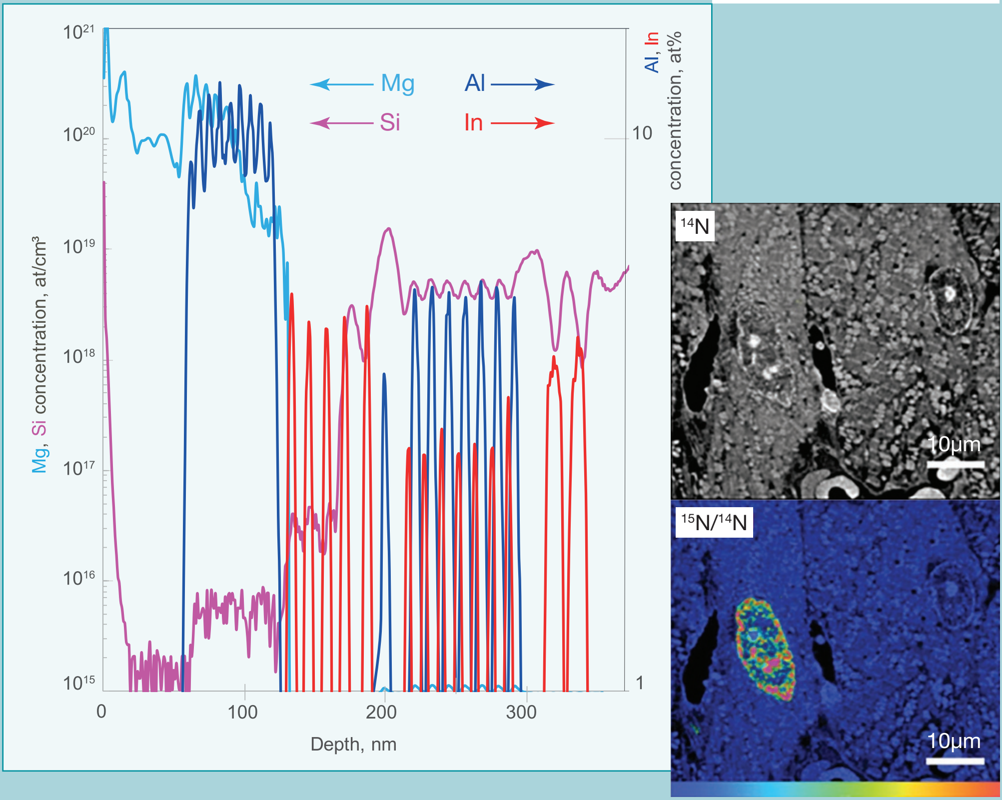
MICROSCOPY AND ANALYSIS



Dynamic Secondary Ion Mass Spectrometry

Essential Knowledge Briefings

First Edition, 2019

CAMECA® SCIENCE & METROLOGY SOLUTIONS
AMETEK® MATERIALS ANALYSIS DIVISION

Front cover images:
Left: Mg, Si, Al, In depth profiles in light-emitting diode (LED) structure. Dynamic SIMS achieves excellent depth resolution and detection limits for matrix species as well as for p and n-type dopants.
Right: Study of cardiomyocyte cell cycle activity in the exercised heart. ^{15}N-thymidine (labeling DNA) was administered continuously for eight weeks to young adult mice undergoing voluntary wheel running versus sedentary activity. Mass ^{14}N image shows histological details, while ^{15}N/^{14}N image demonstrates nuclear ^{15}N labeling (red, 150% above natural ratio) of a cardiomyocyte while the cytoplasm and other cells are at the natural abundance level (blue, 0% above natural ratio). (Right image reproduced from Vujic A, Lerchenmüller C, Wu T-D, *et al*. Exercise induces new cardiomyocyte generation in the adult mammalian heart. *Nat Commun* 2018;9:1659. © The Author(s). http://creativecommons.org/licenses/by/4.0/)

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About Essential Knowledge Briefings

Essential Knowledge Briefings, published by John Wiley & Sons, comprise a series of short guides to the latest techniques, applications and equipment used in analytical science. Revised and updated annually, EKBs are an essential resource for scientists working in both academia and industry looking to update their understanding of key developments within each specialty. Free to download in a range of electronic formats, the EKB range is available at www.essentialknowledgebriefings.com

INTRODUCTION

Surface analysis is the cornerstone of a wide range of scientific disciplines, from materials science and electronics to geology and biology. Localized analysis of solid surfaces can be performed by a range of physical and chemical techniques, with secondary ion mass spectrometry (SIMS) being one of the most popular.

First commercialized by CAMECA in the early 1960s, SIMS involves bombarding the surface of a sample with a focused ion beam and collecting the ejected secondary ions that are representative of the sample surface composition, as shown in Figure 1. SIMS consists of analyzing these secondary ions with a mass spectrometer. Still the most sensitive surface analysis technique available, SIMS provides localized elemental, isotopic and molecular characterization of the sample surface. It can be applied to any solid material that can be maintained under high vacuum, including insulators, semiconductors, metals and even biological samples.

There are two main modes of SIMS analysis:

In static SIMS, a low-dose primary ion beam is applied to a sample, generating atomic and molecular ions from the top monolayers. Static SIMS provides information on the organic and inorganic top surface composition with a main focus on *molecular* characterization. Time-of-flight (TOF) mass spectrometers are well adapted for static SIMS analyses, with their capability for analyzing all masses in quasi-parallel mode, up to a few thousand atomic mass units (amu).

Dynamic SIMS utilizes a high-dose ion bombardment that erodes successive layers of the sample, providing information

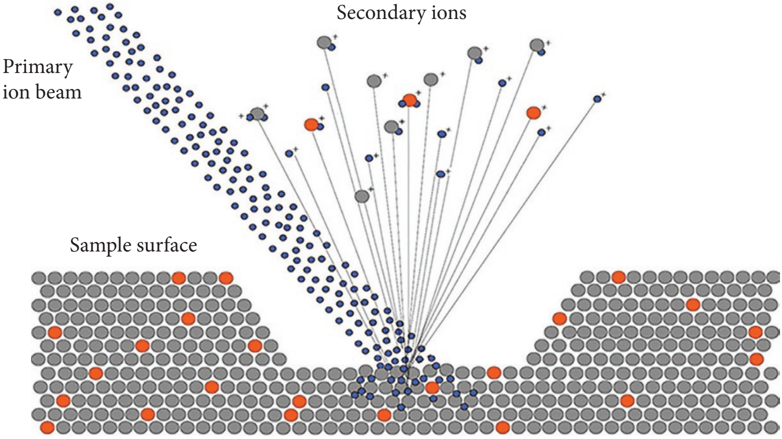


Figure 1. Schematic illustration showing the SIMS sputtering and ionization process. The incident primary ions implant into the surface layers of the sample and trigger a cascade of atomic collisions causing local ejection of atoms, and clusters of atoms, from the surface. A small fraction of the sputtered species will be ejected spontaneously ionized (called secondary ions to distinguish from the incident primary beam). They are collected, then separated according to their mass-to-charge ratio, thus providing elemental and isotopic composition of the analyzed area

about the bulk elemental and isotopic composition over depths that can range from nanometers to tens of micrometers. It is a *destructive* technique by its nature as it is based on sputtering of material. In order to enhance the ionization yield, dynamic SIMS uses *reactive* primary ions (mostly oxygen or cesium) with an energy range between 100eV and a few tens of keV, which split molecules on the surface, so it provides mostly *isotopic* and *elemental* information. Elemental concentration detection limits can reach *parts per billion* (ppb) for many elements. To achieve such sensitivity, a high data rate is mandatory, achieved with *continuous sputtering* (DC mode), the mass analysis typically performed with a magnetic sector or a quadrupole mass spectrometer. Dynamic SIMS can also be performed using a TOF analyzer by combining a low-energy ion beam for sample erosion and a high-energy, pulsed primary ion beam for analysis, but with poorer sensitivity or lower data rate.

In recent years the surface specificity of static SIMS molecular analysis has been expanded to depth profiling using large molecular primary ions (*eg* Ar_{2000}^+). Their use is mostly restricted to organic materials due to a low sputtering yield for inorganic materials. This field is considered here as an extension of static SIMS and will not be treated in this booklet, concentrating on (elemental and isotopic) dynamic SIMS.

This Essential Knowledge Briefing (EKB) will introduce dynamic SIMS in greater detail. It will outline its development, the major components of a typical dynamic SIMS instrument, its major advantages over alternative surface analysis techniques such as electron probe microanalysis (EPMA), and how and where it can be used. Four case studies will provide examples of how SIMS is used in the real world, by leaders in fields spanning life science, materials science and cosmochemistry.

The briefing will end by looking at the future of dynamic SIMS technology, including advances in detection sensitivity and spatial resolution. It will discuss directions that will allow the technique to be applied to a wider range of samples than ever before.

HISTORY AND BACKGROUND

SIMS is based on one simple process: the emission (or sputtering) of secondary ions from the surface of a solid sample bombarded by primary ions, a phenomenon first observed in the early 1900s. The secondary ions emitted from the sample are analyzed and identified by a mass spectrometer. Early prototypes of SIMS were developed in the 1940s, but the first true SIMS instruments weren't built until the 1960s.

In the USA, a team sponsored by NASA (Herzog and Liebl) developed an early dynamic SIMS instrument to analyze Moon rocks. Around the same time, at the University of Paris-Sud in France, Raimond Castaing and his PhD student Georges Slodzian created their own dynamic SIMS instrument, based on a magnetic sector mass spectrometer and an argon primary ion beam bombardment. This first design was taken forward by instrument manufacturer CAMECA and commercialized in 1968. In 1977, the CAMECA IMS 3f, based on a double-focusing magnetic sector mass analyzer developed in collaboration with Georges Slodzian, was launched. Since then, variations of this instrumentation and other specialized SIMS instruments have been developed by CAMECA: the IMS Wf/SCU provides ultra-low impact energy for semiconductor applications, and large-geometry SIMS instruments (IMS 1300-HR^3 and previous models) provide high transmission at high mass resolution for analysis of geological and environmental samples. The NanoSIMS, developed with Georges Slodzian and the ONERA institution, offers optimized lateral resolution and multicollection for a wide range of applications including biology.

In dynamic SIMS, continuous, high-dose primary ion bombardment is used to erode the sample layer by layer, allowing for bulk analysis and depth profiling. Reactive primary ion beam species – oxygen and cesium are commonly used – enhance the ionization yield by several orders of magnitude, enabling detection limits down to ppb level for many elements. The magnetic sector analyzer provides high mass resolution, allowing the elimination of mass interferences, and offers the best sensitivity of all the analyzers for fast in-depth analyses.

A high-performance dynamic SIMS instrument comprises the following main components:

Vacuum: ultra-high vacuum is mandatory to prevent sample contamination and to minimize secondary ion collision with interfering gases as they travel through the mass analyzer. The pumping system in the analysis chamber should be efficient for residual gases (*eg* H_2, H_2O, CO_2, N_2, O_2) to reduce sample surface adsorption affecting detection limits of light elements. Residual gases also affect the measurement of other species through hydride and oxide interferences (*eg* ^{30}SiH–^{31}P) and degrade isotopic ratio precision of atmospheric species (*eg* D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$). The vacuum conditions can be created by a range of pumps, including turbomolecular pumps, ion pumps and titanium sublimation pumps, and can be optimized by degassing of the analysis chamber through high temperature baking. With these technologies, the resulting vacuum in the analytical chamber can reach the low 10^{-10} mbar range.

Ion source: the ion source generates the primary ions, which are focused onto the sample to bombard its surface and create the sputtering effect underlying SIMS. Dynamic SIMS employs two main types of primary ion species: oxygen ions for analysis of electropositive elements (*eg* Li, B, metals, REEs, uranides), and cesium ions (Cs^+) for analysis of electronegative elements (*eg* H, C, N, O, F, P, S).

Primary ion column: mass filtering is included to select the species of interest and remove parasitic species from the ion source. The primary ion beam is then focused with electrostatic lenses and deflected with electrostatic or magnetic deflectors. The beam can finally be rastered (scanned) over the sample surface. Primary beam rastering produces a flat-bottom crater, which is mandatory for depth profiling applications and which is also used for scanning ion imaging.

Collection optics: the sputtered ions emitted from the sample are accelerated, extracted and focused by an electric field. Only the secondary ions of a given polarity can be extracted at any time. In magnetic sector instruments, a high extraction field (few kV/mm) favors an early collection and maximizes the sensitivity of the technique. This design also includes transfer optics after the extraction optics in order to optimize the transmission (sensitivity) of the mass analyzer and the lateral resolution of the stigmatic, ion mass filtered microscope image that is available on some instruments (CAMECA IMS xf series). On such instruments, optical gating using mechanical apertures is employed to reduce crater edge effects that can degrade depth resolution and detection limits.

Mass analyzer: the mass analyzer separates the ejected ions by their mass-to-charge ratio. Dynamic SIMS nowadays mainly employs either a quadrupole or a double-focusing magnetic sector analyzer. A quadrupole mass spectrometer consists of four parallel cylindrical rods and separates ions by their passage through high-frequency oscillating electric fields. The double-focusing magnetic sector mass spectrometer design is based on the coupling of an electrostatic analyzer (energy dispersion) with an electromagnet (mass-to-charge ratio dispersion) through a coupling lens, as shown in Figure 2. This configuration brings ions of a given mass-to-charge ratio but slightly different energy to a focal point. Because the SIMS emission process produces a significant spread of ion energies, a double-focusing mass spectrometer design is required in order to obtain both high sensitivity

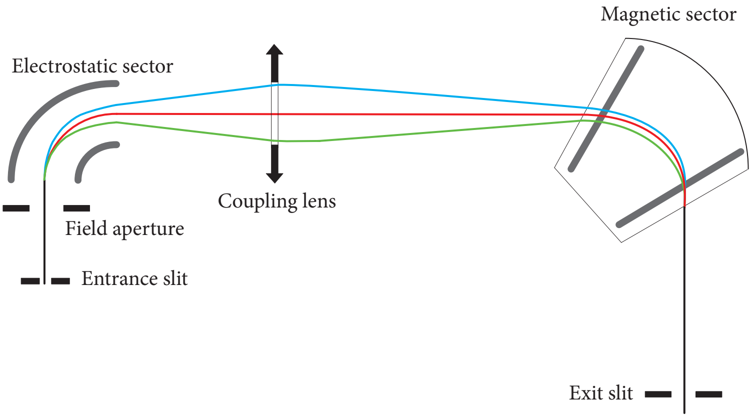


Figure 2. Schematic of double-focusing mass spectrometer configuration, showing paths of ions with different energies (colors) but constant mass-to-charge ratio: from the entrance slit through electrostatic and magnetic field sectors to the detector located after the exit slit. Energy dispersion is minimized thanks to the combination of the electrostatic sector, the magnetic sector and the coupling lens. Entrance and exit slits are adjusted to vary mass resolution. The field aperture allows the analyzed area to be optimized (optical gating)

and high mass resolution. This design includes an energy slit for energy filtering of the secondary ions (adjustable energy bandwidth and offset). A large energy bandwidth can be accepted (up to hundred eV), which makes slight surface potential variations negligible.

Projection optics: positioned after the magnetic sector, this allows the ions to be focused onto the detection system for ion counting. For some instruments (CAMECA IMS xf series), it also allows the mass-filtered microscope image to be projected on an image detector, which is used for instrument tuning or direct stigmatic SIMS imaging.

Detection system: some instruments work in mono-collection mode, elements being acquired one by one by scanning the field (magnetic or radio frequency). Larger magnetic sector instruments include multicollector capability – where an array of detectors allows simultaneous detection of different isotopes or elements – thus ensuring maximum sensitivity and analytical precision.

Detectors: Two main types of detectors are used with dynamic SIMS. For high secondary ion signal intensity (above a few million c/s), a Faraday cup is used to collect the secondary ions and measure the ion current flow. Faraday cups can quantify a large number of ions with high precision, but their response time is too long to be used for ion imaging. The electron multiplier detector is used for lower signals (below ~10^6 c/s). When an ion hits the first dynode of an electron multiplier detector, it initiates secondary electron emission, multiplied through multiple dynodes, resulting in the output of a short pulse of millions of electrons, which can be directly recorded.

It is one of the most sensitive detectors, enabling single ions to be counted, at a high data rate (up to 10^6 c/s range) and with very low background (*eg* <0.01 c/s) for a large dynamic range.

Dynamic SIMS offers many advantages over other surface analysis techniques, especially in terms of its *sensitivity*, as well as both *depth resolution* and *lateral resolution* that allow for depth profiling and surface imaging within a sample. It can detect nearly all elements in the periodic table, including hydrogen, and all isotopes. A wide variety of analyses can be performed (*eg* depth profiles, isotope ratio analyses, ion imaging).

These capabilities have ensured the regular use of SIMS in fields such as materials science, electronics, geology and biology. The semiconductor industry uses dynamic SIMS to measure dopant depth distribution, to identify trace contaminants in computer chips (see Case Study 4) and to analyze novel semiconductor materials (see Case Study 2). In geology, dynamic SIMS has been used to identify trace elements in minerals from terrestrial rocks or planetary bodies and to analyze the isotopic composition of light elements such as hydrogen (see Case Study 3). Dynamic SIMS is also increasingly being used in life sciences for studying a wide range of nanoscale biological processes, including imaging at cellular or intra-cellular level (see Case Study 1).

IN PRACTICE

Typical dynamic SIMS outputs include depth profiling, ion imaging, isotope ratio analysis and mass spectra.

The choice of primary and secondary beam species (and polarity) is made simultaneously: oxygen primary ions are generally used to investigate electropositive elements (*eg* metals, alkalis) as they enhance the ionization of positive secondary ions. Positive oxygen ions (O_2^+) are more common, but negative oxygen ions (O^-, O_2^-) are preferred when bulk insulator samples are to be analyzed as they minimize the charge build-up during sputtering of insulating materials. Cesium primary ions (Cs^+) are generally used to investigate electronegative elements (*eg* carbon, oxygen, phosphorus, sulfur), as well as for semi-quantification of matrix species using the MCs^+/MCs_2^+ cluster technique (see below).

The energy and angle of incidence of the primary ion beam will determine the ion beam penetration and mixing depth, thus lower impact energies are selected for optimized depth resolution. On the other hand, beam focusing improves with increased primary impact energy, thus providing better lateral image resolution.

The intrinsic high sensitivity of dynamic SIMS makes it ideal for detecting and localizing elements at trace level in a solid sample. The ability to accurately measure the species of interest may be affected by the presence of mass interferences (species of a similar mass, often molecular ions). On magnetic sector analyzers, most interfering species can be separated using either high mass resolution or secondary ion energy filtering (see below).

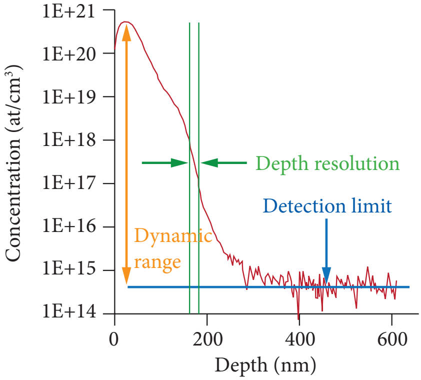


Figure 3. Typical quantified boron dynamic SIMS depth profile obtained on a boron-implanted silicon sample. Depth resolution, dynamic range and detection limit are crucial parameters determined by the sample and convolved with the response of the instrument and selected analysis conditions

It is often of great interest to know the distribution of species versus depth in the sample. Dynamic SIMS is often used for elemental and isotopic depth profiling; the secondary ion intensity is recorded over time for selected species while the sample is eroded by the primary beam. During sputtering, the primary beam is rastered over a specific area of the sample, creating a flat-bottomed crater. Thanks to an electronic or optical gating, the secondary ion signal is collected only from the center of the crater excluding crater edges, optimizing the detection limits and dynamic range of depth profiles that can span over six decades of concentration range (Figure 3).

The sputtering rate determines the analysis time for the depth profile. It depends on the sputtering yield (number of sputtered atoms per incident ion), which is a function of energy, incidence angle and mass of the bombarding species, and which also greatly depends on the sample composition. The sputtering rate can be varied by changing the primary beam current and/or raster size. A high sputtering rate reduces the analysis time and the relative noise contribution from the vacuum. However, one must also consider data point density of the profile; if the sputtering rate is too high, depth information may be lost, especially at interfaces.

A large analyzed volume (large analyzed area and high impact energy) increases the statistics of detected ions and enables higher dynamic range (lower detection limit). The fast DC sputtering used on quadrupole or magnetic sector dynamic SIMS is thus crucial for allowing deep depth profiles with high data rate and very low detection limits.

Depth calibration (conversion of sputter time to depth) is usually carried out by measuring the final crater depth with a mechanical stylus profilometer or by measuring the sputtering rate on a standard sample. Concentration calibration (conversion of count rate to concentration) requires the use of a standard sample as detailed below.

Depending on the instrumentation and selected analytical conditions (primary impact energy in particular), the depth resolution varies from subnanometer to a few tens of nanometers. It can be obtained from a measurement through a steep interface and is usually expressed in nm/decade.

Figure 4 shows shallow B, P and As co-implant profiles in Si, analyzed with impact energy as low as 150eV in order to reduce atomic mixing. Ultra-low energy SIMS can combine subnanometer depth resolution with large dynamic range and accurate near-surface quantification, which is of great interest for semiconductor applications (*eg* measurement of transistor junction depths).

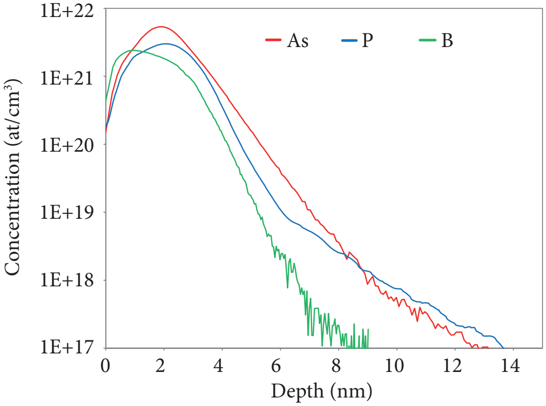
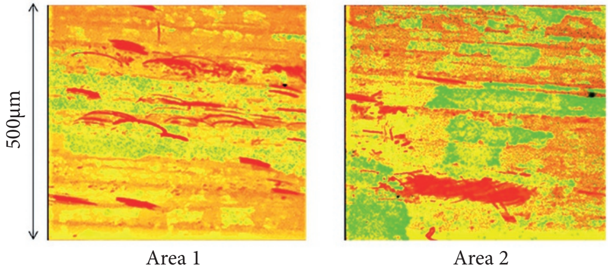


Figure 4. Ultra-low impact energy depth profiling (at 150eV) of B, P and As shallow implants reveals the real distribution within the first 10nm

To perform imaging, the spatial position of each secondary ion must be mapped to the sample surface. There are two ion imaging strategies: the ion *microscope* mode where spatial resolution is determined by stigmatic ion optics, and the ion *microprobe* mode where spatial resolution is determined by the primary beam size (Figure 5).

The ion *microscope* mode is available on CAMECA IMS xf magnetic sector instruments; it allows for high sputtering rates and direct imaging using high beam current, but the



Area 1 Area 2

Figure 5. Example of ion imaging capabilities of dynamic SIMS (microprobe mode), used here to investigate the quality of a tinplate surface. Red: ^{118}Sn, green: ^{52}Cr, yellow: both species. Defects on the sample correspond to red areas (no Cr passivation layer on the Sn coating). Field of view: 500 x 500µm^2

instrumental transmission must be reduced and the lateral resolution is limited to around 1µm.

The ion *microprobe* mode is available on all dynamic SIMS instruments. The primary beam is rastered across the surface and the signal is detected pixel by pixel. In contrast to SEM-EDS/EPMA where analytical resolution is governed by the electron/x-ray interaction volume, SIMS lateral resolution is determined by the primary beam size (down to ~10nm physical limit).

It is possible to obtain 3D volume reconstruction (Figure 6) as well as retrospective depth profiling from ion image stacks recorded sequentially while sputtering in-depth.

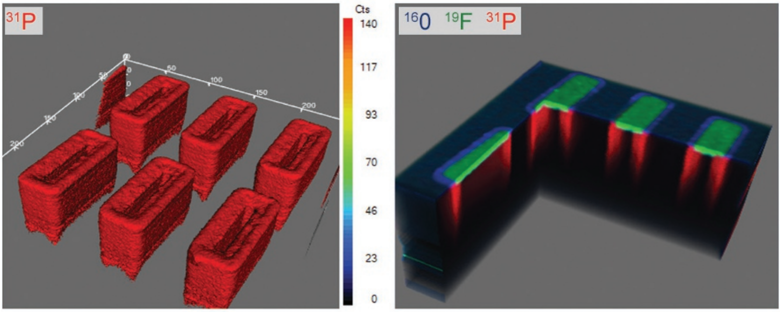


Figure 6. SIMS 3D imaging data obtained on a semiconductor device: P dopant volume distribution (left) and Red-Green-Blue view of three elements, O matrix species and F and P trace elements (right)

Dynamic SIMS is also widely used to measure local isotopic ratios (relative amount between isotopes of a given species) with high accuracy and precision. In addition, the high sensitivity of dynamic SIMS allows isotopes of low relative abundance (minor isotopes) to be measured. Large radius magnetic sector instruments equipped with multi-collector capability (CAMECA IMS 1300-HR^3 for instance)

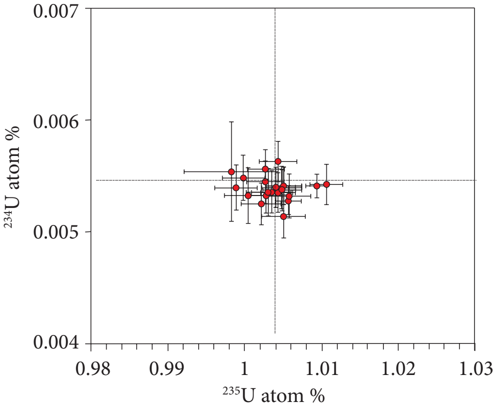


Figure 7. Dynamic SIMS uranium isotopic measurements on a sample containing 1% enriched uranium particles (SRM U010) amongst an environmental matrix. Intersection of dotted lines indicates the nominal values for ^{234}U and ^{235}U atom % for SRM U010

ensure maximum sensitivity and analytical precision for *in-situ* isotope ratio measurements.

Isotope ratio analyses provide crucial information for a wide range of applications: tracking geological processes, mineral dating in geosciences, understanding the origins of the Earth–Moon system (see Case Study 3), or verifying nuclear activities by measuring the uranium isotopic composition of micrometer-sized particles (Figure 7). When used in conjunction with stable isotope labeling (*eg* D, ^{13}C, ^{15}N), dynamic SIMS imaging can measure the distribution, exchanges and dynamics of labeled molecules, allowing it to be used for studying metabolic processes in biological systems (see Case Study 1).

The mass spectrum is another dynamic SIMS analytical output. Mass spectra display secondary ion intensity as a function of mass-to-charge ratio. On magnetic sector analyzers, mass-filtered secondary ion intensities are recorded while scanning the magnetic field. Mass spectra analyses can be performed prior to depth profiling in order to identify the species present in the sample, assess possible mass interferences and select the ions to collect during profile acquisition.

Sample preparation for dynamic SIMS is crucial for obtaining reliable results, but fortunately tends to be relatively simple. SIMS requires that samples are ultra-high vacuum compatible, flat and, ideally, conducting. Several methods have been developed for reducing sample charging while sputtering insulating materials, allowing the analysis of non-conductive samples. In many cases, such samples can be analyzed by simply coating them with a conductive material (see section below). Samples containing water are not compatible with the high vacuum required for dynamic SIMS. Biological samples are generally prepared with methods similar to transmission electron microscopy: fixation, fast freezing, dehydration, resin embedding and microtoming.

Once prepared, samples are mounted into sample holders, together with standards. The sample holder is introduced in a load-lock for pumping down, then the samples can be directly transferred into the analysis chamber. Alternatively, for the analysis of light elements at trace level, samples are often outgassed over several hours in an intermediate storage chamber that can keep multiple sample holders under vacuum for optimized instrument throughput.

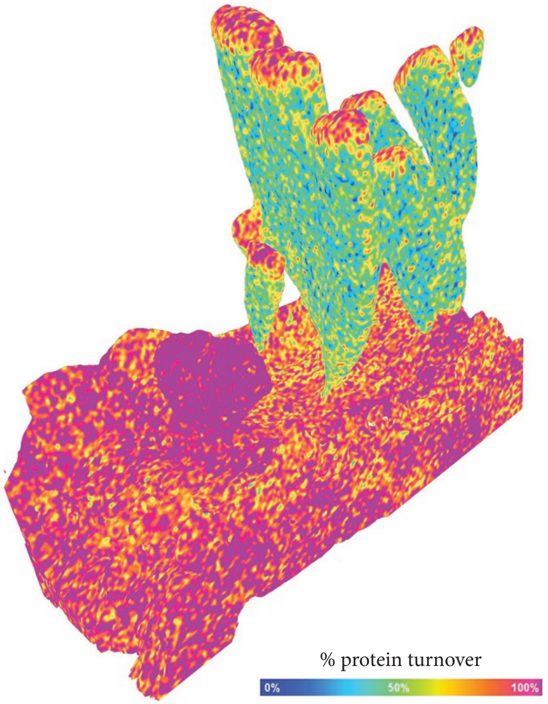
Instruments are equipped with an optical microscope that provides an image of the sample surface and allows sample navigation. Other images of the sample produced by alternative techniques, such as electron backscatter diffraction or confocal microscopy, can also be useful to assess the surface and preselect areas of interest.

CASE STUDY 1. Seeing is believing

In the early 2000s, Claude Lechene of Harvard Medical School and Brigham and Women's Hospital in Boston developed multi-isotope imaging mass spectrometry (MIMS), which combines imaging dynamic SIMS with non-harmful stable isotope tracers to allow users to simultaneously see and measure molecular turnover within single cells.

Lechene began looking at nitrogen, a major component of living matter existing in organisms both as nitrogen-14, which is the predominant nitrogen isotope in nature, and nitrogen-15, which makes up just 0.37% of total nitrogen. Because nitrogen-15 is found at such trace levels compared with nitrogen-14, adding even a very small amount to a sample allows it to be traced.

With the advent of the NanoSIMS, it became possible to simultaneously detect two isotopes originating from the same location, which Lechene says was a boon for quantitation. The signal intensity for an isotope can be highly affected by the composition of the matrix out of which it originates. Thus, in order to evaluate the relative abundance of an element at two locations, one has to eliminate the matrix effect. Lechene thought that using the ratio of two isotopes of the same element will do the trick, because they are likely to undergo the same matrix effect. The isotope of low natural occurrence is used as a tracer, the isotope of high natural abundance is the reference. Any increase of the tracer above natural abundance measures the relative turnover of a molecule containing the tracer at the given location.



With a NanoSIMS 50L we slowly etched a stereocilia bundle of a mouse that had been fed 15N-leucine, a protein precursor. We created 450 XY planes with a Z resolution of approximately 4nm. This allowed us the 3D rendering of quantified protein turnover in the bundle. In contrast to previous studies, direct measurement with MIMS revealed unexpectedly low turnover of protein in hair-cell stereocili. Volume measured is 8 x 8 x 2µm. Incorporation is displayed with a hue saturation intensity (HSI) transformation in which the hue corresponds to the ratio value and the intensity is an index of statistical reliability

Because the NanoSIMS is an ion microscope, Lechene was also able to see at submicronic resolution where the tracers went within a sample.

Lechene recalls his first successful grant application for using MIMS 'was a high-risk, high-impact grant, which offered *a small amount of money to try a crazy idea'. The review came back saying it's certainly high risk because impossible to do, yet certainly highest impact, if doable, by opening a world to explore.*

But impossible it was not, and using a NanoSIMS instrument Lechene was successfully able to visualize and measure protein turnover in stereocilia. This showed that it is possible to label molecules with stable isotopes to both visualize and quantify biological processes at submicrometer scale. It was a huge step forward and was soon applied to follow almost any biological component – DNA, RNA, protein, lipid or sugar – at the single cellular organelle level.

MIMS can be applied to organisms of all scales – from viruses to humans – the possibilities are almost endless.

'An application we are working on at the moment is drug localization', Lechene explains. 'We are labeling drugs with stable isotopes and follow exactly where they go within a cell.'

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CASE STUDY 2. Synthesizing semiconductor crystals

Gallium nitride (GaN) is a semiconductor used in high power and high efficiency LEDs. Tom Mates, technical director of the SIMS facility at the University of California, Santa Barbara (UCSB) in the USA, is using dynamic SIMS to support ongoing research to improve GaN-based technologies.

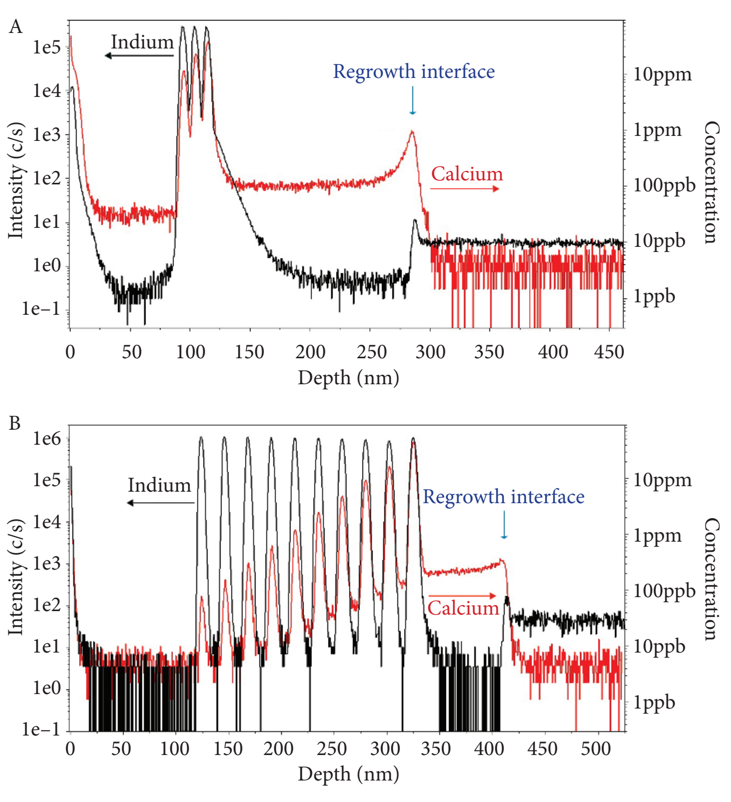
The UCSB materials lab has been using dynamic SIMS since 1997, as it has proved to be an ideal technique for characterizing GaN crystals. 'We are growing devices that involve many layers of material, totaling microns of depth, and we need to characterize them throughout that depth, so dynamic SIMS is really the only way to go for us,' Mates explains.

This is a challenge that simply cannot be met by other surface analysis techniques, such as EPMA. 'Some of the layers that make up our devices are on the order of 5nm thick, and we need to distinguish between one layer and the next,' he says. EPMA cannot provide the depth resolution needed for this, as it combines information from volumes of 1–2µm. EPMA also lacks the extreme sensitivity needed to measure minor dopants and impurities.

A particular interest of UCSB's device designers has been to improve techniques for growing GaN as a substrate for GaN devices. 'GaN-on-GaN structures promise to deliver higher current densities and efficiencies than traditional GaN-on-sapphire. To create substrates for GaN-on-GaN, it's necessary to increase GaN growth rates and lower costs,' Mates says.

To achieve this, UCSB researchers have developed a new system for sodium flux growth of GaN crystals, which increases *growth rates but also impurity levels. Using dynamic SIMS, the researchers can rapidly monitor the incorporation of impurities into GaN crystals during this growth.*

Even with a more conventional growth technique such as molecular beam epitaxy (MBE), dynamic SIMS has proved



SIMS depth profiles of GaN-InGaN structures grown by MBE on top of GaN substrates grown by metal-organic vapor-phase epitaxy. (A) A multiple quantum well structure incorporating a large amount of calcium impurity in the quantum wells. (B) A superlattice of GaN and InGaN grown specifically to trap the calcium impurity

indispensable at pinpointing impurities that are problematic for GaN crystals. In 2016, a group at UCSB was the first to show that calcium in MBE-grown GaN-indium gallium nitride (InGaN) quantum well structures lowers the photonic efficiency of LEDs. They further showed that calcium incorporation is a temperature-dependent process and even developed a new growth strategy to reduce the amount of calcium, which led to an order-of-magnitude increase in LED output power.

Turning his hand to altogether different samples, Mates is also interested in applying the sensitivity and resolution of dynamic SIMS to biological samples. 'The 1μm lateral resolution we can achieve has enabled us to get some very useful images of certain biological samples, and I'm interested to see if we can improve our results in that mode.'

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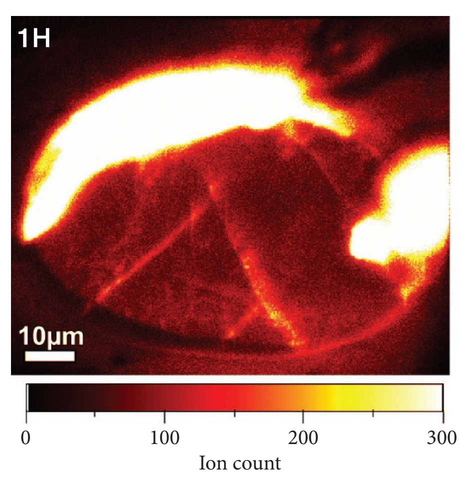
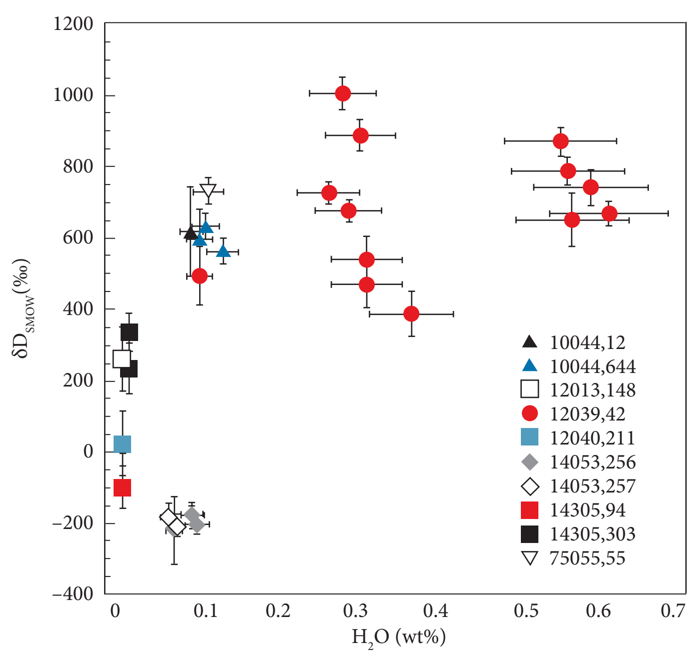
CASE STUDY 3. Measuring hydrogen on the Moon and Mars

Hisayoshi Yurimoto, professor of geochemistry at Hokkaido University in Japan, first started using SIMS in the 1980s. He and his team are interested in two-dimensional microanalysis of hydrogen in geological materials, which are critical to Earth sciences and can only be measured by dynamic SIMS. 'Hydrogen measurements are important to the study of Earth's mantle and volcanoes. SIMS is the only technique to measure the hydrogen content of samples,' Yurimoto explains.



Water content distribution image of apatite crystal in Martian meteorite ALH 84001 using the CAMECA large-geometry with SCAPS detector. Bright areas and lines correspond to terrestrial contamination by absorbed water. The contamination occurs along cracks and micro-fractures. Intrinsic Martian water is preserved in the line-free darker portions (containing small amounts of water). All of the line-free portions show high D/H ratios more than five times larger than the Earth value. (From Greenwood JP, Itoh S, Sakamoto N, *et al.* Hydrogen isotope evidence for loss of water from Mars through time. *Geophys Res Lett* 2008;35:L05203. Reproduced with permission from Wiley)



δD (permil) versus H_2O (wt%) of lunar apatite measured in this study. Three apatite grains are essentially dry (12040,211; 12013,148; 14305,94), and two of these have δD that are difficult to distinguish from terrestrial water. The error bars are 2σ. (From Greenwood J, Itoh S, Sakamoto N, *et al.* Hydrogen isotope ratios in lunar rocks indicate delivery of cometary water to the Moon. *Nature Geosci* 2011;4:79–82. Reproduced with permission from Springer Nature)

The primary focus of Yurimoto's current work is measuring the hydrogen content of samples from other planetary bodies. 'We have measured hydrogen contents and the isotopic composition of minerals from Moon rock and Martian meteorites,' he says.

In 2008, Yurimoto and his colleagues used dynamic SIMS to study the ratio of two hydrogen isotopes – deuterium (heavy hydrogen, 2H) and hydrogen (1H) – in meteorites from Mars.

Measuring these isotopes can help reveal when and how quickly water was lost from the planet.

Comparing the ratios of hydrogen across three Martian meteorites, Yurimoto's group found that water was lost from Mars in two stages – an initial significant loss of water to space, followed by a second, smaller loss, which occurred in the last 4 billion years. They could also determine that the hydrogen ratio in the current Martian atmosphere has remained unchanged for the past 165 million years.

They followed this up with a study of the hydrogen isotope ratios in Moon rock. Determining the amount and origin of water on the Moon is important for understanding the origins of both the Earth and the Moon.

'We found that the hydrogen isotopic composition of the Moon is not equivalent to those of Earth,' Yurimoto says. Instead, he and his team found that heavy hydrogen isotopes are more enriched in lunar rock, suggesting water on the Moon could have come from comets. They believe this occurred shortly after the giant impact event that formed the Moon itself, when the young Earth collided with a protoplanet slightly larger than Mars.

Greenwood J, Itoh S, Sakamoto N, *et al.* Hydrogen isotope evidence for loss of water from Mars through time. *Geophys Res Lett* 2008;35:L05203. (https://doi.org/10.1029/2007GL032721)

Greenwood J, Itoh S., Sakamoto N, *et al*. Hydrogen isotope ratios in lunar rocks indicate delivery of cometary water to the Moon. *Nature Geosci* 2011;4:79–82. (https://doi.org/10.1038/ngeo1050)

CASE STUDY 4. Self-focusing SIMS

Micrometer- to nanometer-scale devices, typically made from semiconductor materials, are now ubiquitous in consumer electronics, and researchers are still actively trying to improve their production and performance. Dynamic SIMS is an essential tool for this type of research.

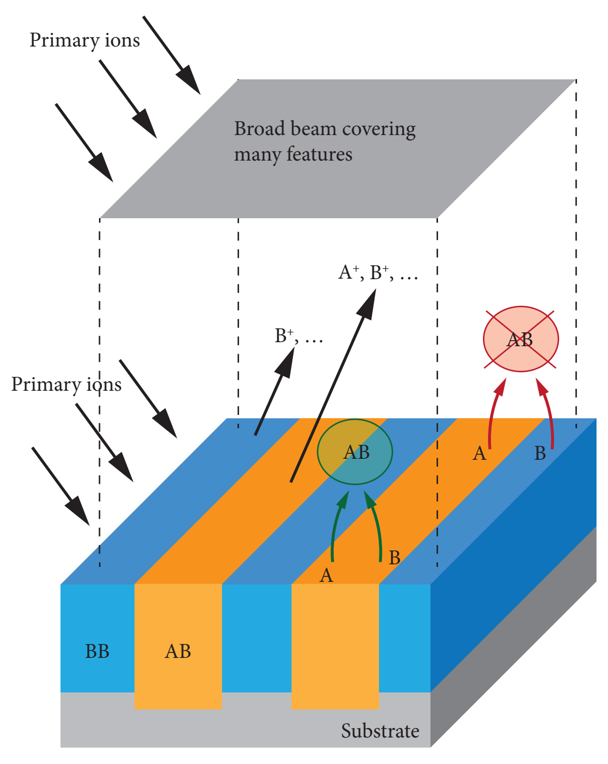
At IMEC in Belgium, a hub for nanoelectronics research, Alexis Franquet takes advantage of dynamic SIMS to detect very low concentrations of dopants and impurities in semiconductor materials. 'I started using SIMS when I joined IMEC in 2005. SIMS is very useful for the semiconductor industries, for applications including deep and shallow implant depth profiling and impurity control,' he says.

Part of Franquet's work now focuses on extending the applications of SIMS, by improving the detection sensitivity, depth resolution and lateral resolution of the technique. Although conventional SIMS offers very high sensitivity, its spatial resolution is limited, which can be a problem when studying semiconductor structures with dimensions of less than 10nm.

'The need to probe doping and composition in very small, heterogeneous 3D devices (<10nm) has led to the paradox of performing analysis with the required 3D spatial resolution, versus the limited statistical relevance of analyzing one small single device,' Franquet explains.

To overcome this problem, Franquet and his colleagues developed self-focusing SIMS (SF-SIMS) to increase the spatial resolution. 'With this new concept, we can overcome the problem of the poor lateral resolution of the SIMS technique compared *to the device dimensions and thus extend the use of SIMS in the semiconductor industries,' he says. 'SF-SIMS relies on the detection of cluster ions (such as AA, AB), which can be formed due to either direct emission or atomic recombination.'*

In direct emission, the constituents of the detected cluster have an obvious origin. But even in atomic recombination, the constituents arise from the same area in the sample. 'The



Schematic representation of the SF-SIMS concept. (From Franquet A, Douhard B, Conard T. Composition analysis of III–V materials grown in nanostructures: the self-focusing-SIMS approach. *J Vacuum Sci Tech B* 2016;34:03H127. Reproduced with the permission of the American Vacuum Society)

formation of secondary ion clusters requires close temporal, spatial and energetic overlap in the emission process of the constituents in order to have a sizeable probability for cluster ion formation,' Franquet says. 'Hence, 90% of the constituent particles of the formed cluster are initially first or second neighbour atoms at the sample surface (ie *their points of origin are very close together, <0.5nm). Therefore, the formation of the AB cluster ion can only occur if both A and B constituents come from the same area.'*

As a result, the information produced by SF-SIMS is confined to the regions containing both ions, which overcomes the lateral resolution limits of conventional SIMS. For Franquet's purposes, this means he can determine the composition of thin films grown in very small volumes. In practice, he applies SF-SIMS simultaneously on several similar structures over a large area to generate an average composition value. Averaging over many devices like this means very large volumes are analyzed, generating high counting statistics and a high signal-to-noise ratio.

Franquet A, Douhard B, Conard T. Composition analysis of III–V materials grown in nanostructures: the self-focusing-SIMS approach. *J Vacuum Sci Technology B* 2016;34:03H127. (https://doi.org/10.1116/1.4943950)

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PROBLEMS AND SOLUTIONS

Dynamic SIMS can be complementary to EPMA, which is based on x-ray emission under electron bombardment: in geology, major elements of mineral phases are quantified with EPMA while the trace elements (*eg* REEs) and the isotopic analyses are performed by dynamic SIMS. It is instructive to compare their respective advantages and weaknesses.

Whereas EPMA is inherently non-destructive, dynamic SIMS is a destructive technique by nature. Hence SIMS should be the last analysis in the sequence for rare or ultra-small samples.

Dynamic SIMS and EPMA both provide the possibility to determine *in-situ*, localized elemental composition, but dynamic SIMS has the additional capability to measure very precise *in-situ* isotopic ratios.

Dynamic SIMS offers superior elemental sensitivity (detection limits below ppm down to ppb level, whereas EPMA is in the range of tens ppm for point analysis). SIMS can also analyze some light elements (H, He, Li) that cannot or hardly be analyzed by EPMA. Note though that a few elements are not so sensitive with dynamic SIMS, such as mercury, zinc, cadmium and noble gases.

Quantification is simple and robust in EPMA, based on the use of pure standards or of known stoichiometry that are easy to create and procure. SIMS quantification is also reliable and simple for low concentrations (below one atomic percent) provided a standard is available with the same matrix composition. For higher concentrations, calibration curves are necessary (see below).

The depth of information is a main differentiator. Although depth information can be reconstructed by varying the primary electron energy, EPMA is basically a volume analysis (interaction volume ~0.1–10µm^3), whereas SIMS is a surface analysis that can be used for *depth profiling* (with ~1–20nm depth resolution).

Finally, the electron/x-ray interaction volume limits EPMA chemical imaging lateral resolution to ~0.5µm, while dynamic SIMS lateral resolution is only limited by the *primary ion beam diameter* that can be focused down to 50nm on a NanoSIMS.

A limitation in both techniques is the absence of direct chemical bonding or valence information. Such information can be obtained through XPS surface analysis, in some cases Auger, or other *surface analysis* methods but with much lower sensitivity.

Matrix effects

As seen above, quantification of dynamic SIMS data – converting secondary ion signal intensities to absolute concentrations – can sometimes be delicate. The fraction of particles emitted from the sample surface that are ionized and sent to the mass spectrometer is highly dependent on instrumental factors (primary beam species, impact and angle of incidence), but also depends on the surrounding chemical environment and hence varies with the chemical composition of the matrix. These are collectively known as *matrix effects* and mean that, for the same concentration of a given element, its signal in a silicon matrix may be very different from its measured signal in a silicon oxide matrix or in a germanium matrix.

Note that the sputtering yield (sputtered atoms per incident primary ion) also varies with the sample matrix composition, so for a multilayer sample the sputtering rate is expected to be different for each layer.

Data quantification requires standard samples with a known concentration of the element(s) of interest and the same matrix as the sample being studied (see below).

One very effective semi-quantitative dynamic SIMS methodology to tackle matrix effects is analyzing MCs^+ or MCs_2^+ ions (where M is the ion of interest and the primary ion beam is Cs^+) rather than M^+ or M^-. The mechanism is indeed a kind of post-ionization (by recombination) of the sputtered *neutrals* (no ionization influence by the matrix) by the sputtered Cs^+ *ions* (that are linear with the primary current). In semiconductors this technique has become a standard to *minimize matrix effects* in III–V compounds.

Standards and relative sensitivity factor

Creating standard samples for dynamic SIMS is primarily achieved using two methods: ion implantation and bulk doping. A depth profile of an ion-implanted sample has the advantage that it provides not only quantification but also detection limit (determined by the average of the quantified signal at sufficient depth), see Figure 3. An important point for a local analysis technique like SIMS is that the standard must be homogeneous over its whole surface.

Depth profiling SIMS is then performed on standard and unknown samples with the same settings. By monitoring the implanted ion signal *and* a matrix signal, a relative sensitivity factor (RSF) that converts secondary ion intensity to concentration can be calculated from the known implanted dose or known bulk concentration in the standard sample. By measuring the same two signals during the analysis of the unknown sample, the RSF can then be applied to quantify the signal of the species of interest (concentration calibration).

For simple matrices (*eg* semiconductors), the procurement or production of standards may be relatively straightforward, and tabulated RSFs exist for many elements in silicon matrices. But for complex samples such as multilayered materials, or in cases where the matrix composition is unknown (such as meteoric samples), quantification is more challenging and several standards may be required. Alternatively, ion implantation is sometimes conducted on a piece of the actual sample being studied.

For life science, when using stable isotope tracers, as the samples are often embedded in resin, the isotopic ratios of the pure resin can serve as an internal natural ratio reference.

Mass interferences

A challenge facing SIMS analysis is the complexity of mass spectra and the potential presence of mass interferences: two atomic species may have the same nominal mass, *eg* $^{28}Si^-$ and $^{12}C^{16}O^-$, and hence appear as a single peak in a low mass resolution mass spectrum. But because their exact masses differ by fractions of atomic mass units, the peaks may still be separated by high mass resolution mass spectrometers. A great advantage over quadrupole analyzers is that magnetic sector analyzers can separate most interfering species using high mass resolution conditions, provided that the required mass resolving power does not exceed the capability of the instrument or does not reduce the sensitivity too much. Another great advantage of the magnetic sector design over TOF analyzers is the independence between the lateral resolution setting (beam size) and the mass resolving power setting.

In some cases, the energy filtering technique may also be used for removal of molecular mass interferences. The secondary ion energy distribution is narrower for polyatomic species (*eg* $^{28}Si^{29}Si_3$) compared to monoatomic species (^{115}In). By shifting the energy band-pass towards the high-energy part of the distribution, it is possible to minimize the molecular peak contribution relative to the atomic peaks; this is the so-called energy filtering technique.

In other cases, appropriate choice of analysis species can avoid the problem of mass interference altogether. For example, in silicon matrix samples, recording $^{54}Fe^+$ rather than $^{56}Fe^+$ that presents a severe mass interference with high intensity $^{28}Si_2^+$ signal, allows quantification of the elemental concentration of iron (Fe) in a sample using the known ^{54}Fe isotopic abundance.

Insulator samples

Because dynamic SIMS is based on sample bombardment using charged particles, sputtering of insulating materials causes charge build-up on the sample surface, which affects the detected secondary ion intensity. Several methods have been developed to reduce sample charging.

The most common method employed for charge neutralization is the use of an electron beam coincident with the ion beam analyses area. As the sample charges positively, electrons provide charge compensation. On magnetic sector instruments, a normal-incidence electron gun delivers electrons to the sample along the axis of the secondary ion optics.

For positive secondary ions, the electrons strike the sample surface at high or medium impact energy. This works well for relatively thin insulating layers, but is more challenging for thick multilayered samples or bulk insulators. Alternatively, ion bombardment using negative O^- or O_2^- primary ions, *without* using the electron gun, is known to alleviate surface charge-up and has been successfully applied to the analysis of bulk insulators such as glasses or mineral samples.

For negative secondary polarity, the high voltage of the sample acts as an electrostatic mirror that decelerates the electrons to quasi-zero eV energy near the sample surface. This results in charge 'self-compensation' that allows charge neutralization even in the case of multilayer or bulk insulator samples (Figure 8).

For low-impact energy measurements on shallow semiconductor structures, optical conductivity enhancement is another complementary means of charge compensation often used in dynamic SIMS (quadrupole or magnetic sector). The sample is illuminated with blue to UV photons in order to generate electrical carriers near the surface favoring charge flow.

For all methods described above, the sample needs in general to be coated with a thin conductive layer around 20–30nm (carbon, gold, platinum being the most used) that provides a path for charge to leak away from the surface to the sample holder.

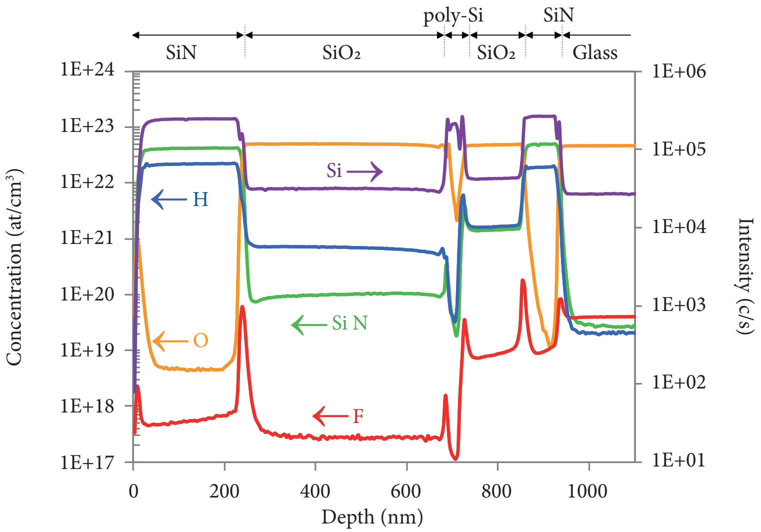

Figure 8. Dynamic SIMS depth profiling in SiN and SiO_2-based multilayer insulating sample using the normal-incidence electron gun. Efficient charge compensation provides excellent signal stability

WHAT'S NEXT?

Dynamic SIMS has matured to become an essential micro-analytical characterization technique. A large part of the development of dynamic SIMS has been driven by the semiconductor industry, but recent advances in instrumentation and analytical protocols have extended its application to many areas other than the semiconductor field.

On the instrumentation side, physics governs. Hence performance improvements for specific applications generally lead to compromises in other parameters. Dynamic SIMS can be defined as an ultra-sensitive surface analysis technique for elements and isotopes with 3D spatial resolution. The main physical directions for future instrumentation are depth scale, lateral scale and sensitivity.

In terms of depth scale, ultra-low energy dynamic SIMS for semiconductors are already using impact energies down to 100–150eV in order to deliver subnanometer depth resolution for measuring low-level dopant profiles on structures with thicknesses of just a few nanometers. The next step will be to run such analyses on small patterns of a few tens of micrometers a side, in a fully unattended mode, including data analysis. With productivity being crucial, brighter ion sources and optimized primary columns can make key contributions.

There is a similar challenge with lateral resolution: as dynamic SIMS is destructive, analyzing smaller objects containing fewer atoms requires much more than simply a smaller primary ion beam size. It requires maximizing the useful yield: ionization (reactive primaries), collection (strong extraction), transmission, mass resolution, parallel collection, detection efficiency and low detection background. The NanoSIMS already meets most of these criteria at 50nm lateral resolution, but the development of new ion sources and associated column designs could further improve the resolution toward the physical limit of the collision cascade, around 10nm.

The other route to analyzing 3D structures of a few nanometers in dimension, much below the primary ion beam size, is to analyze many similar structures in parallel using a self-focusing methodology (SF-SIMS): the polyatomic secondary ion composition is intrinsically determined by its point of emission. Refinements of this method will occur, including correlation with currently available high-resolution electron microscope images of device sections obtained by focused ion beam.

Users of dynamic SIMS are increasingly demanding improved detection limits for atmospheric species, which will require advances in analysis chamber vacuum quality for reduced contamination, especially during slow depth profiling.

As with any widely adopted, maturing technology, users are also demanding usage simplification, while still keeping performance and reproducibility at their peak levels. This is a challenge for manufacturers and will require a close collaboration with users.

A desire of life scientists is the capability to analyze frozen-hydrated samples in order to eliminate, if possible, any risk of relocalization of small molecules during sample preparation. This already partly exists for static SIMS and would be an interesting evolution for dynamic SIMS (also for liquid inclusions in minerals or against roughness developed under bombardment).

Finally, dynamic SIMS users always want to increase the ionization yield in order to improve the sensitivity for specific elements, and to standardize these yields in order to facilitate quantification. For example, some interesting discoveries have been made in detecting surface contamination by coating the sample with graphene, enhancing the ionization by two orders of magnitude. Flooding with a reactive species or gas is another route. Oxygen is largely used today for further enhancing the ionization of electropositive elements in some matrices. Other gases, atomic species or ions could also be tried. This is all based on enhancing the ionization yield, not the sputter yield, as commonly obtained in focused ion beam instruments.

Post-ionization of the sputtered neutrals, by laser, plasma or other means, is another long-awaited potential technique. Possibly new UV laser technologies or other improvements might emerge, opening the way to radical instrumentation changes.

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