed in a continuous mode or as a bar graph. In a continuous mode the peaks are wider as they include counts in between each m/z. Since the intensity or counts are displayed in seven orders in magnitude, in most scans, all the elements are visible which also includes molecular ions. Most software includes a ‘bar graph’ program that integrates all intensities on both sides of a mass number so that the results show bars at most mass numbers. This integration is done with +/- 0.5 amu of each mass/amu positions. This type of analysis provides information on a qualitative estimate of elements present in materials. To understand the specimen better, it is also possible to change the range of integration of bar graphs (as the software would allow) to a value less than +/- 0.5 amu. Since the secondary ion yields vary significantly between the secondary positive and secondary negative ions, it is better to take both positive and negative scans to get a complete idea on all elements present.

To obtain a quantitative elemental analysis, the interfering species must be separated from the nearing elemental ions by performing a high-resolution scan. Since the intensity is sacrificed at the expense of resolution, primary ion intensity may be increased to yield more secondary ions. To reduce analysis time, the software allows operators to perform analysis only in the region of interest. As an example, let us say that we need to find the amount of N₂ in a piece of graphite. H seems to be omnipresent in any material even if the material spends days in high vacuum analytical chamber of the SIMS. Hydrogen and C can react to have C₂H₄ species formed which interfere with N₂. Exact mass of N₂ is 28.006158 and that of C₂H₄ is 28.031299. The mass resolution required in this case is $m/\Delta m = 28.006158 / (28.031299 - 28.006158) = 1110$. The SIMS instrument should have the required resolution to provide the right intensity for N₂. Since most instruments have the capability to measure heights of peaks in a spectrum, it is easy to get a bar graph of the region where the N₂ and C₂H₄ peaks are separated. Fig. 17 compares spectrum with bargraph and the conventional mass spectrum. Fig. 18 shows a higher resolution technique resolves individual peaks at mass 43.0. Data on interference for mostly electronics materials have been listed in Reference 4 (Appendix G).

Depth Profiles: Most analytical applications of SIMS do not emphasize true surface compositional analysis. Rather, depth profiling (from 20 to 2000 nm), trace element or bulk element analysis, and imaging of microstructural features are more common applications of SIMS. Of these, quantitative depth profiling with high detection sensitivity and depth resolution is unquestionably the forte of SIMS. In a depth-profiling analysis, one or more of the secondary ion signals are monitored as a

function of sputtering time (or depth) into the surface or bulk of the specimen or through an adherent thin film or coating. The depth and time are correlated by standardizing the sputtering process. Both bulk or trace element analysis as well as depth profiling come under the heading of depth profiling. Figure 19 shows an illustration of depth resolution in a depth profiling experiment.

Accurate depth profiling requires uniform bombardment of primary beam with no contribution from the crater walls, or the instrument surfaces. It is also expected that the sputtering by primary beam would produce a uniform material removal as the sputtering depth increases. This rarely happens as the rastered beam passes through various material layers through a semiconductor chip. Fig. 20 shows the dependence of sputter yield for various elements as target for a Kr^+ beam. Even with rigorous control of primary beam, the concentration profiles across often do not reveal a sharp edge due to several inherent issues with the depth profiling process. This is largely due to the ion beam mixing process described below.

The ion beam mixing has three effects. They are: recoil mixing, cascade mixing, and enhanced diffusion. The recoil mixing is due to the penetration of the primary beam into the matrix being analyzed. This process not only finds traces of the primary beam material in the matrix and shows up in the analysis, but also changes the sputtering behavior of the matrix. The cascade mixing refers to the effects of the impact by which the inside material shows up on the surface distorting the geometry of the profile. The enhanced diffusion is caused by the creation of vacancies due to the disturbance of lattice around the primary beam impact areas. Direction of diffusion of various species depends on the localized vacancy concentrations and the chemical potential gradients, higher vacancy concentrations increase diffusivities. The mixing depth is directly related to the primary ion penetration depth; it increases with ion energy and decreases with the decrease in incident angle to the sample surface. In depth profiling, during determining the interface width, the beam mixing leaves a trail or decay in the profile as shown in Fig. 21. Here, the trail lasts as long as 180 nm but the interface is shown only at 37.5 nm where the intensity drops by an order of magnitude. The conventional factor could be either 10 (as in Fig. 20) or by a factor e (exponential).

Depth resolution is also characterized by interface width and is defined as the average dimension over which the intensity drops from 84% to 16%. This has been shown in Fig. 22. As an example, Fig. 23 shows an InGaAs/GaAs interface calculation. It shows a 6 nm width with an edge position of 0.135 μm .

It is important to point out that a presence of electronegative elements such as F, O, N, and Cl, the sputtering surface increases yields of secondary positive ions, and similarly, presence of electropositive elements such as Cs increases yields for secondary negative ions. This is the reason why O and Cs primary ions are used to enhance secondary ion yields in SIMS analyses. Thus, the presence or absence of these elements is expected to affect secondary ion yield of a matrix. For elements such as Si or Al, high vacuum level at the analytical chamber does not prevent formation of an oxide layer on a clean metallic surface and is expected to show high levels of O in a depth profile. It is, therefore, advisable to monitor O levels during the depth profile experiments. Operator should also have a knowledge of the growth of these oxides in analytical vacuum levels and should correlate it to the sputter rate.

Depth profiles are often distorted by the presence of dust particulates embedded during manufacture. The elements found in dust and similar contaminants are Si, Ca, Mg, and Al to name a few. In this case, when the depth of the contaminant particle is reached signals for the constituent elements increase significantly and decay sharply when it contaminant is passed. To avoid particulates, a low energy (primary ion) imaging can be done to identify particle free areas and then

perform high energy depth profiling.

As mentioned earlier, the analysis during a depth profile is performed at the center of a crater to avoid affects of crater walls. However, unevenness at the bottom of the crater can also throw the measurements completely off. This may be caused by the shape and non-uniformity of the primary beam. This is due to the primary beam species that may not have the same velocity and spend different times under one of the primary beam lenses. Also, the depth of focus of a primary beam is rather low, therefore, a focused beam at a particular depth may not be at focus below a few nm depths. The crater should be examined and the dimensions should be measured after a depth profile measurement.

It should be recognized that ‘memory effect’ is a significant issue with SIMS analysis. Due to the proximity of the ion collecting lens systems and apertures, the ejected species get deposited on secondary beam path and can show up on the spectrum. Perioding cleaning and replacement of the apertures and lens components or sputtering of matrix for several hours (to deposit matrix material on effected lens parts) are generally utilized to overcome the memory effect.

Isotopic Ratios: While there are special magnetic sector instruments with multiple detectors to collect different isotopes simultaneously (one isotope on each detector), isotopic distribution can be performed on a SIMS instrument if the interference species could be separated. Reference 4 in this write-up lists a good deal amount of interferences. These references have been realized due to significant SIMS research and applications in the micro-electronics discipline. Also, the instrument should have a high enough mass resolution to separate the intensity contributions of all the interfering species. If the interfering species are known, the instrument could be operated in a high-resolution mode and the isotopic ratios could be determined accurately. An example of such analysis is as follows.

If we want to find the isotopic abundances of ^{12}C and ^{13}C in a graphite sample, interference of $^{12}\text{C}^1\text{H}$ with ^{13}C is expected since H is present in every material (a mass scan can verify this). ^{12}C has a mass of 12.000000 amu and ^{13}C has a mass of 13.003355 amu. Hydrogen has a mass of 1.007825, so, the species $^{12}\text{C}^1\text{H}$ would have a mass of 13.007825 amu, which needs to be separated from 13.003355 amu line by the machine. This would require, approximately, $0.004/13 = 0.0003 \Delta m/m$ resolution. Machine now could be set to this resolution and the heights of peaks or intensities of both ^{12}C and ^{13}C could be measured.

In magnetic sector instruments such as Cameca IMS series, the interference from molecular species can be minimized by placing the energy slit away from the center, as shown in Fig.24. This is done manually or it could also be accomplished by electronically by offsetting the secondary ion energies by several eV, as shown in Fig.24. This correction is done at the expense of line intensity.

Light Element Analysis: Light element analysis for elements such as H, Li, Be and B is less complicated. The interference, if any, may come from H since H is present in almost all materials. For interference with H as a species, $\Delta m/m$ value comes out to be relatively high and therefore, instruments with somewhat lower resolution can be utilized for analysis. Line scans and ion imaging are generally performed for segregation and precipitate identification for these elements.

Trace Element Analysis: There are two techniques used in SIMS to take advantage of its analytical capabilities. Since SIMS is capable of analyzing ppm or even ppb level impurity and trace element analysis, small quantities of elements of interest are added to bulk or matrix material to form as standards for their detection and analysis. The other technique is to implant elements of interest to

the bulk matrix. Accurate levels of fluence (ions implanted per unit area) are required to use the implanted surface as a standard for analysis. To be detected by ant technique, the trace element must be present above the detection limit of that element. The detection limit depends not only by the energy of the primary beam, but also on matrix as well as the presence of other elements. Operators of these instruments have a significant role to play by adjusting various instrumental parameters for detection limit determination and trace element analysis.

Impurities and trace element concentrations are usually expressed in terms of atoms/cm³. The instruments, however, provide information of intensity/counts for various masses. The Relative Sensitivity Factor (RSF) is often used to convert intensity to atomic density of impurities in terms of atoms per unit volume. Mathematically,

$$\rho = I_{\text{imp}} / I_{\text{mat}} \times \text{RSF} \dots \dots \dots \text{(Eq. 1)}$$

where, ρ is impurity atom density in atoms/cm³, I_{imp} and I_{mat} are counts of impurity isotope and matrix isotope, respectively. If RSF value is known and counts for impurity and matrix numbers are known, ρ can be calculated. Accurate RSF values are generally calculated, averaged from several readings. RSF values depend not only on the type of machine, it also depends on specimen matrix, primary ion source, and whether the secondary ion is positive or negative. Reference 4 lists RSF values for several matrices for quadrupole and magnetic sector machines.

As mentioned earlier, RSF values are used in most calculations and they need to be established for a particular type of matrix. If Li concentration needs to be determined in an Al matrix for an Al-Li alloy, RSF values need to be established. People in semiconductor industry using SIMS for trace element analysis or doping levels have established RSF values for several matrices as shown in Ref.4. Most RSFs values are determined from implanted standards where the fluence of implanted species is measured accurately using the following formula:

$$\text{RSF} = [\phi, C, I_{\text{mat}}, t] \% [d, \sum I_{\text{imp}} - d, I_{\text{bac}}, C] \times [\text{EM/FC}] \dots \dots \dots \text{(Eq.2)}$$

Where, ϕ is the fluence used in the implant in atoms/cm², C is the number of measurements or cycles of analysis (shown in the x-axis of Fig. 25) used to develop the curve in Fig. 25. d is the depth of crater in cm, measured after the test, $\sum I_{\text{imp}}$ is the sum of impurity isotope counts over the depth profile, I_{bac} is the background intensity for the impurity ion per data cycle, and t is the analysis time in seconds per cycle for the species of interest. [EM/FC] is the counting efficiency ratio for the electron multiplier and the Faraday cup. When matrix intensity is very high, it is measured by the Faraday cup otherwise, the impurity intensity is measured by the electron multiplier (EM). If only EM is used, the ratio of EM/FC is 1.0. A SIMS instrument may have both FC and EM. For trace elements, it is more accurate to work only with EM due to their low-level counts. However, the matrix counts could be very high and trigger FC or reach saturation. In that situation, for a Si matrix, ³⁰Si isotope may be used in place of the intense ²⁸Si.

Fig.25 is a ¹¹B depth profile in Si matrix. It shows a typical profile of an ion implanted sample. The B spike near the surface is due to the oxide and may not show in other ion implanted profiles. ¹¹B has been tracked in this profile experiment since it is the dominant isotope of B. It is also possible to track ¹⁰B during this experiment provided that, ¹⁰B was implanted on to the surface. Generally, one of the isotopes is implanted for standard samples. On the other hand, bulk samples doped with small amounts of elements, dope with natural elements preserving their naturally occurring isotopes and both ¹¹B and ¹⁰B would be expected to be found in that situation and depth profile would be a straight line parallel to the x-axis of the plot for both the B isotopes.

The specimen in Fig.25 has been ion implanted but the plot has been generated in a dynamic SIMS. Several elemental peaks including B and perhaps Si has been documented in the process of generating the plot. Only the B profile has been shown but the others have not been. During this process, the magnetizing current of the spectrometer magnet is varied to make the ions of other species (such as Si) reach the detector and eventually the current is brought back to detect B. This completes one cycle of the total number of 190 cycles are shown in Fig. 25. Boron atom density in atoms/cm³ as a function of depth can be calculated using Eq.1 and the intensities of B and Si form the experiment using the RSF value calculated using Eq.2. The crater depth can be measured by a profilometer and when divided by the number of cycles, etching depth per cycle can be obtained to obtain Fig.26.

Ion implantation standards for SIMS are popular but care must be taken for the production of precise standards. They include selection of an appropriate isotope, levels of impurities in the implanting beam, if any, precise measurement of fluence levels and its implanting energy, as well as possibility of ionic interferences. Ion implanters are now available with energies up to one or more MeV capable of implanting masses up to 200 amu.

Applications and Interpretation:

From the very onset of the development of commercial SIMS systems with the associated primary ion sources, and spectrometers, SIMS has emerged as a very useful tool in all kinds of analysis. Due to its ability to analyze monolayers of surface materials complementing other analytical tools such as X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy, and its ability to detect analyze all elements, and that it can analyze very thin layers of metals for its dopant, it has become an invaluable tool for the analysis of micro-chips. Modern SIMS are complex and are very expensive due to their complexity. With advancements in primary ion sources, cluster guns, imaging capabilities, SIMS is useful for investigating almost all kinds of materials problems. Application of SIMS has been described in most of the previous chapters, however, due to constant and ceaseless instrumental developments, its applications can extend to far reaching capability than they exist today. This development is being augmented by ever shrinking size of electronic appliances warranting smaller and precise analytical capabilities from the instrument manufacturers.

General applications of SIMS analysis includes (1) depth profiling to characterize thin and shallow layers of deposits in terms of thickness, composition, and trace elements in microelectronics for both conductors and insulators, (2) measurement of layer thickness in layered engineering materials, (3) contamination analysis, (4) isotopic ratio and abundance analysis, (5) imaging capabilities of ion species (in addition to imaging of elements),and (6) general failure analysis where failure is investigated using SIMS as a tool. What follows are examples of cases where SIMS has been successfully employed in resolving or analyzing problems that cannot be done by other analytical instruments such as electron microscopes or electron microprobe analyzers.

Example #1: Analysis of hydrogen using SIMS is simple since there is no interference near amu 1.0. However, hydrogen being mobile, complexities in hydrogen analysis in SIMS arise as the hydrogen atom migrates into the high vacuum analytical chamber. Mobility of hydrogen also increases due to the impact of primary ions near the crater area. This is especially true in case of

ferritic steels where the body-centered cubic structure allows higher hydrogen diffusion. Analysis of hydrogen in steels is particularly important as the steels suffer from hydrogen embrittlement and lose significant mechanical properties due to the presence of hydrogen.

Ref. 10 describes a technique to cool the SIMS stage to around 83° K using a Cameca IMS-7f machine to minimize the hydrogen mobility effect. The authors have used an annealed low carbon ferritic steel and charged it with hydrogen using 20% NH₄SCN aqueous solution. The hydrogen charged and uncharged specimens were analyzed using Cs⁺ primary source and monitoring H⁻ secondary ions. Fig. 27 shows depth profiles for hydrogen charged and uncharged specimens. There are several specimens for repetition of this analysis. It is not unusual to see some hydrogen in any specimen as it is inherent to any metal or alloy. Fig. 27 (b) for the hydrogen charged specimens shows higher levels of H and places where the H is spiked represent regions of H traps such as dislocation tangles, pileups, twins etc. The bottom parts of both (a) and (b) show monitoring the stability of the primary Cs beam.

Fig. 28 of Ref. 10 shows variation of sputtering rate and how it effects the H count rate. Between 1200 and 1300 secs. of sputter the raster size was reduced by a factor of nine increasing the corresponding H count rates by a factor of 4 during that period for both the charged and uncharged specimen.

Example #2:

Al-Li alloys are used in light structures for their low density, stiffness and strength. Alloys such as 2090, 2195, and C-458 are used in spacecraft structures. Stringers of alloy 2090 in the form of rolled strips sections used as support structures in NASA Space Shuttle propellant tanks, were found to be cracking. The manufacturer of the strips indicated that it is due to the depletion of Li at the surface during heat treatment of the strips and such depletion would be indicated by large grains at the surface. The cracked stringer was analyzed for Li depletion using a Cameca IMS-6f where the cross section of the stringer material was polished mounted and analyzed. Since edge retention is difficult during polishing, the sample was sandwiched between two alloys: 2219 and C-458. Al-2219 is an Al-Cu alloy with no Li but C-458 is an Al-Li alloy with nearly same Li as 2090. The three strips were welded by spot welding away from the analysis area. Fig. 29 shows the microstructure of the 2090 stringer with large grains near surface. Also shows a hardness impression taken to identify the location of the large grain inside the SIMS instrument. Fig. 30 shows line scans across the large grain areas in the stringer sample at the center with 2219 alloy on the left and C-458 on the right. The Li depletion was not evident on the 2090 material. Later on it was found that the cracking was due to anomalies in the heat treatment during the manufacture of the strips.

Example #3:

Contributions of SIMS analytical capabilities to geochemistry and cosmo-chemistry cannot be over emphasized. These are topics of university courses having references to several books on the subject. Major SIMS manufacturers such as Cameca Instruments (models such as IMS 1300-HR³, Nano SIMS 50L, and KLEORA) have designed their SIMS models to ease analysis of very small particulates found either on ground or as extraterrestrial powders commonly known as "Stardust" (Ref.11).

One of the great discoveries in cosmochemistry in the last century was the fact that primitive meteorites contain tiny mineral grains that condensed around dying stars. These grains survived a myriad of destructive environments, including the immediate surroundings of their parent stars, the

interstellar medium, the molecular cloud that collapsed to form the solar system, the solar nebula, meteorite parent bodies, breakup of those bodies, and subsequent atmospheric entry. There were a number of hints of the presence of these grains over the years, mainly from strange isotopic patterns of the noble gases. These grains are commonly referred to as “pre-solar grains,” although the more evocative name “stardust” is often used. Because it is now clear that these grains formed around individual stars with little apparent subsequent modification in the interstellar medium. Note that the name is also used for the National Aeronautics and Space Administration (NASA’s) Stardust mission, which returned dust grains from Comet Wild 2 and from the contemporary interstellar medium.

The mineralogy, textures, chemistry, and isotopic composition of stardust from meteorites is expected to provide direct evidence of processes that occurred in individual stars and complement observations by more traditional astronomical methods. Stardust from meteorites samples a number of different types of stars, including asymptotic giant branch (AGB) stars, part of the normal stellar evolution of stars 1.5 to 4 times the Sun’s mass, as well as core-collapse supernovae and novae. Diamond, silicon carbide, and graphite are common types of stardust but are thermodynamically unstable in the solar nebula, so their survival places constraints on physicochemical conditions in the solar nebula.

Stardust grains are small, although the largest grains can reach a few tens of μm in diameter, such grains are very rare, and most grains are of μm -sized or less. For this reason, laboratory study of stardust has driven advances in analytical technology and progress depends on further improvements in spatial resolution and analytical sensitivity. While isotopic analysis in geoscience is generally done by instruments such as ICP-MS (where the samples are dissolved and then converted to a plasma needing more sample material), and the stardust samples (particles) being fine, instruments such as Nano SIMS 50L are advantageous to use. In fact, larger particles could provide localized analysis giving repetitiveness and more precise analyses.

In the stardust analyses several isotopes are monitored including Si, C and O. In Fig.31 (Ref. 12) shows the variation of O isotopes in meteorites, terrestrial as well as lunar samples. In this figure, a plot between $^{17}\text{O}/^{16}\text{O}$ (in y-axis) vs. $^{18}\text{O}/^{16}\text{O}$ (in x-axis) should be straight line with slope of $\frac{1}{2}$ according to the theory of isotopic fractionation. The terrestrial and lunar samples follow this slope, however, meteorite or their components fall on a slope of 1.0. In this figure, δ is defined as

$$\delta^{18}\text{O} \text{ (in parts out of 1000)} = [(^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{standard}}] \times 1000.$$

Example #4: Development of SIMS instrumentation has grown following needs of the SIMS market. One of the developments associated with the TOF SIMS is the LEIS (Low Energy Ion Scattering) technique. In LEIS the sample surface is bombarded by noble ions with low energy. As these ions are scattered and collide with surface ions, they conserve their energy and momentum through the impact. By measuring and scanning the energy of the scattered ions, the mass of the scattering ions on surface, and hence the composition, of the surface is known. The product of a LEIS scan is a graph between intensity of the scattered secondary ion (y-axis) and energy of the ions (x-axis) coming from the surface.

In a conventional LEIS the peaks are indicated by scattering of surface ions are buried in the background and are hard to detect. However, when a mass filtering is applied, the back ground is reduced significantly and the detection limits are improved (see Fig.32, Ref. 13).

Reference 13 shows an application of LEIS technique in detecting Mo diffusion across a B₄C barrier deposit. The composite as shown in Fig.33 (top) has five layers and was heated to 500°C

for different times to induce Mo diffusion. The second part (bottom) of Fig.33 shows the plots of intensity vs. ion energy for different heat treatments. With no heating (annealing), the O surface peak is seen but with no indication of any Mo surface peak. However, as the heating continued at 500°C, the curves shift to right in to the Mo background zone indicating increasing diffusion of Mo to the surface.

Currently, there are three dominant manufacturers of SIMS machines. They are: Physical Electronics Incorporated (PHI), (www.phi.com); Cameca Instruments (www.cameca.com), and Iontof GmbH (www.iontof.com). All the three have application sections in their websites that can be accessed for a complete and advanced application of their SIMS instruments. Application of SIMS is evolving as the components analyzed by the SIMS instruments are shrinking in size day by day. It is always worthwhile to visit these websites as they have examples of advanced applications, continuously developing capabilities, and SIMS applications for new materials.

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- (5) “Cameca IMS-6f operator training” handbook, Analytical Instrumentation Facility, NC State University, page 48.
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<https://www.google.com/url?sa=i&source=images&cd=&cad=rja&uact=8&ved=2ahUKEwj1ouzAyqzgAhWMnFkKhdfSBLMQjRx6BAgBEAU&url=https%3A%2F%2Fserc.carleton.edu%2Fdetails%2Fimages%2F8384.html&psig=AOvVaw2hgB35b6VRQtQrfr4w6we0&ust=1549730578932071>
- (8) Physical electronics: phi.com – internet site -
<https://www.google.com/url?sa=i&source=images&cd=&cad=rja&uact=8&ved=2ahUKEwiOmlrOy6zgAhUMSN8KHbu9BoAQjRx6BAgBEAU&url=https%3A%2F%2Fwww.phi.com%2Fsurface-analysis-techniques%2Ft-of-sims.html&psig=AOvVaw1DR8GKPdtyEbssT2UXWNB5&ust=1549730896259307>
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- (13) Qtac 100 (Quantitative Top Layer Characterization” Iontof website - www.iontof.com

SIMS Figs.

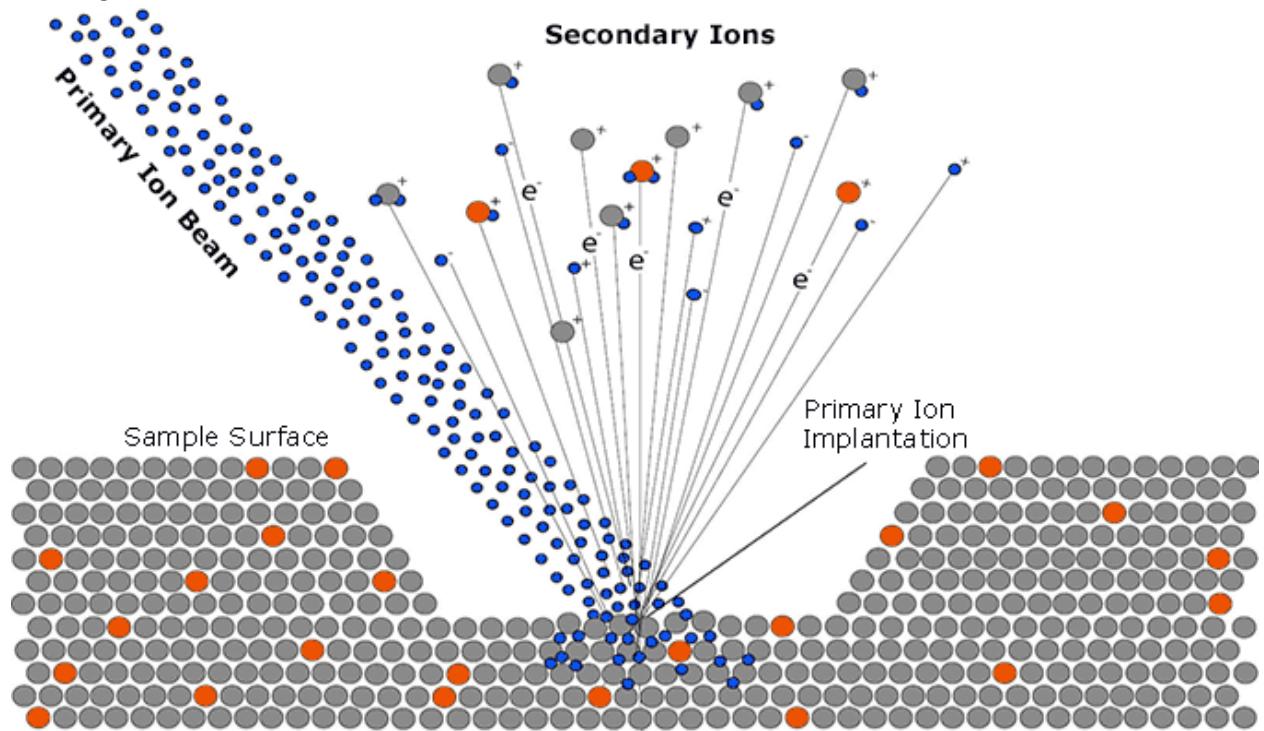


Fig. 1 – The SIMS process. Shows the impinging primary beam in to a crater (sample) and the emanating secondary ions consisting of secondary ions of the matrix and impurity atoms (orange color) with single and double charges (could be more than two charges also) and electrons. Secondary ions could be positively or negatively charged or could be neutrals. (Ref. 2, Cameca Instruments website).

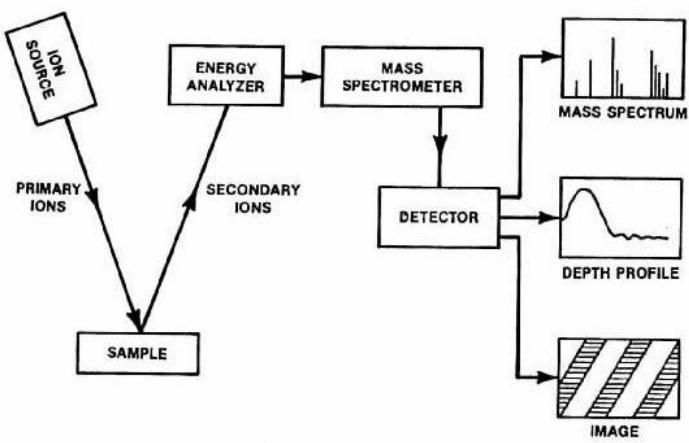


Fig.2 – A schematic of a SIMS system. It shows how the signals are processed to obtain various analytical results. The entire system is under high vacuum for the ease of ionic movement. (Ref. 4, page 1-8).

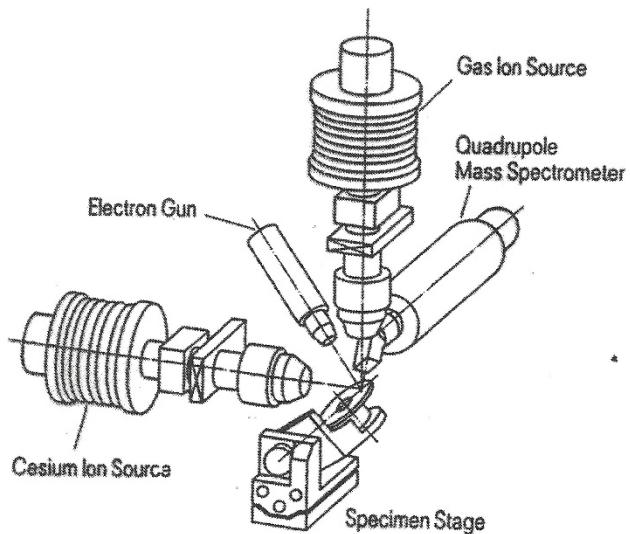
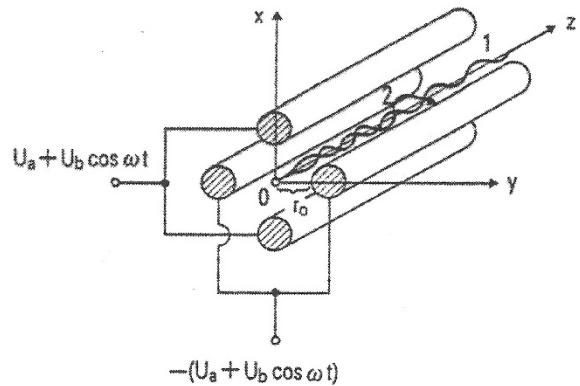


Fig.3 – Schematic of a Quadrupole mass spectrometer (bottom). The top diagram shows the four rods and how they are charged alternatively. The secondary ions travel along the z -axis before they are detected at the far end of the z -axis. (Ref.5, page 48).

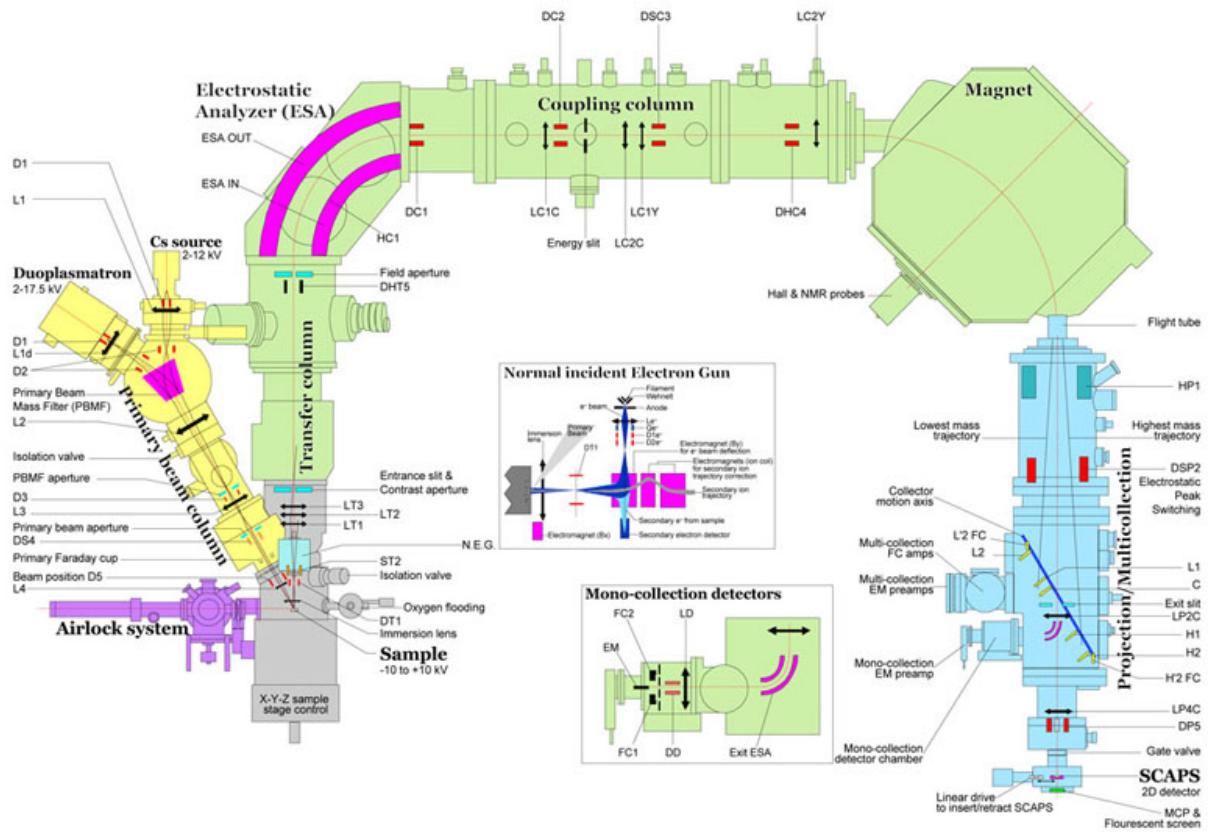


Fig.4 – Schematic diagram of IMS-1270, a magnetic sector instrument.
Courtesy of Cameca instruments.

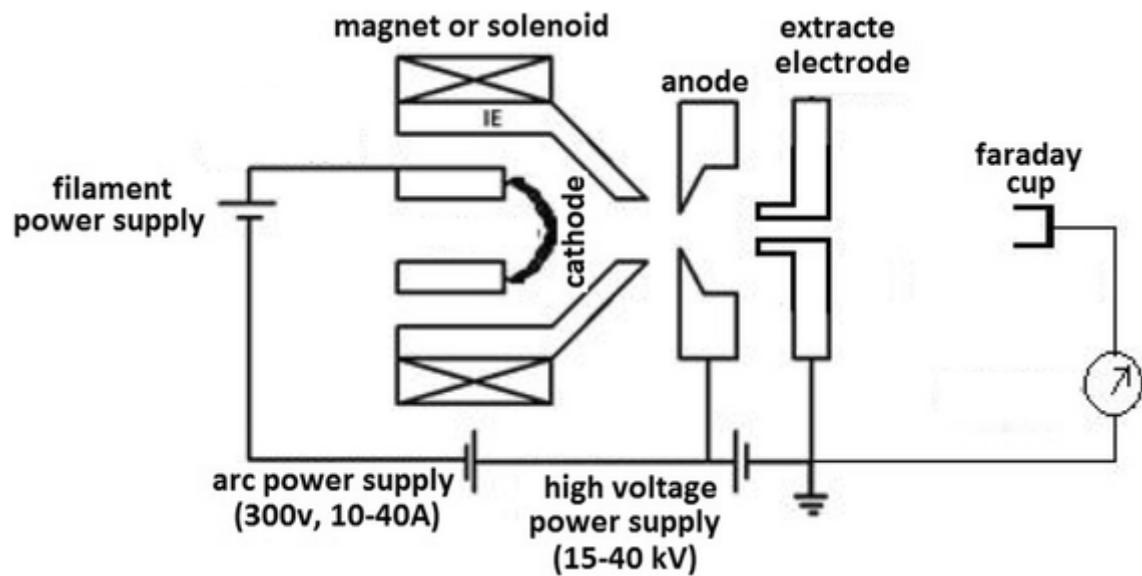


Fig. 5- Schematic of Duoplasmatron, a source for Oxygen. (Ref. 6).

- | | |
|--|------------------------|
| ① High voltage input | ⑤ Tungsten plate |
| ② cesium chromate pellet (not reactive to air) | ⑥ Reservoir filament |
| ③ Reservoir | ⑦ Ionizer filament |
| ④ Ionizer | ⑧ Extraction electrode |

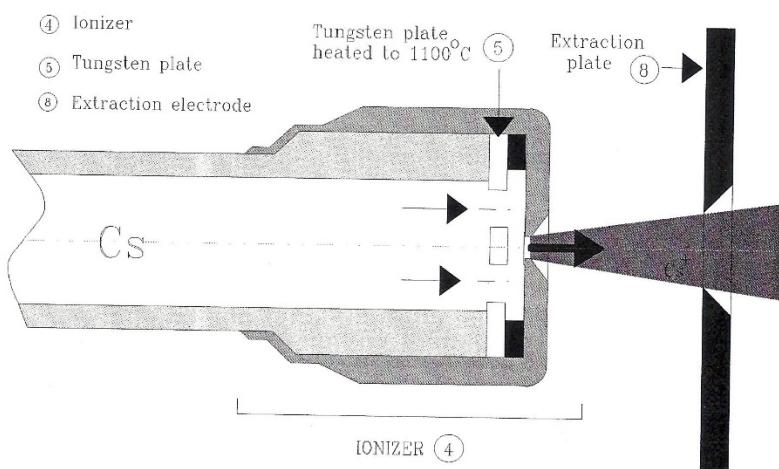
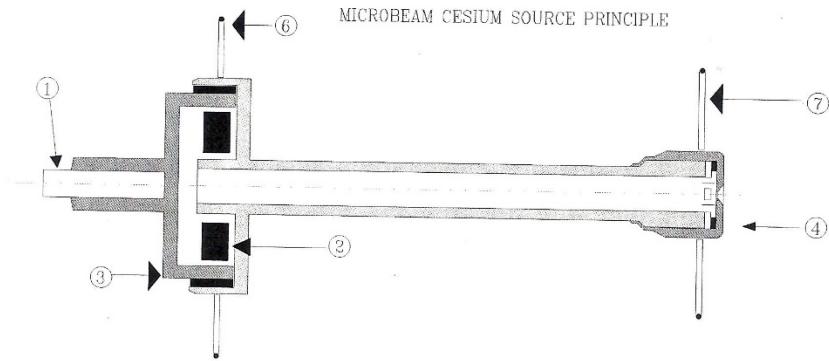


Fig.6 – A schematic of a Cs source. Bottom part shows the details of ionizer. (Ref.5 page 107).

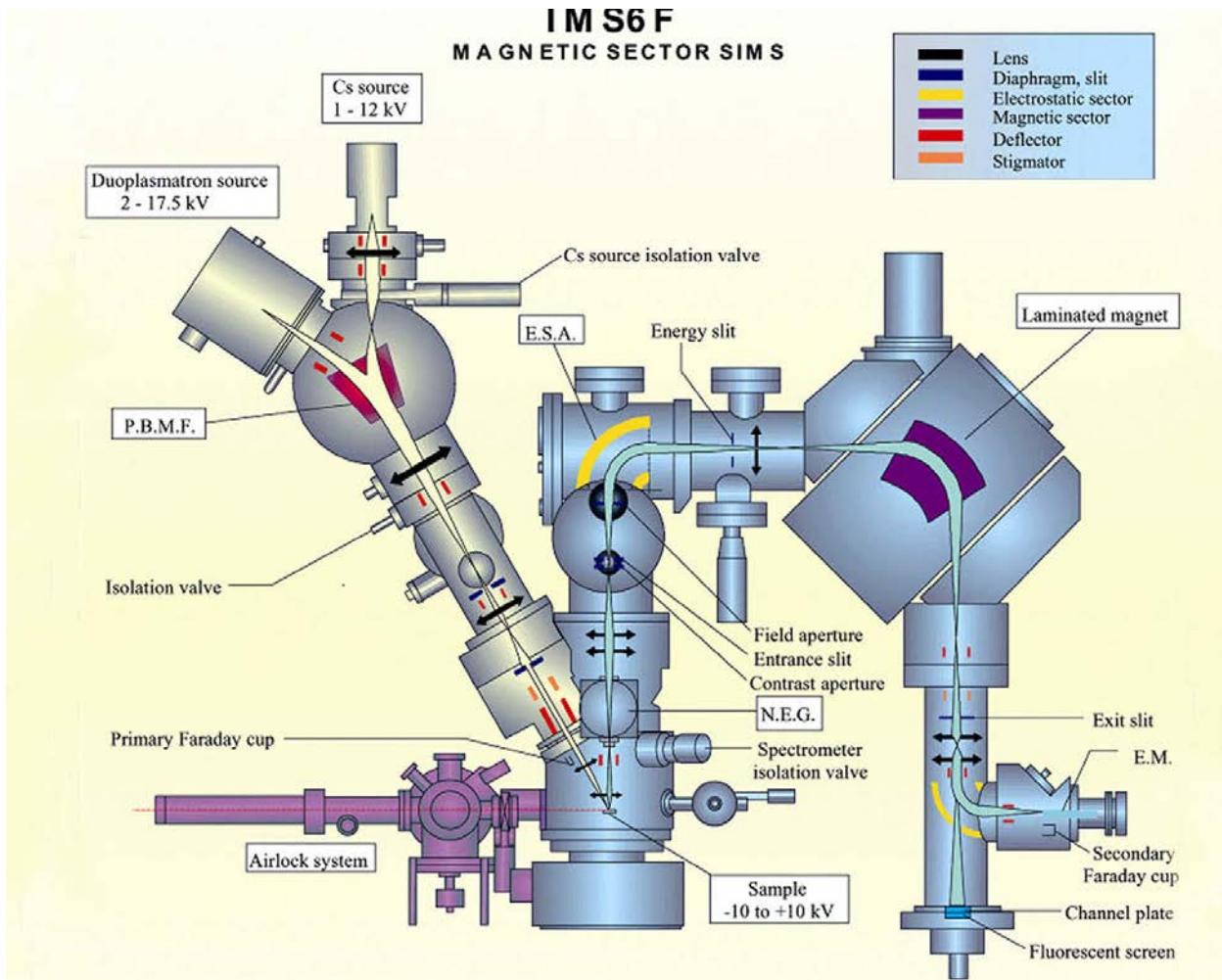


Fig. 7 – Secondary section of an IMS-6f made by Cameca Instruments.
The secondary section is in blue. The primary section is on left with a golden color. (Ref.2)

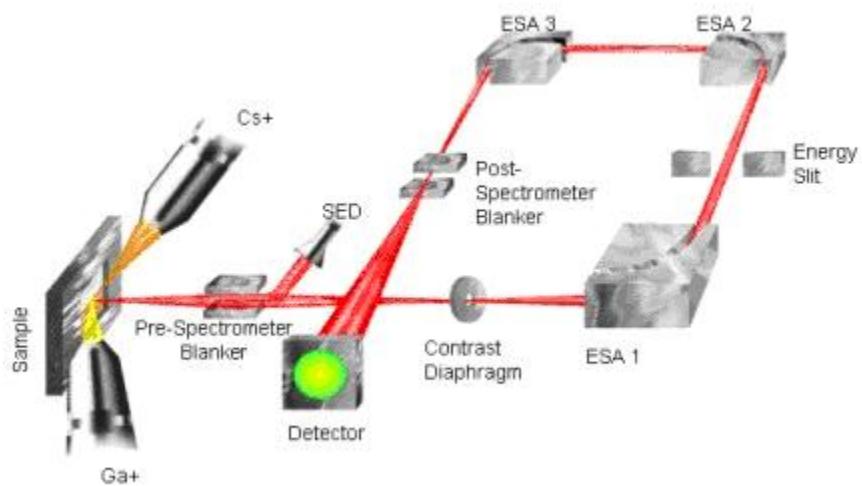
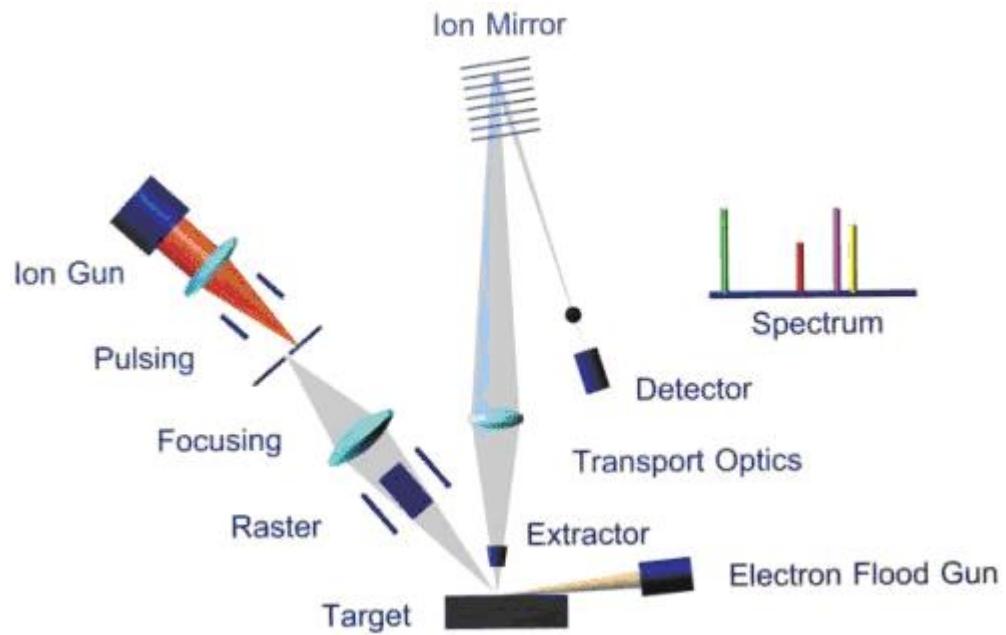


Fig. 8 – Schematics of two types of TOF SIMS. Top – Cameca – ION TOF design (Ref.7), Bottom – TRIFT TOF SIMS by Physical Electronics (Ref.8).

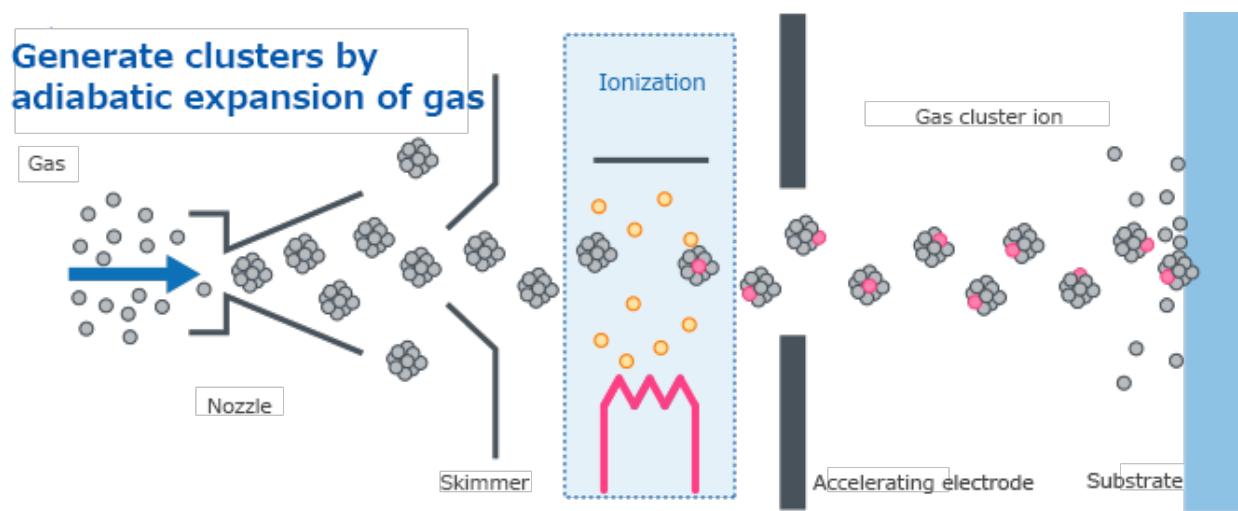
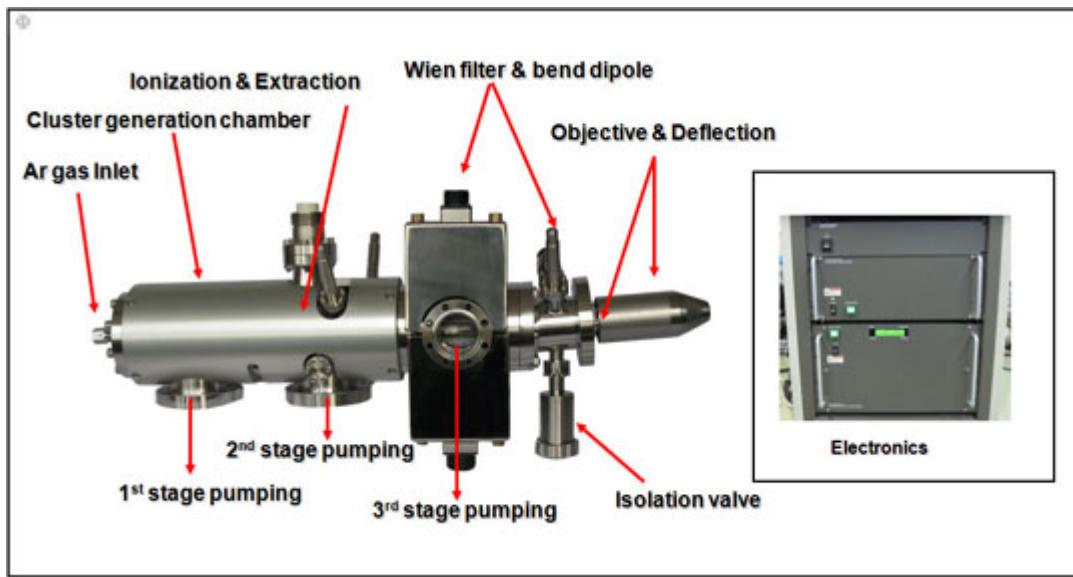


Fig. 9 – Cluster ion gun. Top – external view and Bottom-schematic of ion production. (Ref. www.ulvac-phi.com).

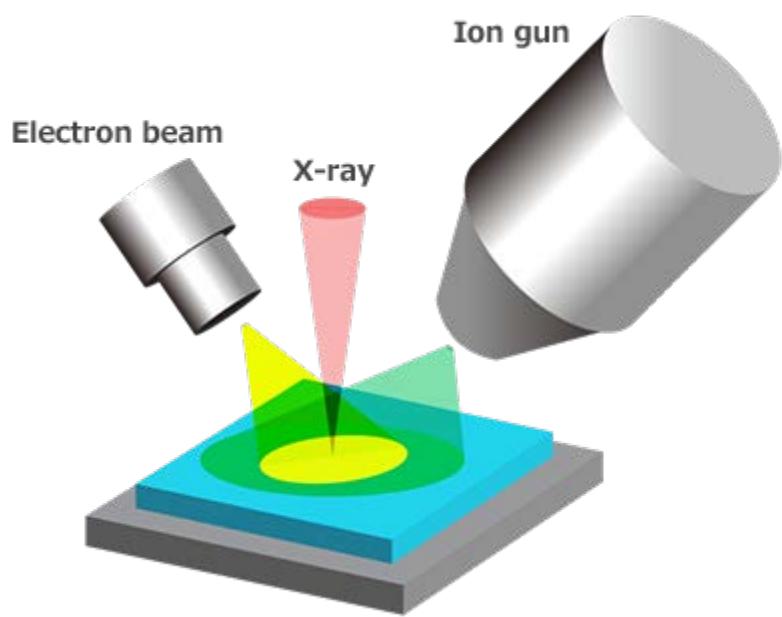


Fig.10 – Dual beam Charge neutralization. (Ref.
www.phi.com.)

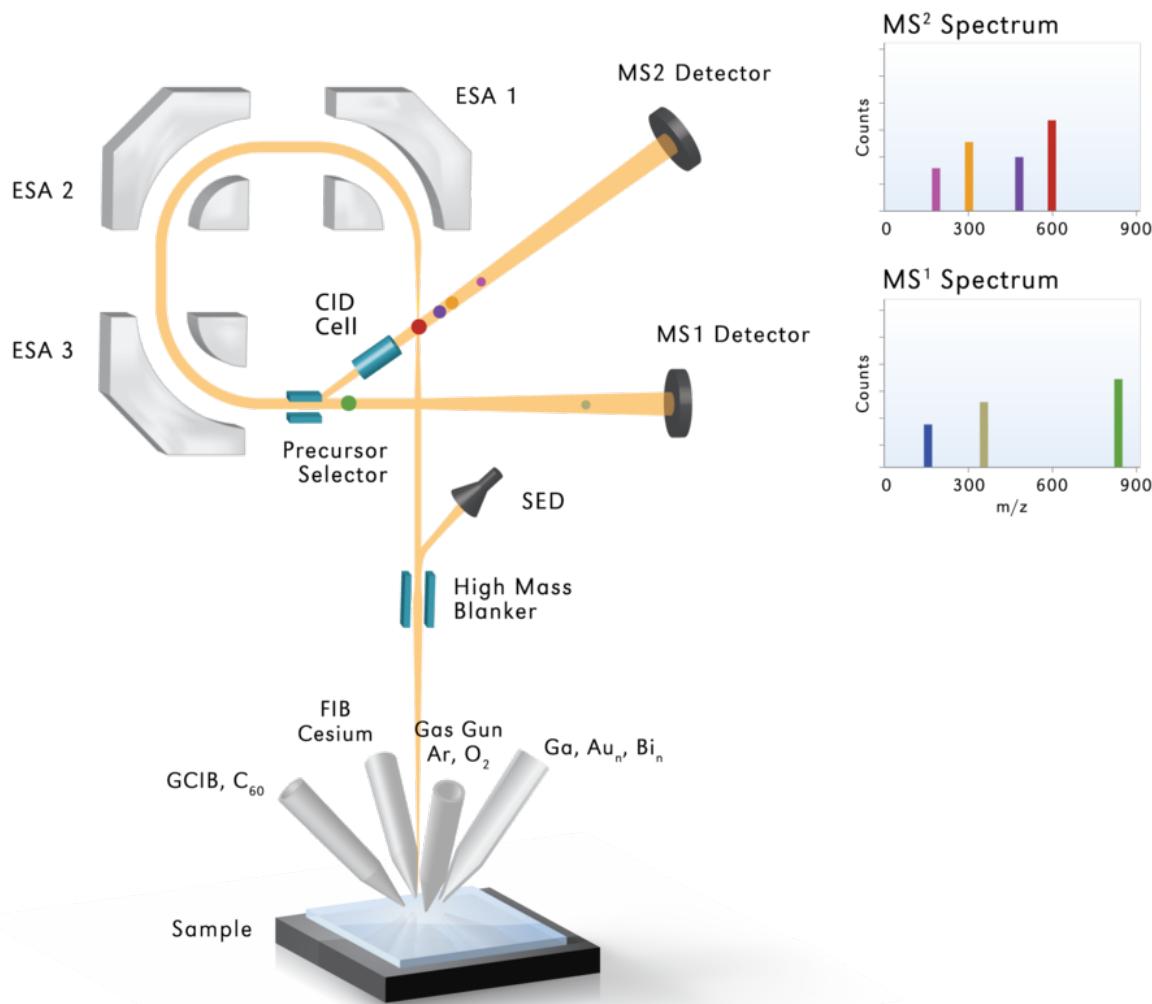


Fig. 11 – Schematic of a TOF SIMS with two MS detectors. Simultaneous detection is possible in both the detectors increasing the characterization capability of the TOF SIMS. See Section “Applications and Interpretation” for sample details (Example #2).

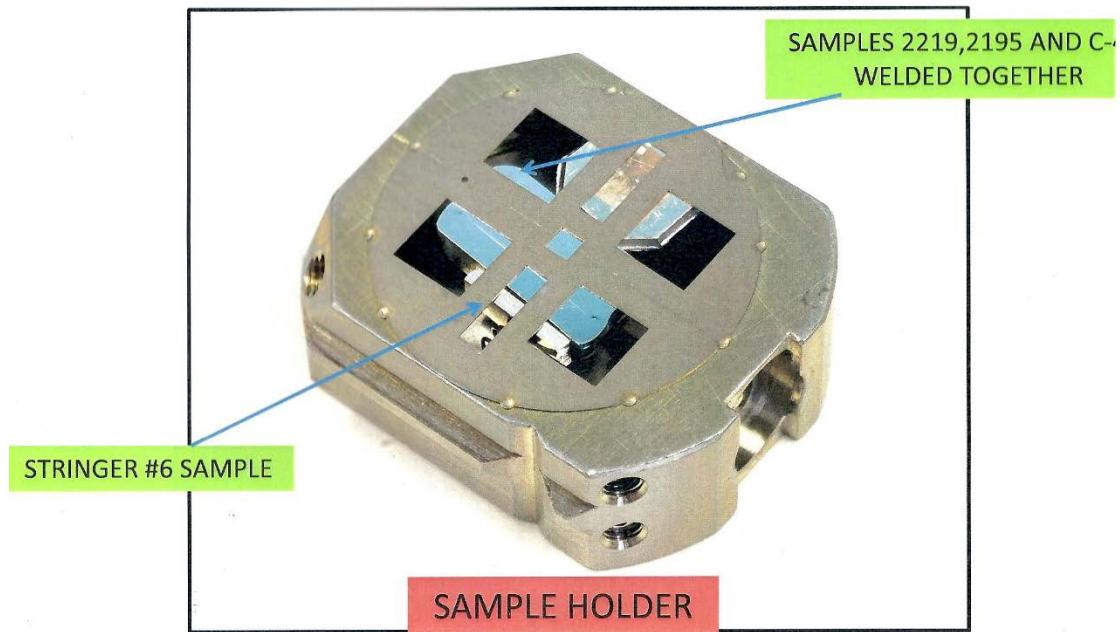


Fig.12 – A photo of the sample holder for Cameca IMS-6f with samples inside. The Cameca grid needed for beam alignment is on top-right of the sample. All samples are being supported by springs from the bottom. Sample details are shown in section “Applications and Interpretation”, example #2.

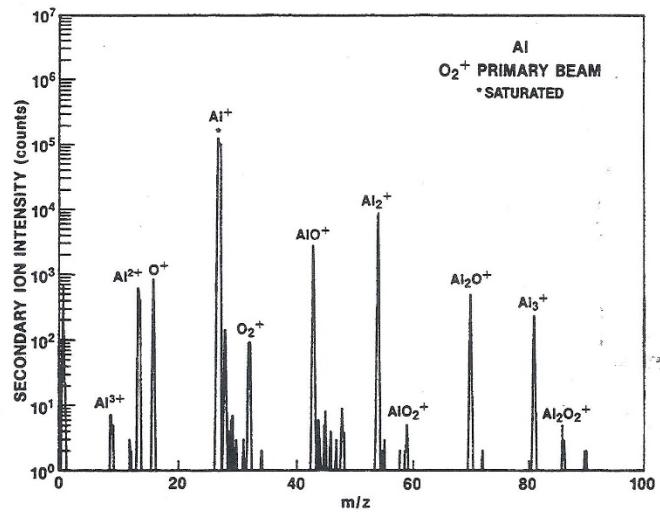


Fig. 13 – Spectrum from an Al sample using O₂⁺ beam. Secondary ions collected are all positive ions. (Ref 4, page: Appendix H-17)

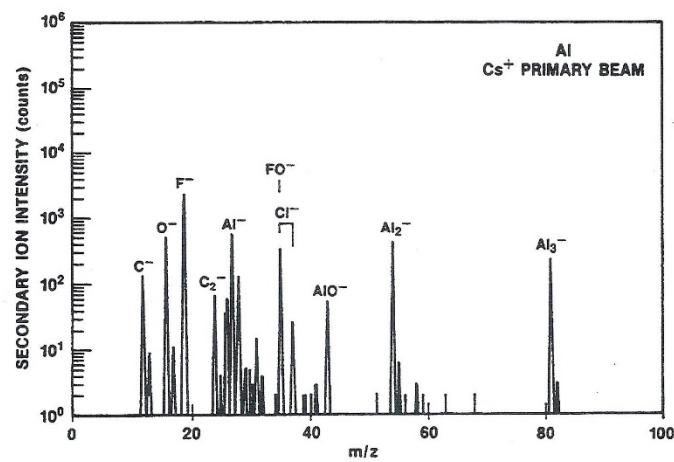


Fig.14 – Same as Fig.12 but analyzed with a Cs^+ primary ion. Secondary ions are collected are negatively charged species. (Ref. 4, page: Appendix H-17)

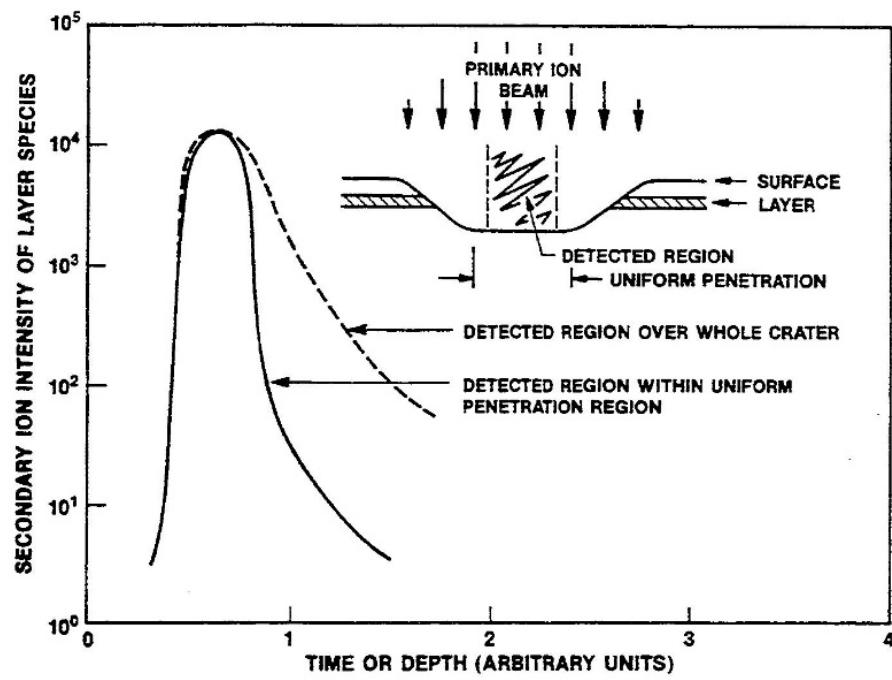
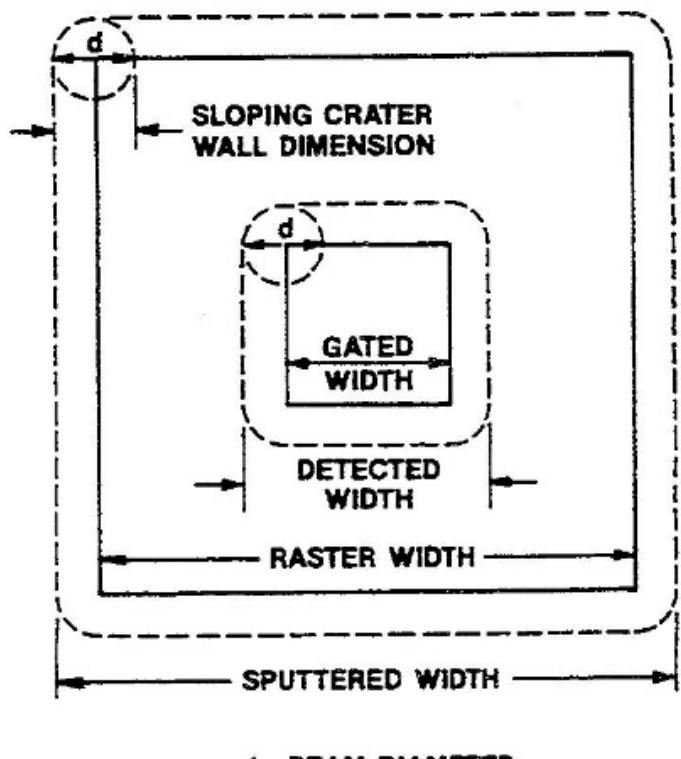


Fig.15 – Shows ideal area to be focused for depth profile analysis.
Also shows how the results vary if the entire crater is analyzed. (Ref.4, Fig. D on page I-9).



d=BEAM DIAMETER

Fig.16 – Detected area for ion probe operation at the bottom of the crater. Diameter d is added to gated length and width for area estimation. (Ref. 4, page 1.5-2).

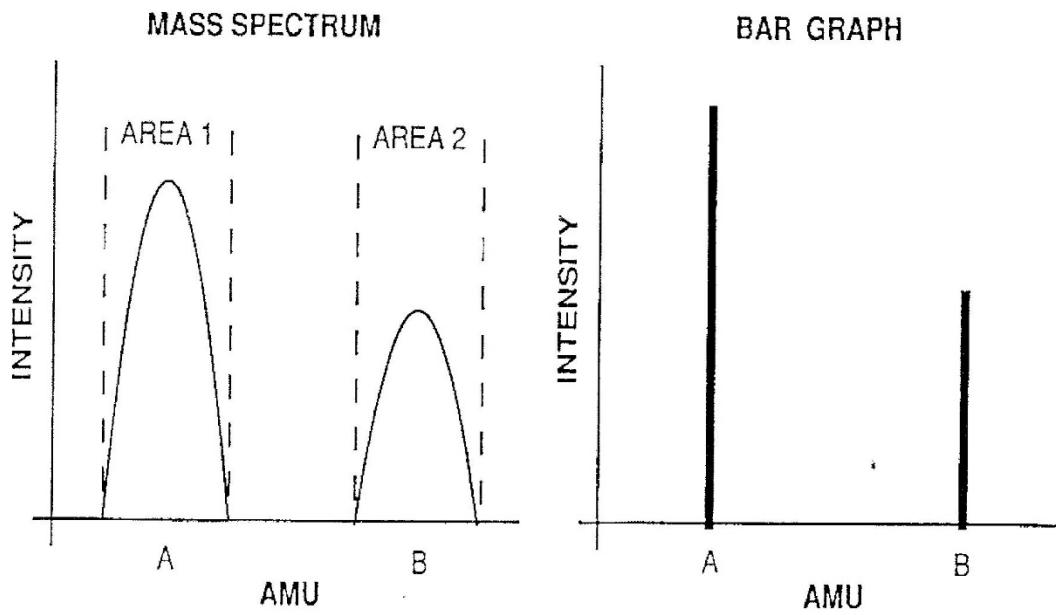


Fig.17 – Shows how the intensity is integrated in a bargraph spectrum from the mass spectrum. (Ref. 5, page 28)

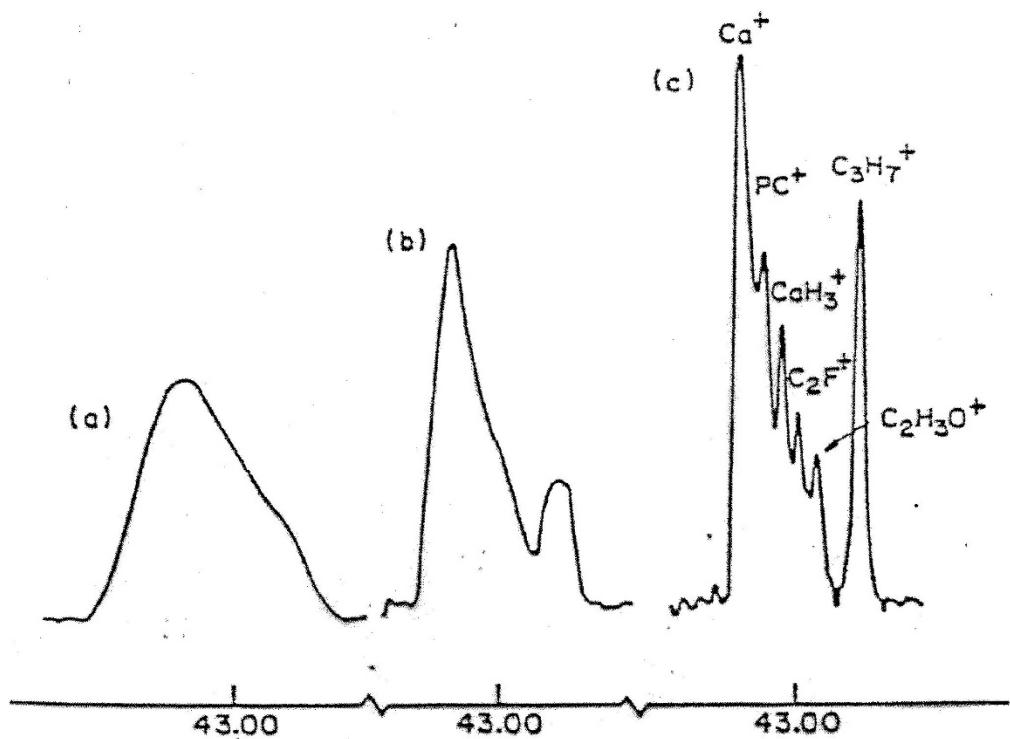


Fig.18 – Shows the effect of having a high-resolution machine. Mass 43 is acquired at (a) 300, (b) 1000, and (c) at 3000 resolution ($m/\Delta m$). (Ref. 5, page 42)

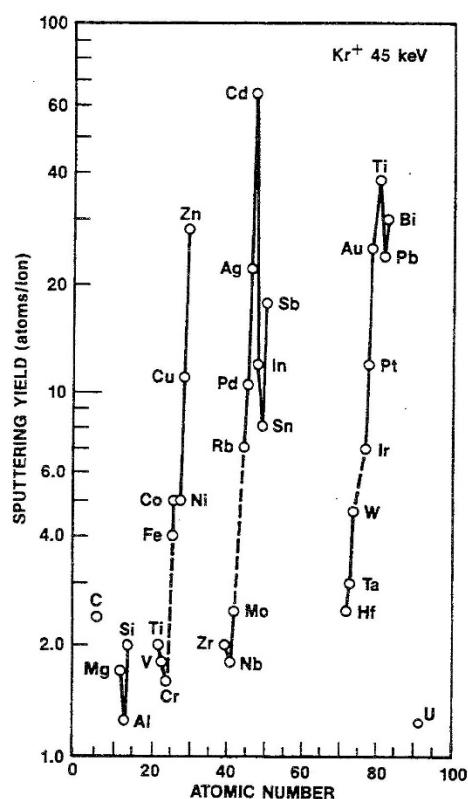


Fig.20 – Shows the dependence of secondary ion yield on the atomic number. Yield for Kr^+ primary ions at 45KeV. (Ref.4, Fig. 1.4 – A).

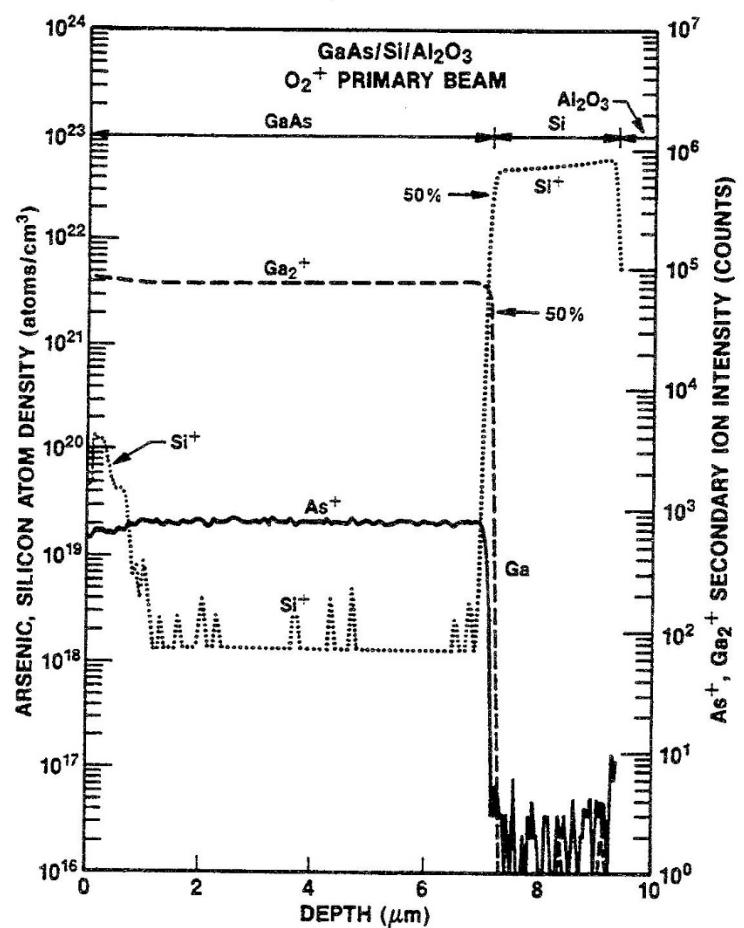


Fig.19 – Shows an example of elemental variations in depth profiling. It is a GaAs/Si/Al₂O₃ structure. As and Si are quantified and Ga and As are shown as counts. (Ref. 4, page 2.1-7).

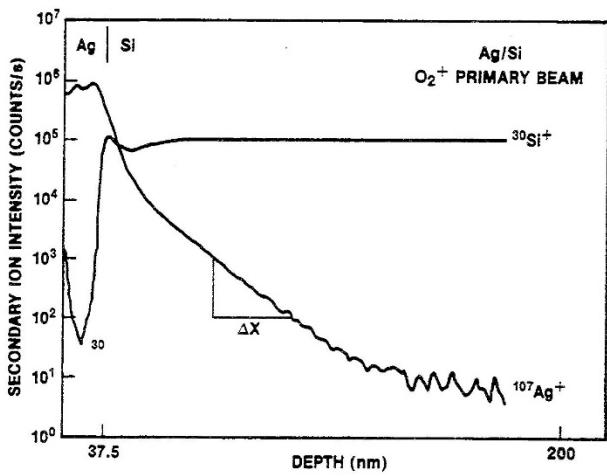


Fig.21 – Determination of decay length for Ag on Si. The decay length shown here is for an order of magnitude decrease in intensity. (Ref. 4, page 2.1 – 6)

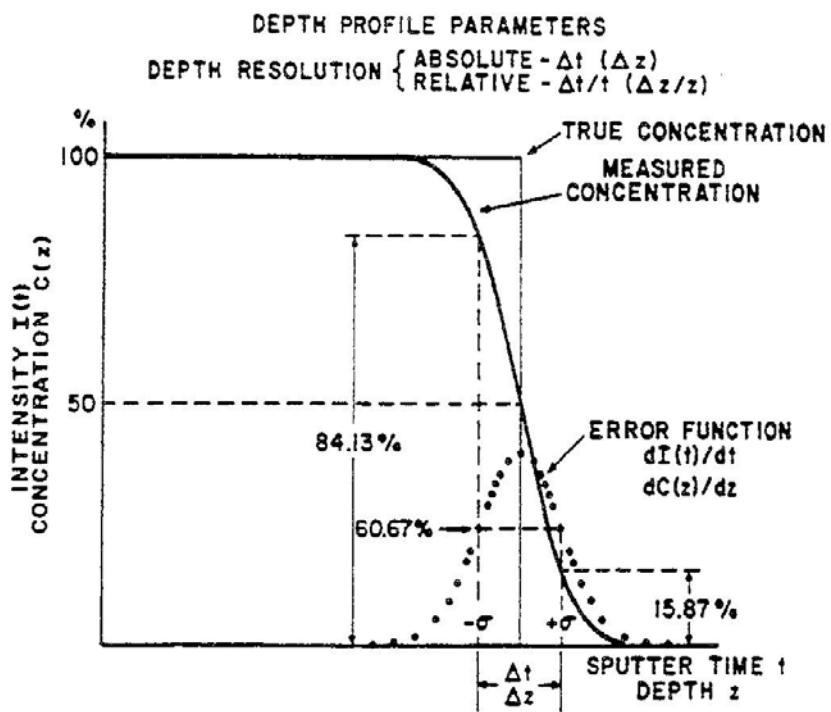


Fig. 22 – Shows Depth profile parameters for an analysis of an interface described in terms of sputter time and depth. The error function is the derivative of the interface curve and the $+/- \sigma$ points correspond to 84 and 16 percent of maximum intensity. (Ref. 4, Fig. 2.1E).

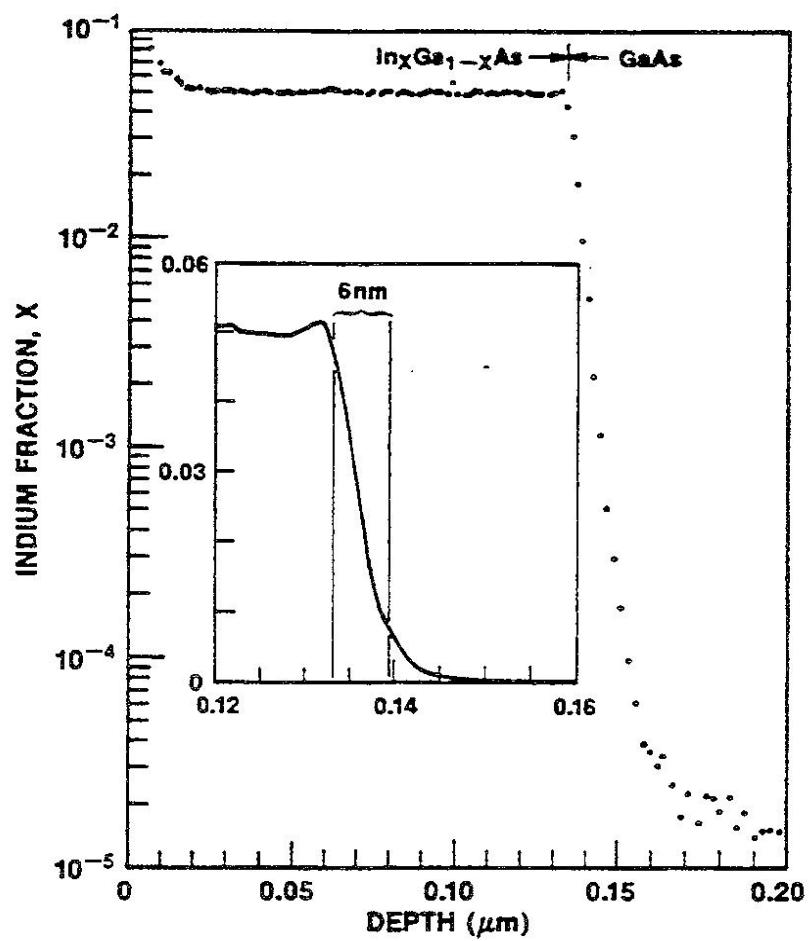


Fig. 23 – Interface width determination for a thin IN Ga As layer on a GaAs substrate. Analyzed using a quadrupole instrument. (Fig.2.1F in ref. 4).

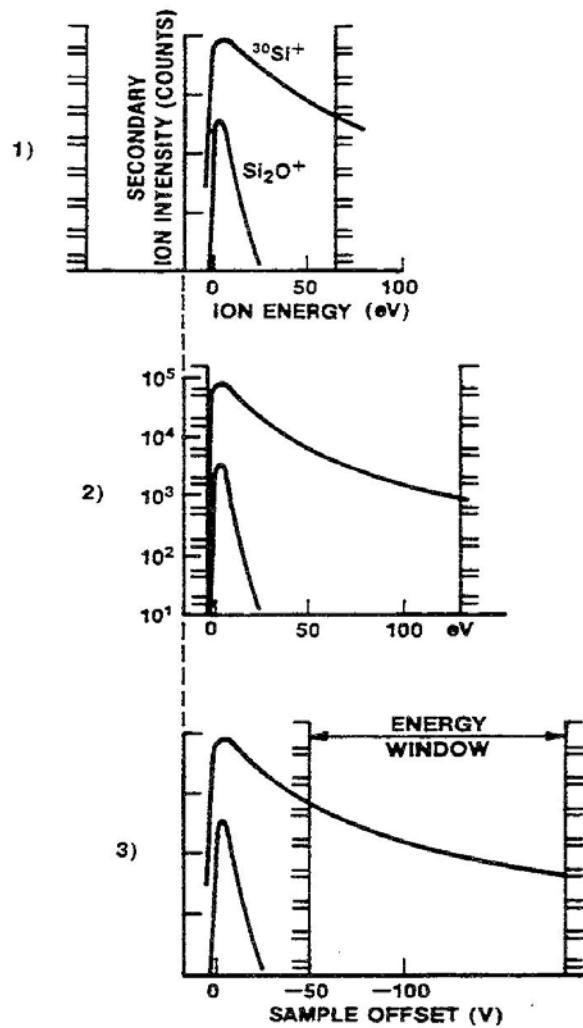


Fig. 24 – Placement of the energy slit (see Fig.7) to achieve maximum separation between the Si and molecular ion Si_2O (interfering with Si ion) to get proper Si counts. (1) shows both distribution and no slit translation, (2) partial energy window translated, and (3) complete translation and equivalent voltage offset to get proper Si counts without interference. (Ref. 4, page 1.8-4).

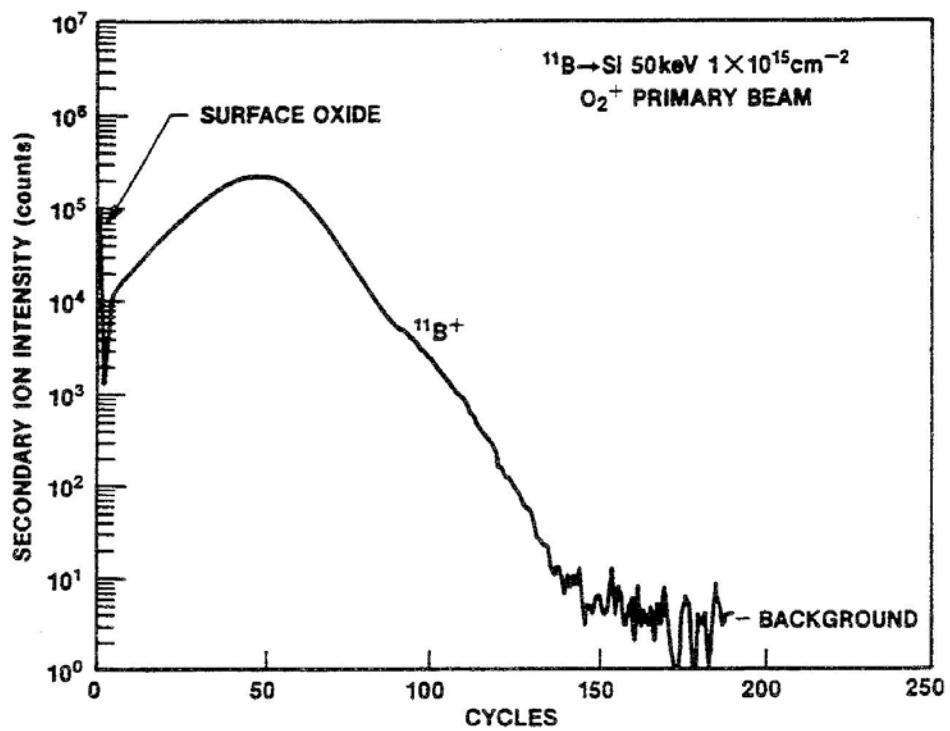


Fig. 25 – Raw data obtained from Cameca IMS – 3f machine for a depth profile of ^{11}B ion implant into Si. (Ref. 4, page 3.1-9).

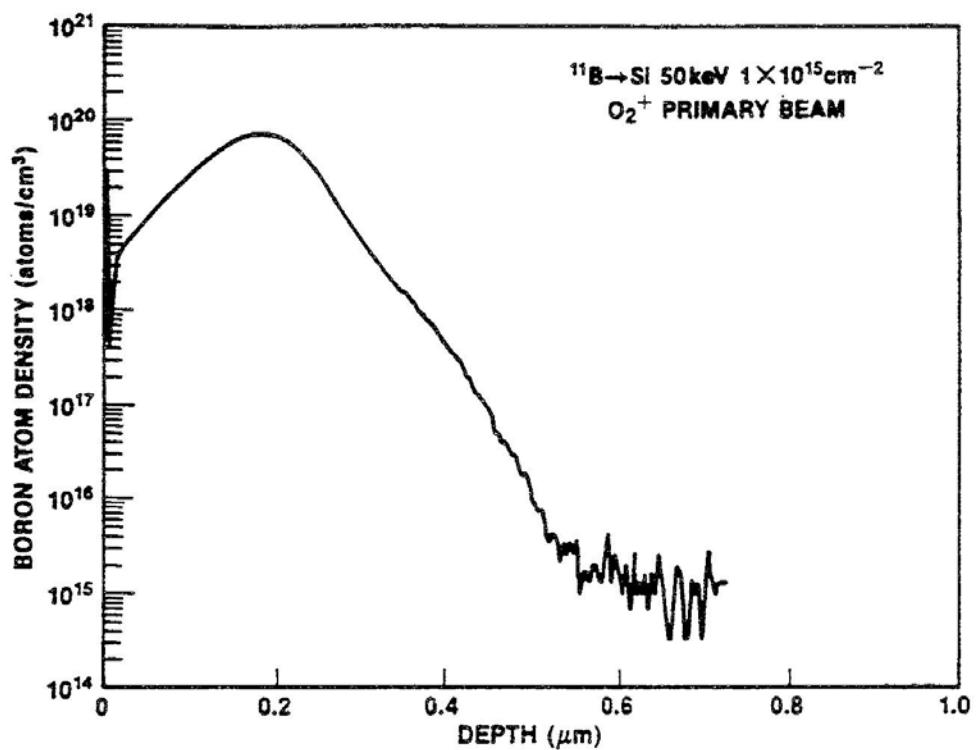


Fig. 26 – For the same raw data as in Fig. 25
but now reduced to atomic density. (Ref. 4,
page 3.1-9).

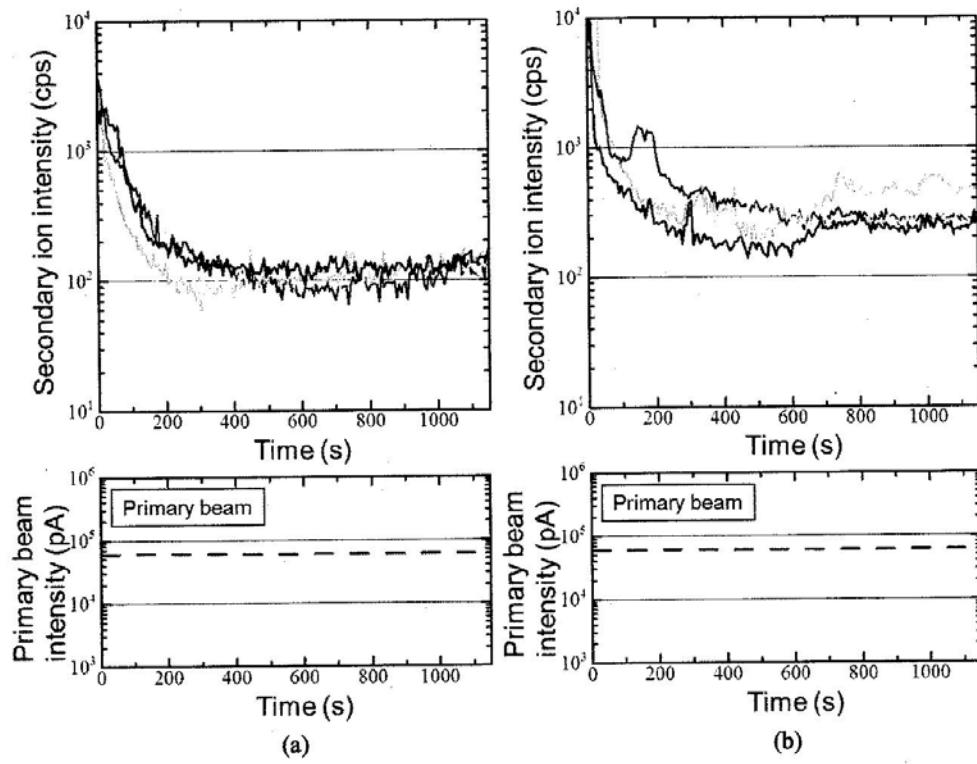


Fig. 27 – SIMS profiles and primary beam intensities (bottom graphs) of uncharged (a) and charged (b) steel samples. (Ref. 10)

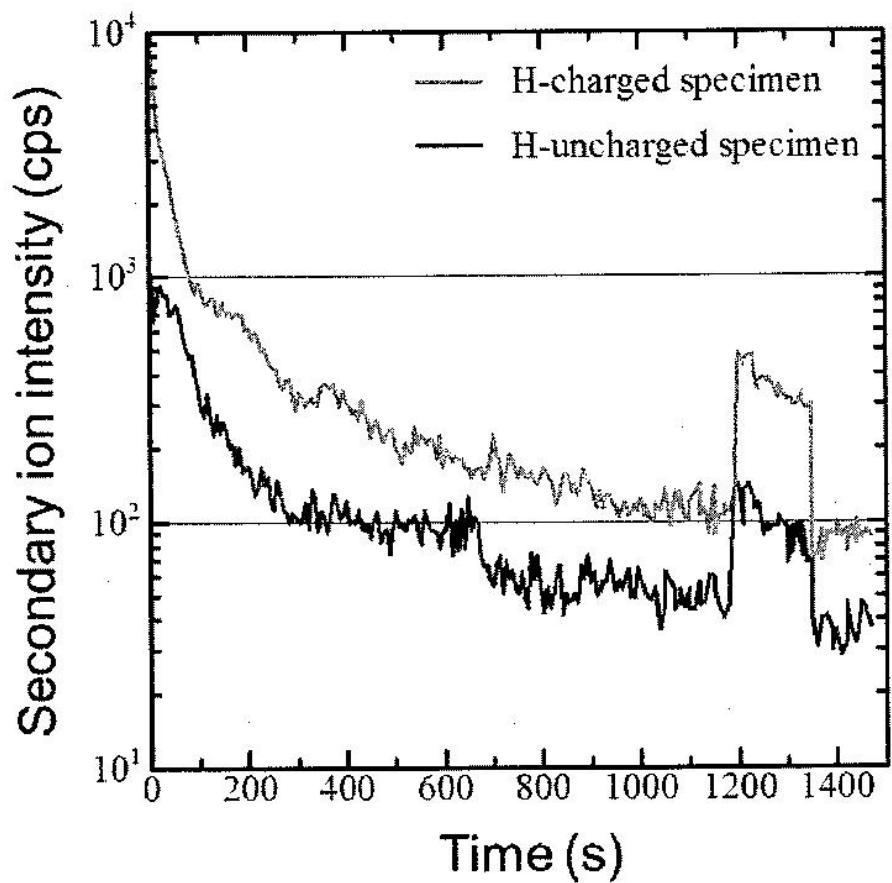


Fig. 28 – Secondary ion intensities for both charged and uncharged specimens. Between 1200 and 1350 seconds, the raster size was reduced from 150 to 50 μm . The reduction in raster size increased intensity. (Ref. 10).

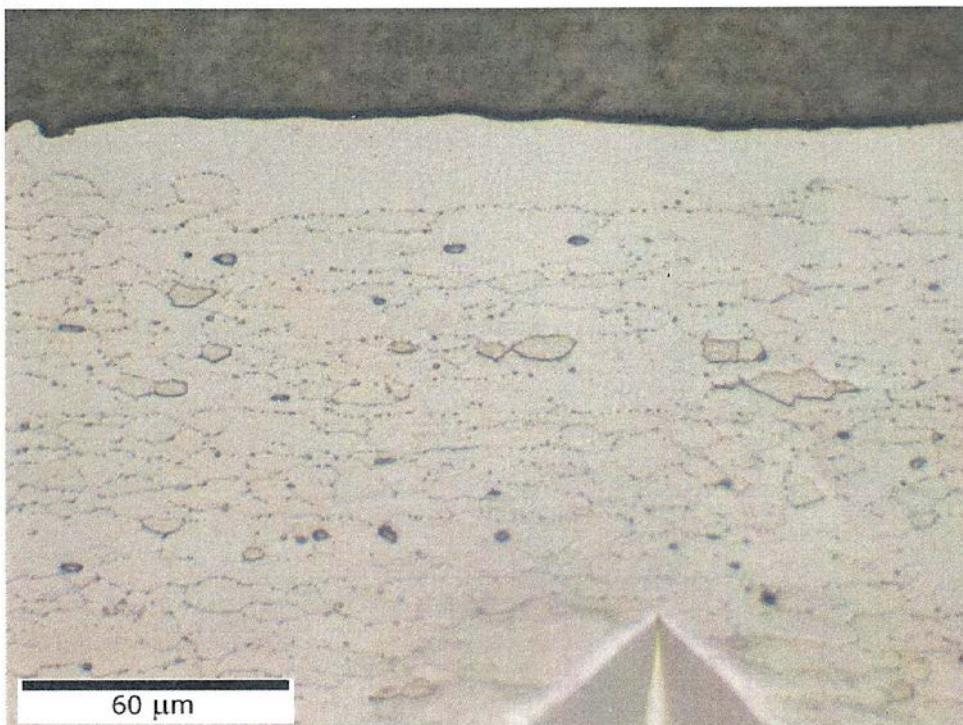


Fig. 29 – Microstructure of the Al stringer showing large grains at the surface. A diamond hardness impression at the bottom is for location identification needed for subsequent analysis. (Ref. NASA Lab.)

NASA MSHE

Stringer #6 sandwiched between 2219 (left) and C-458 (right)

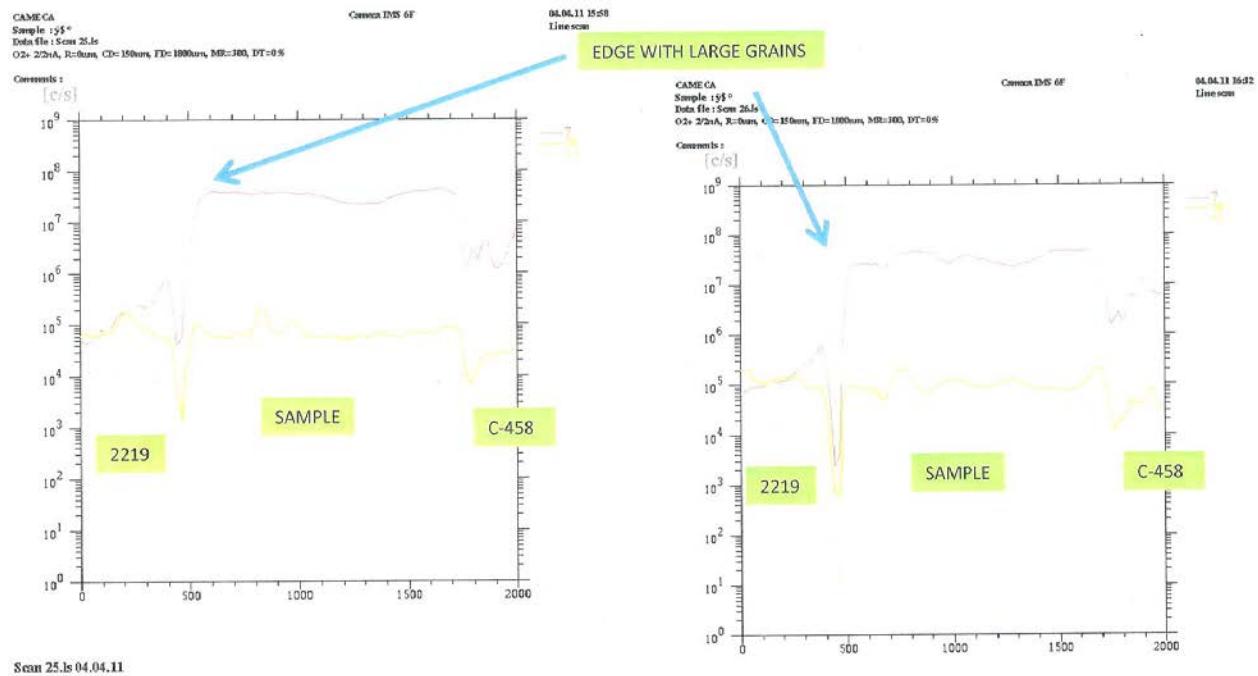


Fig. 30 – Shows linescans for Li at the edges of stringer where large grains existed. Sharp falls in Li counts indicates no Li loss near large grains. (Ref. NASA Lab)

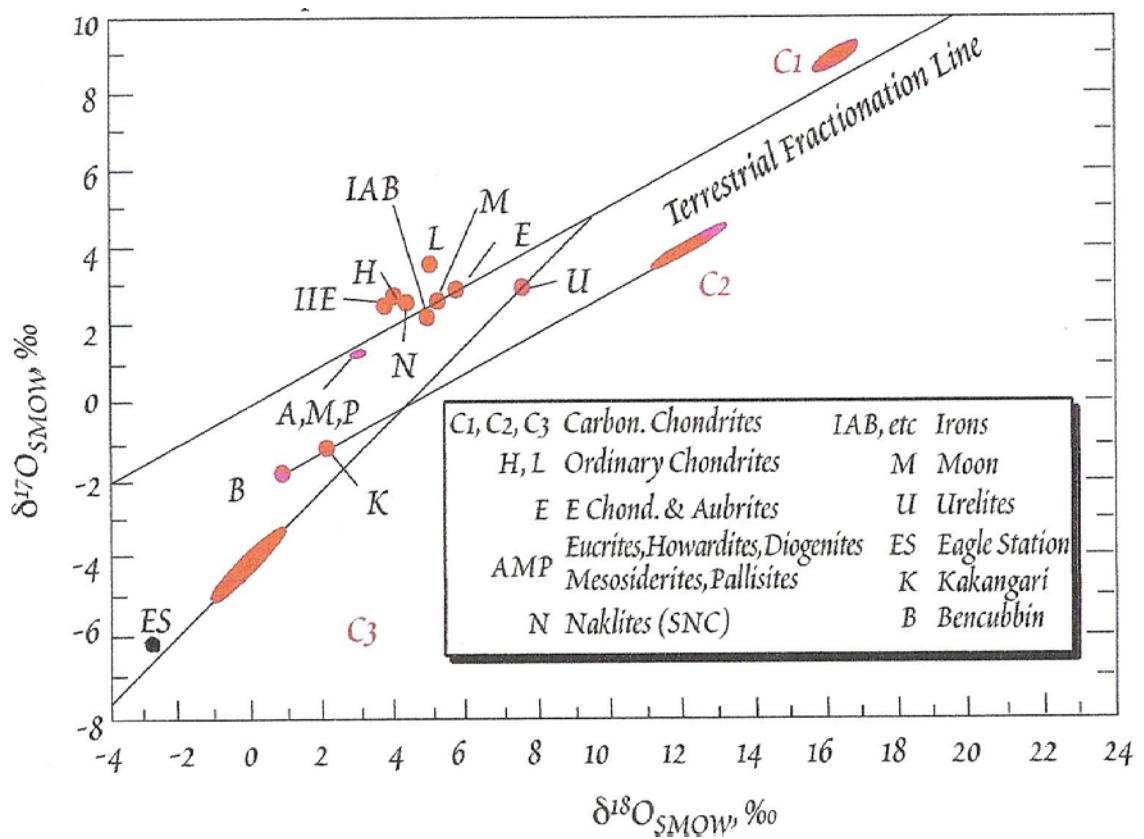


Fig. 31 – Oxygen isotope variations between terrestrial and extraterrestrials objects. (Ref. 12).

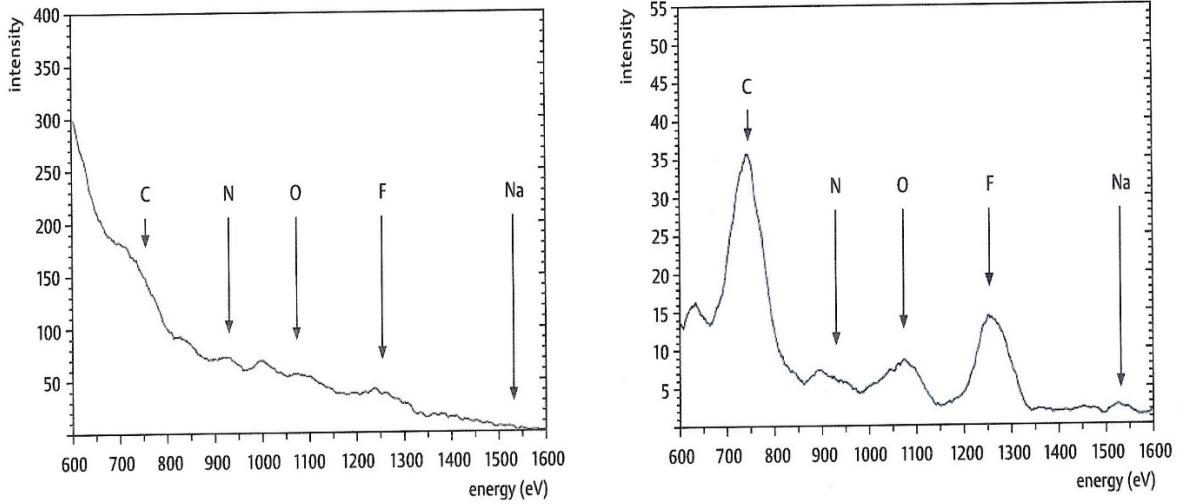


Fig. 32 – LEIS spectrum of a polymer with (right) and without (left) time-of-flight mass filtering. Mass filtering improves background and peak shapes. (Ref. 13)

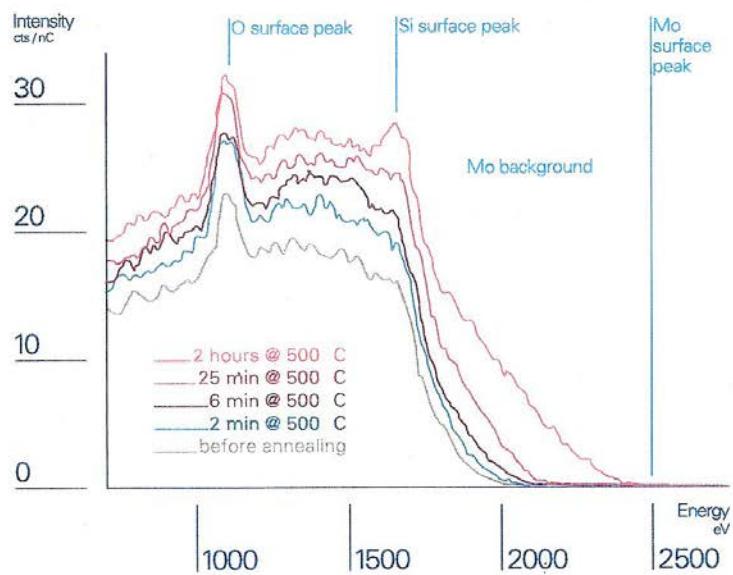
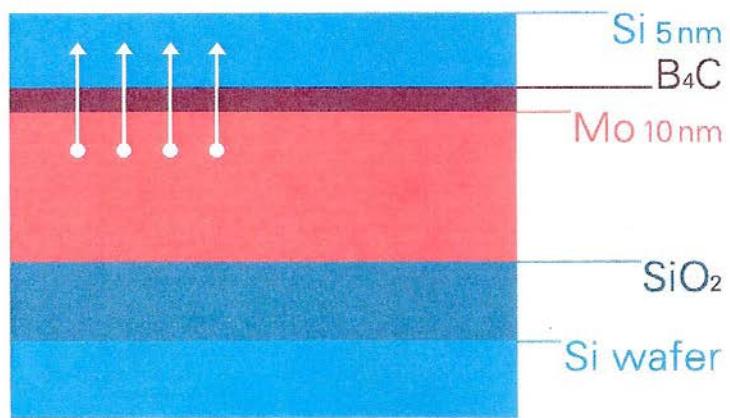


Fig. 33 – Diffusion measurements using the LEIS (Low energy ion Scattering) technique. Top shows the various layers in a Si wafer and the bottom shows the energy of scattered secondary ions. Mo diffusion is seen in annealed samples. (ref. 13).